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CONTRIBUTIVE RESEARCH AND DEVELOPMENT

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4126 Linden Avenue
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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This Technical Report gives a summary of the research performed in the materials and physical sciences in support of the Wright Laboratory Materials Directorate under a Contributive Research and Development contract. The report contains an abstract covering the nature of the research and the results for each of 208 tasks completed under the contract.

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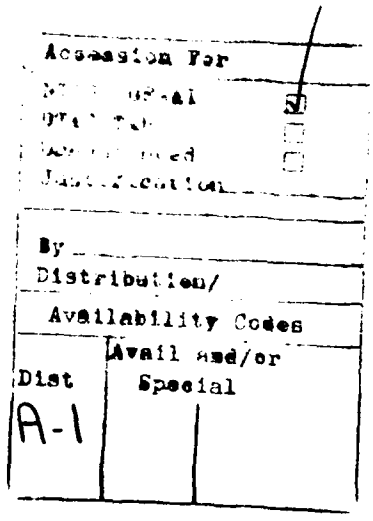

Preface and Acknowledgements

This Final Technical Report was developed under Air Force Contract F33615-88-C-5402, Contributive Research and Development. This contract was sponsored by the Wright Laboratory, Materials Directorate, Wright-Patterson Air Force Base, Ohio 45433-6533. The Materials Directorate Project Managers were Ms. Kristine Lark and Ms. Susan Kirchoff. The SYSTRAN Project Manager was Mr. Milton Zellmer.

1.0 OVERVIEW

This final report for Contract Number F33615-88-C-5402 describes the objectives and accomplishments of SYSTRAN Corporation from contract inception to the end of the technical effort on 31 December 1990.

During this period, SYSTRAN has administered this Contributive R&D contract in response to the need to provide highly specialized scientists for short-term studies vital to the objectives of the Wright Laboratory.

1.1 Approach

Meeting the contractual requirements for this effort, SYSTRAN has provided all technical and administrative management control over the project and the assigned researchers.

SYSTRAN has identified and assigned a principal researcher(s) for each task requested by the Government. These researchers have conducted investigations in the physical and engineering sciences and have provided a level of effort in accordance with task assignments. The effort involved theoretical and analytical studies, measurement techniques, and evaluation of systems, devices, and concepts. Areas of investigation included chemistry, solid and plasma physics, metallurgy and ceramics, nondestructive evaluation and solid mechanics. A majority of the technical work was conducted at Wright-Patterson AFB in Laboratory facilities.

SYSTRAN has exercised management control over all the administrative aspects of the contract including budgets, schedules, and project management reports. All support requirements including software, graphics, and documentation have been provided by SYSTRAN's support staff. All reports have been prepared in accordance with CDRL requirements.

2.0 ACCOMPLISHMENTS

At the completion of this ongoing research effort, 208 separate tasks had been issued. Of these 208 tasks, 12 were canceled. Of the remaining 196 tasks, 6 were administrative tasks.

For each technical task completed under this contract, a final report was submitted upon completion of the technical effort. Abstracts of these final reports are included in this document. Each abstract provides a summary of major activities for each completed task. No abstract has been prepared for either administrative or canceled tasks.

2.1 Documentation/Graphics

SYSTRAN has completed all documentation and graphics requirements. Quarterly R&D status reports were submitted for each task. In addition performance and costs reports were submitted monthly for each task, accounting for current and cumulative manhours and funds expended per task. Manhour expenditure charts were prepared. Final technical reports were submitted for each completed task from the original input of each researcher. SYSTRAN has provided all graphics support for presentations and documentation.

2.2 Software

Software developed under any of the technical tasks has been delivered at the completion of the task. Software was delivered on the media supporting the computer system within the Materials Directorate Branch for which the research was performed. User's manuals/instructions were developed and submitted to support this software.

2.3 Equipment

All equipment and materials purchased to perform a specific task during the project have been transferred to the Government.

3.0 TASK ABSTRACTS

This section contains abstracts for all technical tasks completed under this contract. Abstracts appear in numerical order by Task Number.

TASK: 1

TASK TITLE: Determination of Structure-Property Relationships of Novel Candidate Base Stocks for Advanced Lubricants

TASK OBJECTIVE: To investigate the effect of controlled variations in the molecular structure of novel base stocks on their tribological properties.

SCIENTIST: Harvey L. Paige, Ph.D.

DESCRIPTION OF WORK:

The aim of this investigation was to explore the possibility of developing advanced, high-temperature liquid lubricants using molecular modeling and computational chemistry to replace expensive experimental portions of development.

In the course of this study the following activities were accomplished using perfluoropolyalkyl ethers:

- identification of compounds and the limiting carbon:oxygen ratios
- correlation of formation enthalpies with ionization potentials
- evaluation of thermodynamic stabilities
- investigation of strategies for evaluating the strengths of individual bonds

Overall, the computational results on the perfluoropolyalkyl ether oligomers have not shown a clear direction for synthesis work. Based on results of the investigation, it is recommended that synthesis efforts concentrate on examples of the most, and least, stable compounds so that reliability of calculations can be tested.

Due to the lack of experimental data on perfluoropolyalkyl ethers, the following activities were accomplished using chlorotrifluoroethylene oligomers, aliphatic and aromatic hydrocarbons, and a selection of other compounds:

- identification of the structure of the compound
- determination of viscosity, formulation enthalpies, and ionization potentials
- study of thermal and thermoxidative stabilities
- investigation of attracting forces pertaining to viscosity.

Pressure differential scanning calorimetry was useful in determining correlations between calculated parameters and properties such as thermoxidative stability.

Thermogravimetry as a measure of volatility was found to have reproducible results with the protocol used in the study and described in the final report.

Interpretation of results led to the following conclusions:

1) Molecular modeling and computational chemistry can be used to deter costs in the

development of high temperature liquid lubricants.

2) Correlations such as those between calculated polarizability and viscosity are possible.

3) Computational measures of relative stabilities of structural variations are difficult due to lack of experimental data and due also to the extraordinary stability of the compounds studied.

TASK: 2

TASK TITLE: Molecular Composite Processing

TASK OBJECTIVE: To develop innovative processing approaches to fabricate molecular composite in bulk form for structural applications.

SCIENTIST: Allan S. Crasto, Ph.D.

DESCRIPTION OF WORK:

The aim of this task was to establish techniques for processing three-dimensional composites and to investigate the influence of process variables on the microstructure and mechanical properties of the resulting products.

Molecular composite solutions were prepared and coagulation of these solutions was observed using the following processes:

1) wet filament technique
2) direct block coagulation
3) lamination of extruded film
4) microwave drawing of extruded fiber.

During processing of molecular composite solutions via wet filament technique, the mechanical properties of filaments were observed over a range of pressures and temperatures.

Direct block coagulation was studied as a potential means of eliminating interfacial boundaries which would result in superior mechanical properties. Research included the following methods:

1) Observation of coagulation from methane sulfuric acid (MSA) and sulfuric acid (SA) solutions
2) SAXS studies of the wet coagulated blocks
3) Examination of freeze-fractured surfaces by scanning electron microscopy (SEM)
4) Thermogravimetric analysis
5) Observation of diffraction patterns.

Interpretation of results led to the following conclusions:

- Direct block coagulation does not eliminate interfacial boundaries. Interfacial area is greater than in specimens made from molded filaments and has to be reduced along with voids and poly-p-phenylene benzobisthiazole (PBZT) aggregation before superior products can be attained; a change in matrix resin to PEEK may be required for further optimization of coagulation and consolidation parameters.

- Lamination of extruded film produced better bonding between the plies of the thinner bars. Further modification of the press cycle may be necessary to improve bonding in thick bars. Interleaving films having low and high PBZT/nylon ratios could be attempted to obtain a better product.

- Tensile tests on extruded fibers treated under varied conditions revealed no difference in properties within the limits of experimental error, indicating that either the fiber did not absorb energy or the energy absorbed was insufficient to cause significant change.

TASK: 3

TASK TITLE: Interfaces in Ceramic Composites

TASK OBJECTIVE: To study and alter the mechanical behavior of the fiber/matrix interface in ceramic composites.

SCIENTIST: Amy J. G. Jurewicz, Ph.D.

DESCRIPTION OF WORK:

This task is an extension of work previously performed in which a vacuum hot-pressing technique was designed for sample fabrication. This technique approximates conditions required for processing a full ceramic-matrix composite and can be easily adapted to high temperature/pressure systems since it does not rely on properties specific to glasses. Early pull-out and push-out test designs used a goniometer to orient the sample and to center it in the load train.

The aim of this project was to refine the previously developed sample fabrication technique, to improve the pull-out test apparatus and procedures, and to implement the previously designed push-out test apparatus and procedures. Mechanical parameters were determined for several SiC/glass systems. Appropriate control measures varied both with the type of glass and with the hot-press die. Changes to the pull-out test entailed replacing the aluminum goniometer with a sine-vice and lining the pneumatic grips with aluminum foil.

The task involved the collection of load-displacement curves and their interpretation, as well as analytical modeling of the derived data. Measurements were made with single-fiber push-out and pull-out tests using samples and test fixtures designed for the project. Parameters included peak load, load drop, and frictional load. Given appropriate mathematical models for the system, these parameters could be used to bound the shear strength and the coefficient of friction for each interface. The load drop was used to recognize and avoid samples damaged during post-process handling.

As a result of this study the following projects are recommended for future research:

- Clarify the analytical analyses to reduce scatter in the peak-load and load-drop data. One way might be to correct for porosity present along the interfaces of samples already tested by examining each track and estimating the percentage of voids.

- Adapt the current techniques to testing high temperature materials at use temperatures. Molybdenum tooling might be necessary for systems in which the fibers would react with the graphite dies. Load displacement curves could be measured using modified push-out tests.

graphite dies. Load displacement curves could be measured using modified push-out tests.

TASK: 4

TASK TITLE: Electrical and Magnetic Properties of High Temperature Semiconductors

TASK OBJECTIVE: Explore the magnetic properties of thin film and bulk superconducting ceramics and relate to electrical behavior.

SCIENTIST: Iman Maartense, Ph.D.

DESCRIPTION OF WORK:

The aim of this project was to establish a highly sensitive magnetic susceptibility facility and to use it in evaluating the quality of superconducting materials.

The following effects of long-term annealing on superconducting properties of BiSrCaCuO were investigated:

1) temperature dependence of electrical resistivity before and after annealing
2) temperature dependence of the AC susceptibility in various AC fields for annealed and unannealed samples
3) backscattered SEM images of annealed and unannealed samples
4) powder x-ray diffraction (XRD) patterns for the materials before and after long-term annealing.

The presence of two superconducting granular phases in sintered 1112 BiSrCaCu2010 was established by AC susceptibility and direct resistivity measurements, confirming previous reports. The step-wise nature of the superconducting transition remained after long-term annealing, even though the phase with Tc_110 K increased in apparent volume at the expense of the low-Tc phase. The latter phase was much reduced in fractional volume, while its Tc increased from 63 K to 76 K. The attendant reduction in the XRD intensities attributed to this 2122 structure suggested that the low-Tc phase can have a variable composition resulting in a range of well-defined Tc values.

The bulk superconducting transition, defined by the onset of zero resistivity, coincided with the temperature below which the AC susceptibility and loss behaviors show the strong AC field dependence which is a characteristic of weak-link ceramic superconductors. Despite the presence of a large volume fraction of 110-K material, the bulk transition occurred at a temperature which is considerably lower than that of the grains themselves This fact again demonstrates that granular connectivity, based on percolation-limit arguments, is not the governing principle which determines the bulk behavior. As seems to occur in all the superconducting ceramics, the intergranular weak-link structure dominated the overall properties. It takes only a small amount of insulating or normal-state material at the grain boundaries to uncouple neighboring grains.

Long-term annealing appeared to improve the bulk properties by reducing or converting the inert intergranular matrix, or by decreasing the number of grains which are small than the penetration depth effective at a given temperature, thereby raising the onset temperature of the weak-link conductivity. This occurred in spite of the higher void fraction present after annealing, presumably resulting from preferential growth in the platelet planes, which has the effect of increasing the three-dimensional extent of the sample. The lack of improvement in the critical

current density, inferred from the susceptibility data, was probably a result of the increased porosity. Work on denser samples is required to test this hypothesis.

The results do not support the model proposed by Tarascon et al. of low-Tc grains enclosed or shielded by the high-Tc phase. Such a geometry is not consistent with the apparently independent behavior of the low- and high-Tc phases observed in both the resistivity and susceptibility measurements. In fact, the low-Tc phase is seen to be a crucial component in the weak-link junction network, which should not be the case if this phase is totally, or even largely, hidden inside the high-Tc material.

It is difficult to deduce the exact phase relationships in the Bi-Sr-Ca-Cu-O system due to the sluggish growth kinetics of the phases. The situation is further complicated by bismuth volatility which results in a time-dependent change in the sample composition.

The behavior of bulk material ceramic superconductors near Tc was investigated with attention to the following areas:

1) relationship between the applied DC field and the upper critical temperature of the annealed sample
2) temperature dependence of the susceptibility near high T_c onset of the annealed sample
3) temperature at the AC loss maximum as a function of AC field in zero DC field, for the annealed sample
4) temperature dependence of the AC loss in the annealed sample for various applied DC fields
5) temperature at the AC loss maximum as a function of DC field for the annealed sample.

The magnetic properties of superconducting thin films were also investigated with consideration given to the following areas:

1) temperature dependence of the AC susceptibility and the AC loss of 1-2-3 film for various AC fields
2) temperature dependence at the AC loss maximum as a function of AC field in zero DC field
3) temperature dependence of the AC loss in an AC field and the differential of the associated susceptibility data.

TASK: 5

TASK TITLE: Infrared Absorption of Defects in Gallium Arsenide

TASK OBJECTIVE: To determine the role of the EL2 defect in the behavior of semi-insulating gallium arsenide.

SCIENTIST: Omar Manasreh, Ph.D.

DESCRIPTION OF WORK:

Despite extensive investigations on the midgap native defect known as EL2 in GaAs, its atomic structure is still a matter of controversy. This project was undertaken in order to apply complementary investigation by different experimental techniques. The object of this study was to use monochromatic light concurrent with the infrared absorption technique to study the effect of irradiation and annealing on the EL2 defect in liquid-encapsulated Czochralski (LEC) Gallium Arsenide.

An important and unusual aspect of the EL2 defect is the presence of an optically induced metastable state, $EL2^*$. Several effects such as conductivity type change, neutralization of shallow acceptors, persistent photoconductivity, excitation of traps, and changes in the optical properties of the sample are observed after transforming the EL2 defect from its normal state, $EL2^0$, to $EL2^*$. Nevertheless, the mystery of EL2 lies in understanding its metastable state, $EL2^*$. No IR absorption spectrum, EPR spectrum, or electric properties have been observed for $EL2^*$. The $EL2^0$ to $EL2^*$ transition can be achieved by illuminating the sample with white light or $\sim$ 1.1 ev monochromatic light at low temperatures ($<$ 120 K). This memory effect is removed in most samples by heating them to temperatures $\geq$140 K.

Many attempts have been made to transform the EL2 defects from EL^* to $EL2^0$ by photon irradiation. Some of these attempts were based on a relatively high intensity laser irradiation with a single or a few values of photon energy. Others were confined within a narrow range of monochromatic light. None of these attempts have been able to provide a clear picture of the structural nature of $EL2^*$.

IR absorption measurements for EL2 were obtained using a CARY 2300 spectrophotometer, closed cycle refrigerator, and a monochromatic spectrophotometer using photoquenching. A separate monochomator was used for photo-induced recovery measurements.

Interpretation of results led to the following conclusions:

(1) The photo-induced recovery data collected during this project shows for the first time that the EL2 defect can be completely transformed from the metastable state to the normal state by using monochromatic light with low light intensities.

(2) EL2 may be coupled with other defects at temperatures below 50K.

(3) The Auger deexcitation process does not seem to play an important role in the photo-induced recovery.

(4) The V_{As} is speculated to act as an acutator for the EL^* to EL^0 transition.

(5) The experimental measurements support the EL2 family of levels concept.

These experimental measurements may play an important role in determining the atomic configuration of the metastable state of the EL2 defect. A modification of the present models of EL2 is required in order to account for the present measurements.

TASK: 6

TASK TITLE: Molecular Beam Epitaxy Growth of Gallium Arsenide Films

TASK OBJECTIVE: Develop improved materials and processes for production of gallium arsenide and related compound semiconductor epitaxial films by molecular beam epitaxy (MBE).

SCIENTIST: David H. Tomich

DESCRIPTION OF WORK:

The aim of this investigation was to determine optimum conditions for MBE growth of doped and undoped GaAs. Insitu analysis of the epitaxial surfaces was performed using the following:

- Auger microscopy (SAM or AES)
- Reflected high energy electron diffraction (RHEED)
- Low energy electron diffraction (LEED).

Exsitu analysis was also performed using the following:

- Secondary ion mass spectometry (SIMS)
- Raman spectroscopy.

Gallium arsenide buffer layers were grown on wafers. The growth process was observed during experiments which altered the wafer sources, cleaning procedures, chemicals, facilities, temperature, and irradiation.

Different combinations of factors led to various improvements in production as updated in documentation.

TASK: 7

TASK TITLE: Polymers

TASK OBJECTIVE: Semi-empirical computations of the nonlinear optical properties of ordered polymers.

SCIENTIST: Jorge Medrano, Ph.D.

DESCRIPTION OF WORK:

The aim of this investigation was to study and develop computer software for the theoretical calculation of nonlinear optical properties of ordered polymers.

Two different approaches can be used for the prediction of second order hyperpolarizabilities of molecules. In the Sum-Over-States (SOS) approach the calculations are made for the unperturbed molecule and perturbation theory is applied to these states to calculate hyperpolarizabilities. In the Finite-Field (FF) approach, determination of molecular wave functions is made on the perturbed molecule including the field, and the hyperpolarizabilities are obtained by numerical differentiation of the energy or the dipole moment with respect to the appropriate electrical field components. The FF approach was used to check calculated values against experimental results and agreement was very good. Nonlinear optical properties of some oligomers of thiophene were also calculated.

For the calculation of polarizabilities and hyperpolarizability tensors of polymers, a decision was made to try a sawtooth-like periodic electrical potential. The program necessary to perform these calculations has been completed.

In an effort to correlate molecular electronic structure with nonlinear optical properties, a mathematical theory of bonding and valence is being developed to interpret in pictorial terms the

electron density in each repeat unit of a periodic system.

TASK: 8

TASK TITLE: Polymers

TASK OBJECTIVE: Rheology and processing of ordered polymers

SCIENTIST: Kung-Hwa Wei, Ph.D.

DESCRIPTION OF WORK:

The aim of this project was to investigate the rheology and rheooptical properties of rigid-rod polymers and their relationships with fiber spinning strength operation. Three areas were studied.

Rheology of PBT/PPA Dope

A series of dynamic viscosity measurements of 15% PBT/PPA dopes at different temperatures was undertaken to determine whether the geometry of the dopes would affect the viscosity measurement. Results showed that when the temperature is above 130 °C and at a frequency higher than 1 rad/s, the geometry has little effect on viscosities of these dopes. At a temperature below 130 °C, there is a difference in viscosity curves caused by the geometry. This behavior is not exactly the same as that of high molecular-weight thermoplastic liquid-crystalline polymers, in which the geometry has no effect on the viscosity.

These dopes also behave differently under shear deformation in a steady state as opposed to a dynamic mode. As frequency increases, steady-state viscosity drops more sharply than complex viscosity. One might speculate the steady state mode is much more effective than the dynamic mode in aligning rigid-rod molecules since the direction of the rotation is unchanged in the former mode.

A study of phase transition under temperature sweeps was carried out using PBT/PPA dope with stainless steel parallel plates. Results showed clearly defined phase separation at approximately 270 °C.

Rheology and Fiber Spinning of Dihydroxy PBT/PPA

The viscosity curve was investigated at different temperatures and an attempt was made to determine whether the viscosity rise was caused by physical transition or by chemical reactions.

Various compositions of copolymer dopes were spun, tension dried, and heat treated in order to determine dope properties and processing conditions.

Dihydroxy PBT fibers were spun, coagulated in iodine/potassium iodide solution, and tension dried in order to improve the compressive strength of fibers.

Flow-Birefringence Study on the Spinning Line

This study was carried out on molecular orientations in flows of rigid-rod polymer solutions on the fiber spinning line. The objectives were to quantify the orientation of rigid-rod polymer molecules and also to determine and to optimize effects of dope concentrations and processing

variables on the mechanical properties of fibers. By measuring light intensity, the resultant phase angle could be determined. From the thickness of the film and the wavelength of the light source, the birefringence could be determined. Problems encountered were how to measure the film thickness in the spinning line and how to maintain a uniform thickness film. The current approach is to design a film die with a longer channel length and to reduce the thickness of the film so that fringes will result from phase angles only.

TASK: 9

TASK TITLE: Polymers

TASK OBJECTIVE: Processing Ordered Polymers

SCIENTIST: Swapan K. Bhattacharya, Ph.D.

DESCRIPTION OF WORK:

One of the major constraints of using poly-p-phenylene benzobisthiazole (PBZT) based fibers as a structural material in airplane design is their relatively poor compressive strength in comparison to carbon fibers. Tailoring the molecular nature of fibers by introducing potential thermally reactive crosslinking agents such as polymers offers promise for improving compressive strength of the fibers. The object of this study was to investigate processing conditions for spinning new ordered polymers into fibers, addressing compressive strength and other mechanical properties.

The characteristics of the PBZT/Fluorene copolymer (with 10 mole percent of fluorene) were studied, examining fibers after each stage of processing by using an optical microscope to check surface or internal defects and to measure the diameter of the fibers. A thin film was produced and found to be birefringent at room temperature when examined under the optical microscope in cross-polarized light, assuring that rigid-rod molecules were aligned in some preferred direction. The rheological behavior of the solution was studied as a function of temperature. Fiber processing was conducted through dry-jet wet spinning and subsequent tension drying of the fiber. Thermal stability of the as-spun fibers was examined. Contrary to expectations, hydrogen evolution was not observed.

Heat treatment of the fibers was conducted, varying temperatures and maintaining constant tension. Solubility of the fibers was determined in methane sulphonic acid (MSA) before testing for mechanical properties. Fibers which were insoluble or only partially soluble in MSA were tested for tensile and compressive properties. Pure PBZT fibers were also heat treated for comparison of physical and mechanical properties with the PBZT/FL polymers. Tensile and compressive properties were evaluated from single filament tests.

Solubility and rheological studies provided direct evidence that some form of crosslinking in PBZT-FL is achieved in the solution state, since pure PBZT is still soluble under similar conditions. Other research reveals that PBZT crosslinks around 320 °C in solution. The conclusion can be further strengthened by the fact that the dynamic viscosity of the PBZT dope decreases monotonically under the 70 to 200 °Ctemperature range. In an effort to determine if crosslinking can be achieved in the solid state (or fiber form) and to determine whether the crosslinking achieved in PBZT-FL fiber is due to the presence of fluorene, the following activities were performed:

- Specimens of PBZT/FL and pure PBZT were prepared, varying temperatures and residence times inside a Lindburg oven in a nitrogen atmosphere.

- To examine extent of crosslinking, the degree of swelling and solubility in MSA of the heat treated fibers were compared.

No difference was observed in the solubility behavior of PBZT/FL in comparison to pure PBZT. However, PBZT/FL fibers showed more swelling than PBZT fibers at temperatures between 600 and 650 °C.

Another attempt was made to achieve crosslinking in the fiber state by heating the extruded fiber, coagulating in water, and processing as usual; however, the dynamic viscosity remained unaffected by isothermal heating.

A spinning experiment was conducted by heating an as-extruded sample for 3 hours at 200 to 210 °C in nitrogen. The fibers showed blisters, stuck together, and appeared brittle after coagulation in water. Fibers cured in air at 200 °C were not brittle, did not show blistering, but were stuck together implying that it may be possible to find a time-temperature sequence for crosslinking to occur in the uncoagulated as-extruded gel fiber without losing tenacity.

These experiments did not prove or disprove the possibility of crosslinking in such a system. The effects of thermally induced crosslinking were examined with reference to tensile and compressive properties of the fibers. Interpretation of results led to the following conclusions:

- Incorporation of a five-membered ring through fluorene moiety in PBZT showed a potential route to enhance the inherent uniaxial fiber compressive property.

- The limited experimental data on PBZT-FL system suggest that contrary to the polymer solution, the crosslinking in solid state is not sensitive to the detection techniques used in the current investigation.

- The tensile properties and x-ray crystal structure of PBZT remain unaltered by incorporation of 10 mole percent of fluorene.

Suggestions for future research based on results of these experiments include the following:

(1) Experiments should be conducted with a higher mole percent of fluorene in PBZT to establish and demonstrate the significance of crosslinking.

(2) Solid state C^{13}NMR may be a useful technique for studying crosslinking in the PBZT/FL system.

TASK: 10

TASK TITLE: Electrical and Optical Properties of High Temperature Superconductors

TASK OBJECTIVE: Exploit the recently discovered class of superconducting ceramic materials for applications in electronic and opto-electric devices.

SCIENTIST: Nils C. Fernelius, Ph.D.

DESCRIPTION OF WORK:

The aim of this task was to survey the rapidly growing literature in high temperature superconduction and identify application opportunities in the Air Force systems. The main sources of information for this task were libraries at the following institutions:

- Wright State University
- Wright-Patterson Air Force Base
- Air Force Institute of Technology
- University of Dayton
- Penn State University.

Major breakthroughs in high temperature superconductivity were noted to include the following work:

- BiSrCaCuO exhibited superconductivity with critical temperatures at 78K and 105K. This is the first high temperature superconductor which did not contain a rare earth.

- University of Arkansas and IBM Almaden achieved superconductivity at 125K with a TlCaBaCuO compound. Sandia has made films of the compound with outstanding current carrying properties.

- Bell Labs reported that a $Ba_{0.6}K_{0.4}BiO_3$ perovskite exhibited superconductivity near 30K. This is the first high temperature superconductor not containing copper.

Technical writings were evaluated and professional organization meetings, technical talks, and briefings were attended.

A review was made of recent and on-going research in superconductivity conducted by the following groups:

- Superconductivity group at WPAFB

- Physics Department at Ohio State

- UDRI Group

- Edison Materials Technology Center (EMTEC)

- Ohio University in Athens

- University of Dayton.

TASK: 11

TASK TITLE: NDE Signal Processing Research

TASK OBJECTIVE: Identify and/or develop improved signal processing methods for the quantitative extraction of flow information from ultrasonic and x-ray data and images.

SCIENTIST: Prasanna Karpur, Ph.D.

DESCRIPTION OF WORK:

The aim of this project was to explore the usefulness of a two-dimensional pseudo-Wiener filter for ultrasonic image enhancement in nondestructive evaluation (NDE) applications.

Experiments conducted during this investigation demonstrate that the method improves resolution in both surface images and internal images in composite material and stainless steel. For a successful implementation of the technique, the following steps are necessary:

- Any edge discontinuity must be removed by subtracting the average edge amplitude from the entire image.

- The PSF and the image amplitudes should be normalized to identical ranges.

- If the transducer is known to have a symmetrical field, an analytical Gaussian PSF can be used in place of the experimentally obtained PSF of the transducer.

TASK: 13

TASK TITLE: Spectral Response of Metal-Insulator Composites

TASK OBJECTIVE: To develop the theory of particle size effects upon the spectral characteristics of metal particles embedded in a transparent host.

SCIENTIST: John Zetts, Ph.D.

DESCRIPTION OF WORK:

The purpose of this effort was to extend the Maxwell-Garnett theory of absorption by small metal particles to include size effects upon the performance of metal insulator composite absorption filters. Three works which remain as cornerstone theories for predicting the optical/dielectric properties of inhomogeneous media are compared and recent modifications to them are discussed:

- Maxwell-Garnett (MG) theory predicts optical absorption of a two-component inhomogeneous mixture, yielding an expression for the effective dielectric function (EDF) of such a medium in terms of the dielectric functions of the metal spheres and of the insulating matrix.

- G. Mie, using a different approach, published a theory of the absorption and scattering of light by small metal spheres.

- Bruggeman published an alternative theory which later became known as the effective medium theory (EMT) or as the Bruggeman self-consistent (BSC) theory.

Using silver as the metal component and glass as the insulator, the investigator gleans general trends for the absorption bands (predicted by the theory) and derives nearly exact analytical expressions for location, strength, and width of the absorption bands. These calculations were based on the classical model for electromagnetic properties of metals developed by Drude in 1900;

however in some cases the dielectric function of the metal does not behave according to that model.

Discussions are presented to explain modifications to the calculations which were designed to accommodate particle size dependence, shape variations, and clustering.

Interpretation of results leads to the conclusion that MG theory is moderately successful in predicting the absorption properties of metal-insulator composites, with the degree of success increasing as the metal volume fraction (MVF) approaches zero.

TASK: 14

TASK TITLE: Validation of ALPIDT by Physical Modeling

TASK OBJECTIVE: To develop heat transfer coefficients for use in Analysis of Large Plastic Incremental Deformation Thermal (ALPIDT) and to measure die/workpiece interfacial friction coefficients in order to model precision forging of aerospace alloys.

SCIENTIST: Vinod K. Jain, Ph.D.

DESCRIPTION OF WORK:

The aim of this task was to develop interface parameters and physical properties of workpiece and roll material for modeling the USAF TiAl sheet rolling process.

The task required experimental determination of the following parameters:

1. Friction factor as a function of pressure, lubricant film, and surface roughness.

2. Heat transfer coefficient between TZM and TiAl as a function of pressure and lubricant film.

3. Contact electrical resistance as a function of pressure, temperature, and lubricant film.

4. Physical properties: electrical resistivity, thermal conductivity, specific heat, and coefficient of thermal expansion of TZM and TiAl as a function of temperature.

Lubricants affect workpiece surface quality, grain structure, mechanical properties, dimensional consistency, and load and energy requirements. They also affect separation between the workpiece and die and promote long die life. The ring compression test is useful in predicting the function factor between TiAl rings and TZM dies. Preparations were made to accommodate performance of TiAl ring compression tests, measurement of the heat transfer coefficient, and measurement of contact electrical resistance:

- Selection of 700-ton press due to its high temperature chamber which can provide an inert environment.

- Redesign and fabrication of dies and tooling to accommodate the TZM-TiAl combination.

- Determination of physical properties by Thermophysical Properties Research Laboratory (TPRL), Purdue University.

TASK: 15

TASK TITLE: Optimization Methods for the Forging Process

TASK OBJECTIVE: To identify opportunities for employing advanced optimization methods into the forging design process using modern analytical techniques for effective use in the processing of materials.

SCIENTIST: Ramana Grandhi, Ph.D.

DESCRIPTION OF WORK:

The purpose of this research project was to evaluate the feasibility of using an interdisciplinary environment in the manufacture of a turbine disk, a forging process. The goal was to integrate manufacturability considerations with a strength design for improving performance, manufacturing cost, and efficient use of expensive materials. A multilevel approach was used which stressed the following:

- Integration of multiple disciplines
- Optimization among competing requirements
- Design for performance and manufacturability
- Shape design.

A turbine disk forging process simulation was performed using the slab method. This was followed by a strength analysis using Axisymmetric Finite Elements.

Design optimization involved the following:

- Selection of performance function and design variables
- Shape description using B-splines or Bezier functions
- Sensitivity analysis with respect to design parameters
- Solution of numerical optimization problem
- Automatic mesh generation.

TASK: 16

TASK TITLE: NDE Theoretical Ultrasonics Research

TASK OBJECTIVE: Develop and derive new theoretical models of wave propagation in multilaminated composite materials.

SCIENTIST: Adnan Nayfeh, Ph.D.

DESCRIPTION OF WORK:

The purpose of this research project was to investigate the mechanical problem of the simulation of ultrasonic wave propagation in various types of composite materials. New theoretical

models were to be derived for the description of guided waves in multilaminated fibrous composites. This area was chosen for detailed study for the following reasons:

(1) When an acoustic beam propagating in a fluid falls onto the surface of a plate, mode conversion between the acoustic wave and a guided plate wave will occur if the fluid wave vector projection equals the wave vector of the guided plate wave which then loses its energy through radiation damping to an acoustic wave in the fluid.

(2) In the propagation of guided electronic waves and beam reflection in orthotropic plates fully immersed in a fluid, the onset of strong node conversion between the two wave types is accompanied by a sharp minimum in the magnitude of the reflection coefficient.

(3) If a fluid is present on only one side of the plate, the reflected field contains all (or most if there are absorptive losses) of the incident energy.

This study demonstrated experimentally the reflection of a finite acoustic beam from an isotropic solid plate coupled on one surface to a fluid, and calculated the response of a similarly coupled orthotropic plate to an acoustic plane wave. The investigation introduced viscous damping into the reflection model, particularized the calculation to an isotropic solid, and approximated the finite beam by an integral of the plane wave reflection coefficient times the spatial beam transform over the incident wavevector. The effects of viscosity and the finite beam on the reflected field are separately demonstrated and generally good agreement is found between model calculation and experiment. It is shown that the finite beam alone modifies the plane-wave reflection coefficient substantially, whereas the introduction of viscosity exerts a smaller but still important influence.

TASK: 17

TASK TITLE: NDE Research in Fluid-Coupled Plates

TASK OBJECTIVE: Derive and extend experimental and theoretical understanding of fluid-coupled ultrasonic waves in low-density, uniaxial composite materials.

SCIENTIST: Stanislav Rokhlin, Ph.D.

DESCRIPTION OF WORK:

The purpose of this task was to investigate by computations and by experiments the problem of ultrasonic guided waves in plates with the goal of elucidating the influence of fluid coupling, initially on isotropic materials, with eventual extensions to unilaxial composite plates of low-mass density. This study involved the deformation of leaky Lamb wave (LLW) spectrum in fluid-loaded plates and was undertaken to resolve an inconsistency identified below:

(1) If an elastic layer is loaded by an ideal liquid, the propagation of Lamb waves will be accompanied by radiation of energy into the liquid if the phase velocity of these waves exceeds the sound velocity in the liquid. For this reason Lamb waves in a plate loaded by a liquid are called "leaky Lamb waves."

(2) It has been generally accepted that for most practical cases the Lamb wave spectrum is only slightly perturbed due to the presence of the liquid. Such small perturbations may be easily calculated by series expansions in the ratio of the liquid density to the plate densities. It has been shown that the velocity is perturbed only in the second order term,

and the attenuation in the first order term. This approximation was thought to be satisfactory in all cases of practical significance, except near the cutoff frequencies.

(3) In contrast, investigators have recently found that for leaky Lamb waves in a fluid-coupled graphite-epoxy composite plate there appears a strong anomaly which completely changes the topology of the S_o mode as a function of frequency. They have also shown that the same anomaly may be induced in calculations in an aluminum plate immersed in heavy liquids.

In the course of this project, topological variations in the spectrum were examined under fluid loading as well as global modifications of LLW spectrum in heavy liquids. Interpretations of results led to the following conclusions:

(1) Regarding the nature of the anomalous dispersion of leaky Lamb waves, understanding of the spectrum topology is dependent upon consideration of the full complex wave spectrum consisting of both propagating and nonpropagating modes. Increasing fluid-solid density ratio leads to interaction and mutual exchange between portions of various mode branches, the first and most prominent of these being the interaction of the S_o and S_1 modes at low frequency.

(2) As the fluid density increases from zero to infinity, the plate waves are gradually transformed from a Lamb wave spectrum in a free plate to one appropriate for plate mixed boundary conditions. A plate with such boundary conditions admits a solution corresponding to a nondispersive bulk longitudinal wave. As the fluid density increases, calculations show a piecewise transformation of various modes to the predicted longitudinal wave V_1. By successive interchange of mode segments whose wavespeed is near V_1, a mode branch develops which displays less and less dispersion around the bulk longitudinal wavespeed. For fluid-solid density ratios of about 3, the wave spectrum has entirely lost its Lamb wave character. Above a density ratio of about 10, the propagating branches have completely transformed to a spectrum for the mixed boundary conditions.

TASK: 18

TASK TITLE: Advanced Base Fluid and Additive Synthesis

TASK OBJECTIVE: To provide technical guidance to WL/MLBT in-house and additive synthesis programs.

SCIENTIST: Christ Tamborski, Ph.D., Fluidics, Inc.

DESCRIPTION OF WORK:

The purpose of this project was to provide technical consultation and advice to WL/MLBT programs. Assistance was delivered in several technical areas:

(1) For the nonflammable hydraulic fluids program data were provided for inclusion in guidelines for the synthesis and manufacture of chlorotrifluoroethylene-based fluids.

(2) Experimental data were reviewed for inclusion in two manuscripts: "Perfluoroalkylation of Bromoheterocyclic Compounds via Perfluoroalkylcopper Intermediates," and "Polyfluoroalkylation of Bromoaromatic Compounds via Perfluoroalkylcopper

Intermediates."

(3) A literature search was performed to acquire information on reduction procedures for chlorosilanes resulting in hydrides used in the synthesis of silahydrocarbon fluids for hydraulic fluids application.

(4) A Materials Laboratory contractual review was attended and topics reviewed included model compounds synthesis, model fluids synthesis, and additives for antirust and lubricity improvement for chlorotrifluorethylene fluids.

TASK: 19

TASK TITLE: Development of Model Ceramic Composites

TASK OBJECTIVE: Development of a model composite system for determination of basic principles governing the behavior of brittle matrix composites.

SCIENTIST: Amit Chatterjee, Ph.D., Adtech Systems Research

DESCRIPTION OF WORK:

The purpose of this project was to evaluate several experimental techniques and associated mathematical formulations for characterizing the fiber matrix interface which would lead to a better understanding of the processes of crack propagation and failure of these composites. This research was precipitated by the following:

(1) Considerable efforts are being made to control the interface or interphase strength in ceramic composites but there is a lack of adequate experimental techniques to quantitatively determine these properties.

(2) The relationships between chemistry, mechanical properties, and composite performance have not been well established.

A major concern in the choice of systems is the thermal expansion mismatch, between the fiber and the matrix, which leads to different residual stress states in composites. The objective of this research was to explore the feasibility of producing model unidirectional composites and studying the effect of the residual stress states produced by the thermomechanical mismatch on the failure modes in these systems.

Glass matrix composites were selected as the fiber-matrix system due to ease of fabrication, low cost, and high performance. Other favorable attributes included its viscous flow characteristic, low density, and physical and chemical stability at elevated temperatures. The choice of fibers was limited to availability of those having a uniform diameter, stability at high temperatures, and nonreacting with the matrix; therefore, a silicon carbide fiber was chosen.

Processing parameters were established and specimens fabricated. Then the specimens were tested, determining dependencies of composite properties on constituent properties.

TASK: 20

TASK TITLE: Behavior of Rapidly Solidified Titanium Alloys

TASK OBJECTIVE: To investigate behavior of titanium alloys exposed to rapid solidification.

SCIENTIST: Challapalli Suryanarayana, Ph.D.

DESCRIPTION OF WORK:

The aim of this task was to investigate the nonequilibrium behavior of titanium base alloys and intermetallics, performing theoretical calculations to predict magnitudes of results and to compare predictions with actual experimental data.

Rapid Solidification (RS) and Mechanical Alloying (MA) can result in one or more of the following constitutional and microstructural modifications which can strengthen the alloy and contribute to the enhanced mechanical behavior of the systems:

(1) refinement of grain size, second-phase particles, or segregation patterns
(2) extension of solid solubility limits
(3) formation of nonequilibrium crystalline or quasicrystalline intermediate phases
(4) production of metallic glasses.

Experimental techniques used to characterize the material included: transmission electron microscopy, optical microscopy, x-ray diffraction, and differential scanning calorimetry/differential thermal analysis.

Specific systems were investigated and results obtained leading to the following conclusions:

(1) Consolidation of titanium-magnesium alloys using hot-isostatic pressing or vacuum-hot pressing was not satisfactory.

(2) X-ray diffraction patterns recorded from niobium-silicon and titanium-silicon alloys indicate formation of amorphous phases.

(3) Intermetallic phases, especially based on titanium, have potential for high-temperature applications. The rate of coarsening of the dispersoids in the MA alloy is much slower than in the RS alloy, and results suggest that mechanical alloying can be a better processing method than rapid solidification for achieving a homogeneous distribution of the dispersoids.

TASK: 21

TASK TITLE: Inference and Knowledge Representation

TASK OBJECTIVE: To provide a processing engineer with the ability to prototype new and existing manufacturing control methods.

SCIENTIST: Anca L. Ralescu, Ph.D.

DESCRIPTION OF WORK:

The aim of this investigation was to develop useful techniques for designing a knowledge-based automated process control system capable of supporting different inference strategies and capable of enhancing the current qualitative physics theory by including the capability to reason about relations in terms of their strength.

The Conceptual Structures theory presented here provides a dynamic knowledge representative structure whose basic features are type hierarchy and the join operation. Several of the theory features are yet to be investigated. The architecture of the proposed knowledge base was described in layers and examples were provided to illustrate the theory application.

TASK: 22

TASK TITLE: Growth of Novel Thin Film High Temperature Superconductors

TASK OBJECTIVE: Growth and characterization of new novel composition high temperature superconductive films for microelectronic interconnect technology.

SCIENTIST: Spencer K. Porter, Ph.D.

DESCRIPTION OF WORK:

The purpose of this project was to improve methods for making superconducting materials and thin films. The investigator formulated, annealed, and prepared substrates of bismuth, strontium, calcium, and copper to serve as targets for pulse laser evaporation. Experimental techniques for making and characterizing the materials included thin film x-ray diffraction and Auger electron spectroscopy. Mixed oxides were synthesized by solid-state reaction, calcination, pressing, and sintering.

A theoretical study of the magnetization curves was conducted and a model was formulated for the action of the superconducting oxides.

TASK: 23

TASK TITLE: Heuristic Engineering Design Assistance

TASK OBJECTIVE: Provide assistance to a design engineer by using heuristic programming techniques and cumulative fatigue damage theory to model past performance.

SCIENTIST: George R. Doyle, Jr., Ph.D.

DESCRIPTION OF WORK:

It was the purpose of this project to develop a system to estimate past performance and reliability by extending stress concentration theory to apply to geometric features in finite plates of aluminum, steel, or titanium. The system addressed fatigue damage and other fatigue theories in order to analyze parts with stress concentrations.

A system was created in Common LISP and gives the user choices in specifying features, loadings, and various material properties. The program determines the possibility of crack initiation over a specified number of loading cycles.

TASK: 24

TASK TITLE: The Surface Primitive Approach to Design with Features

TASK OBJECTIVE: To develop knowledge-based expert system tools which will aid in Computer Assisted Design for Manufacturability.

SCIENTIST: K. R. Halliday, Ph.D.

DESCRIPTION OF WORK:

The aim of this project was to formulate a generic procedure for constructing the features used in Computer Assisted Design systems from the set of Surface Primitives and to investigate the use of associative database management systems.

Activities consisted of the following:

(1) A standard set of mechanical parts was collected. A graphical representation was constructed for each part and descriptions of components were placed in an associative database.

(2) A comprehensive set of design features was identified, described, and placed in an associative database.

(3) Parametric descriptions of the individual surface primitive elements were identified, constructed, and associatively linked.

(4) A general attributes list for surface primitive elements was identified and defined.

TASK: 25

TASK TITLE: Product/Process Design

TASK OBJECTIVE: To formalize product design and manufacturing process design activities reflecting advanced producibility concepts.

SCIENTIST: John P. Eimermacher, Ph.D.

DESCRIPTION OF WORK:

The purpose of this project was to identify potential areas where advanced computer technology could be used to automate design activities. Data were gathered which identified information requirements, procedures, and relationships to design activities which could be used for AI/expert system development.

Product design efforts were investigated to determine the steps that are consistently taken during the iterative process. A table was constructed to demonstrate considerations and constraints which impact process design. Concurrent engineering concepts were discussed with attention to integrating business, design, and manufacturing operations to facilitate and enhance efficiency of producibility. Interaction requirements associated with the product development cycle are addressed throughout the development phase, involving appropriate functional departments within the organization.

TASK: 26

TASK TITLE: Analysis of Thick Laminates

TASK OBJECTIVE: To determine the number of independent constants that will describe the behavior of thick laminates under in-plane and bending loads.

SCIENTIST: Steven P. Wanthal, Ph.D.

DESCRIPTION OF WORK:

The goal of this research was to develop displacement based finite elements which can model both transverse-shear and transverse-normal deformations in a thick laminate. Displacement based elements are the most widely used variety of finite elements because they are accurate and simpler than hybrid stress elements.

Three quadrilateral finite elements were developed for the analysis of thick laminated composite plates. The elements differ in their ability to model the transverse-normal and transverse-shear strains in each laminate layer. All three elements are based on a layerwise modeling approach which has proved to be very accurate in the analysis of thick sections with severe transverse-shear effects.

The first element is the simplest of the three and works well for moderately thick plates in which the transverse-normal strains can be ignored. The second element is shown to be comparable to the first element except it has the ability to model transverse-normal deformation also. The third element is the most complex, but shows the ability to model transverse-shear deformation more accurately than the first and second elements. The third element also converges faster than the others, allowing problems to be modeled using fewer degrees of freedom.

These finite elements have the capability to analyze thick laminated composites under severe transverse-shear deformation. The layerwise approach allows the deformations within each layer to be modeled instead of assuming a single function to approximate the deformation shape for the whole laminate thickness as previous finite elements have done. These finite elements can be of use to engineers who need to analyze thick composite laminates more accurately than previous simplified elements have allowed.

TASK: 27

TASK TITLE: NDE Signal Processing Research

TASK OBJECTIVE: Identify and/or develop improved signal processing methods for the quantitative extraction of flaw information from ultrasonic images.

SCIENTIST: P. K. Bhagat, Ph.D.

DESCRIPTION OF WORK:

The aim of this project was to define the limitations and range of applicability of deconvolution procedures in assessing the deleterious effects of noise. The study attempted to extend existing signal processing routines to extract flow information from ultrasonic image data generated in a noisy environment to identify algorithms which are least sensitive to the noise yet capable of providing good defect resolution.

Current techniques of signal processing which are based on time series modeling of data provide sound mathematical insight but seldom consider physical aspects. Inversion procedures used for flaw sizing assume known source wavelet and noise statistics. Building on time series models several alternatives were investigated to quantify noise spectrum relating to operating data. Main areas of interest included the following topics:

- Model Based Deconvolution
- Nonharmonic Signal Decomposition
- Noise Analysis
- Adaptive Filtering Approach
- Software Development and Implementation
- LMS Algorithm.

Programs developed during this study were tested for accuracy in modeling time series data with excellent agreement. Results indicate that ultrasonic data can be modeled in terms of time series, and meaningful interpretation of noise spectra can be made.

TASK: 28

TASK TITLE: Analysis of Patched Repair of Composite Laminates

TASK OBJECTIVE: To model a damaged composite laminate with a doubler as reinforcement.

SCIENTIST: David Chu, Ph.D.

DESCRIPTION OF WORK:

The purpose of this project was to develop an efficient algorithm as part of a finite element method of analyzing damaged composites under different operational conditions.

Extensive discussions were undertaken with experts in the area of specialization in order to determine the algorithm and the appropriate model. Information was compiled and input parameters determined. The resulting system consists of the following:

- Two separate systems to be integrated later, namely a pre-processing part and a numerical calculation part
- User friendly mouse-menu and window control system
- System modules, the main work residing on the Material Library module
- Control at sub-command level
- Boundary condition module consisting of bending and in-plane displacement
- Graphical interface to the operator.

TASK: 29

TASK TITLE: Polymers

TASK OBJECTIVE: Synthesis of Ordered Polymers

SCIENTIST: Mark Sinsky, Ph.D.

DESCRIPTION OF WORK:

The purpose of this task was to investigate the synthesis of thermo-oxidative stable aromatic-heterocyclic polymers to be used as components in molecular composites or in the application requiring nonlinear optical activity.

Experimentation included variation of polymerization conditions and conventional characterization:

- Acidic solvents
- Oxidative cyclization
- Monomers in polycondensation reactions
- Temperature
- Hydrogenation.

The preparation of 1,7-diphenylbenzo [1,2-d:4,5-d^1]-diimidazole-2,6 dimethanol was accomplished in a five-step synthetic sequence in nearly 10% overall yield.

TASK: 30

TASK TITLE: Thermal Fatigue in Ceramic Matrix Composites

TASK OBJECTIVE: To evaluate the effect of mean stress on thermal fatigue in ceramic matrix composites.

SCIENTIST: Robert C. Wetherhold, Ph.D.

DESCRIPTION OF WORK:

The objective of this project was to evaluate the role of mean stress and residual stress on the thermal fatigue life of a representative ceramic matrix material, assessing the cyclic and mean strain which the material matrix undergoes.

Analytical modeling of the stress/strain behavior was designed to permit a full range of inelastic behavior of the composite constituents as well as to allow for nonequilibrium behavior of mechanical properties. Varying temperatures and loads to produce elastic cyclic strain in combination with inelastic strain allows prediction of dimensional stability and evaluation of lifetime implications of thermo-mechanical fatigue.

Experimentation led to the following conclusions:

- There is an environmental effect as well as a mean stress effect

- The dead load does not affect the permanent set of the material
- Environmental surface degradation was demonstrated.

TASK: 31

TASK TITLE: Processing Maps for Moldable Raw Materials

TASK OBJECTIVE: To develop constitutive equations for the class of moldable raw materials which includes liquid and solid metals.

SCIENTIST: Venkat Seetharaman, Ph.D.

DESCRIPTION OF WORK:

The goal of this task was to develop constitutive equations derived from a dynamic material model to predict material behavior during the solidification process. Interest in expanding the scope of the casting models in order to predict the micro/macrostructure and compositional distribution occurring at different locations of the castings was precipitated by the following:

(1) Traditional models of solidification have focused on heat transfer aspects and are used for calculation of paths of isotherms through shaped castings.

(2) Major concern of these models is to predict the hot spots in castings and risering systems.

(3) Numerical models based on the Finite Difference Method (FDM) and the Finite Element Method (FEM) have been used successfully in the design of complex castings.

(4) It is now possible to provide quantitative descriptions of the solidification phenomena and to fit solidification microstructures into a logical framework.

Investigations into calculating the thermodynamics of solidification took into consideration the following:

(1) In the case of macroscopic solids the solidification rate increases through levels of equilibrium:

- Full diffusional (global) equilibrium
- Local interfacial equilibrium
- Metastable local interfacial equilibrium
- Interfacial nonequilibrium

(2) In microscopic solids the free energy of a small particle increases inversely with its size or radius of curvature.

(3) Nucleation processes play a key role in the solidification of castings by controlling to a large extent the initial structure type, size scale, and spatial distribution of the product phases.

Information required for the casting microstructure model included:

- Chemical composition of the alloy
- Thermophysical properties of the alloy
- Geometry and size of the mold
- Thermophysical properties of the mold

Investigators conducted detailed studies on macrostructure, morphology of the solid-liquid interface, and microsegregation.

In the process of constructing a dynamic model for casting the following activities were accomplished:

(1) A dynamic material model for plastic deformation, chemical reactions, and hydrodynamics was investigated.

(2) Comparative features of deformation and casting were discussed from the dissipation theory viewpoint.

(3) Interrelationships between solidification velocity and temperature gradient were determined for a given system.

(4) Rapid solidification experiments were studied as an example of interface reaction kinetics in high-mobility systems in which interface motion cannot be thought of as heat-flow or diffusion limited.

TASK: 32

TASK TITLE: Rapid Solidification of Titanium Aluminides

TASK OBJECTIVE: To evaluate the effects of alloy chemistry on the behavior of a rapidly solidified Ti_3Al alloy.

SCIENTIST: Dan Eliezer, Ph.D.

DESCRIPTION OF WORK:

The objective of this study was to subject advanced titanium alloys to hydrogen degradation at different partial pressures, temperatures, and soak times in order to perform thermochemical evaluations of results using electron microscopy.

Embrittlement by hydrogen depends on the details of the specific hydrogen interaction and transport processes involved and on the anticipated design application of the material. Although the primary form of degradation of titanium base alloys is hydride formation, a form of lattice bond interaction can occur as well.

The experimental procedure was carried out on the Ti-24Al-11Nb alloy. Interpretation of results led to the following conclusions:

(1) The formation of hydrogen induced main transgranular cracks, microcracks among the needles of the acicula microstructure, and fine microcracks within the needles.

(2) Selected area electron diffraction patterns and x-ray studies revealed the existence of a hexagonal phase, with lattice parameters close to the alpha-2 phase and the existence of a new ordered phase that can be produced by a small distortion of the alpha-2 phase.

(3) The results of the cathodic hydrogen charging process revealed the formation of a hydride phase, probably based on the Ti-Nb-H composition.

TASK: 33

TASK TITLE: Engineering Analysis of Fracture of Composites

TASK OBJECTIVE: To perform engineering and experimental analyses on the fracture surfaces of composite materials.

SCIENTIST: S.C. Max Yen, Ph.D.

DESCRIPTION OF WORK:

The purpose of this task was to conduct a theoretical analysis of fracture surfaces formed when specimens having different ply orientations failed, and then to develop a test plan, specimen configuration, and test fixture to evaluate crack growth rate effects on topology. A detailed stress analysis and design of a composite rotor blade began with the mathematical modeling of the rotor into a composite skin and a foam core.

Factors considered in the determination of loading conditions included:

- Shear force and bending moment due to weight
- Shear force and bending moment due to drag
- Centrifugal axial force.

Methods used to determine stress distribution in composition skin and foam core due to transverse-shear force, bending moment, and axial force included:

- Transformed section method
- Stress distribution due to axial force
- Failure Criterion
- Assessment of factor of safety.

A computer program was written in BASIC to perform analytical procedures including geometrical modeling, calculation of loading condition, generation of the transformed sections, and determination of the factor of safety. Other work involved:

- Evaluations of the stiffness and strength of rotor using different materials and laminates
- Set up of step-by-step design procedures
- Introduction of a proposed manufacturing process
- Recommendations for study of engineering aspects of analysis, design, and manufacture of composite rotors.

Interpretation of results of this analysis led to the following conclusions:

- A rotor made of composite skin and foam core is achievable

- Composite rotor is much lighter than a steel rotor and has a higher factor of safety
- Design of the rotor requires stress analysis on every cross sectional area, not just the end section which may not be the most critically stressed region.

TASK: 34

TASK TITLE: Polymers

TASK OBJECTIVE: Computer Modeling of Ordered Polymers

SCIENTIST: Barry L. Farmer, Ph.D.

DESCRIPTION OF WORK:

The researcher investigated the conformations of new ordered polymers via computer modeling techniques designed to address their solubility and mechanical properties.

A survey was made of the possible conformational effects of various substituents at the ortho position of the phenyl ring in poly-p-phenylene benzobisthiazole (PBZT) and poly-p-phenylene benzobisoxazole (PBO) molecules. Methyl, ethyl, hydroxyl, tertiary-butyl, and benzthiazole substituents on PBZT and methyl, ethyl, hydroxyl, t-butyl, and phenyl substituents on PBO were investigated with the following findings:

(1) The parameter for the torsional potential for the rotation about the single bond between phenyl and heterocyclic rings was determined using semiempirical molecular orbital calculations.

(2) Figures were presented to show each molecule with the atoms labeled to define the torsion angles, the contour map of the energy versus the torsion angles, and a view of the molecule in the lowest energy conformation.

A molecule of the pendant PBZT was built using the ChemX default geometrical parameters. The lowest energy conformation resulted from a cyclic optimization of each of the molecules when the two ends are different.

In studying the conformational properties of the polyphenylenes the torsional parameter value was determined to be two to three times that found most appropriate for the rotation about a single bond between rings in PBZT and PBO.

In building molecular fragments for analyzing the trajectories of rigid-rod polymers, the optimized repeat units were coupled together within the ChemX environment. Investigation demonstrated that the introduction of one or a series of fluorene units has a dramatic effect on the trajectory of the polymer molecule.

TASK: 35

TASK TITLE: Polymers

TASK OBJECTIVE: Synthesis of Ordered Polymers for NLO Properties

SCIENTIST: Richard S. Valpey III, Ph.D.

DESCRIPTION OF WORK:

The aim of this task was to synthesize a new class of monomers for use in developing rigid-rod aromatic heterocyclic polymers which would be expected to exhibit strong nonlinear optical (NLO) behavior. Synthesis of the requisite monomers included studying polycondensation conditions.

Interest in this area has been stimulated due to DOD developing new materials for aircraft structural components which traditionally have been manufactured from metals with high-strength polymers. Particular attention is focused on rigid-rod aromatic heterocycles which when processed properly possess extraordinarily high tensile strength-to-weight ratios. These materials whose properties can be altered through the manipulation focus thick beam elements. Particularly, it solves the so-called "locking phenomenon," which is a major drawback of the other elements, and it will permit very fast and accurate analysis of thick beams.

Thick Plates

A special software was designed for the finite element analysis of rectangular composite panels. The 16-node thick-plate element with transverse shear was retained. A faster method for the formation and assembly of the stiffness matrices was derived and tested. It reduces the corresponding time to about 30% of its previous value and the total time is about 65% of its value. Further time improvements can be anticipated from possible future extensions of the method used. The requirements for the development of a user-friendly input part of the program were defined.

TASK: 36

TASK TITLE: Efficient Finite Element Analysis for Micromechanics

TASK OBJECTIVE: To use finite element models to simulate failure of unidirectional composite materials under tension and compression.

SCIENTIST: George Verchery, Ph.D.

DESCRIPTION OF WORK:

The objective of this task was to use finite element analysis to efficiently model fiber matrix and interfacial strength of a unidirectional composite and to predict the mechanisms of failure through a progressive model. The task was divided into two parts.

Thick Beams

A theoretical analysis was performed and a new close-form solution was established for thick beams with transverse-shear (Timoshenko beams). From this solution, a new formulation for a thick beam finite element was derived for shape functions, elementary stiffness matrix, and consistent loads. This element provides a significant improvement, it solves the so-called "locking phenomenon," and permits very fast and accurate analysis of thick beams.

Thick Plates

Special software was designed for the finite element analysis of rectangular composite panels. The 16-node thick plate element with transverse-shear was retained. A faster method for the formation and assembly of the stiffness matrices was derived and tested.

TASK: 38

TASK TITLE: Further Investigation in Global-Local FE Model

TASK OBJECTIVE: Investigate the influence of different constituents and flaws on the response of layered composites.

SCIENTIST: Ten-Lu Hsaio, Ph.D., Adtech Systems Research, Inc.

DESCRIPTION OF WORK:

The aim of this project was to gain understanding of optimum performance capabilities of composites by using the global-local finite element model to predict the stress fields in composite laminates. In this model, 3D elasticity problems are transformed into 2D problems in a self-consistent approach that features realistic satisfaction of boundary and interface conditions. The study includes:

(1) The analysis of bending effects of laminates under prescribed uniform transverse load.

(2) The analysis of edge effects in laminates under applied uni-axial uniform tensile stress or strain.

(3) The analysis of edge effects in laminates under applied uniform curing temperature.

A set of boundary value problems was studied by local and global-local approaches: bending, thermal load, uniform inplane tensile stress, and uniform inplane tensile strain load.

Both local and global-local models were formulated using the weighted displacement or actual displacement and interlaminar stress components. Interpretations of results led to the following conclusions:

- The results of interlaminar stress components and weighted displacement for thermal load, inplane uniaxial tensile stress, and inplane uniaxial tensile strain load from the local model have the same trend as the literature predicts

- Convergence study of the global-local model indicates that the results for the constant strain applied load case are more stable than those for the constant tensile load case.

TASK: 39

TASK TITLE: X-Ray Synchrotron Topographic Studies in GaAs

TASK OBJECTIVE: Determine defect structure in selected GaAs samples, to include best grown materials, by synchrotron topography.

SCIENTIST: Stuart R. Stock, Ph.D.

DESCRIPTION OF WORK:

The objective of this project was to prepare x-ray topographs of GaAs samples at a synchrotron x-ray source and to analyze the results.

The project began with discussions on previous results and planning of future experiments. Experimentation was conducted at Stanford Synchrotron Radiation Laboratory (SSRL) and at the National Synchrotron Light Source (NSLS) to obtain polychromatic x-ray topography of the selected GaAs samples.

Based on analysis of results, the hypothesis that persistent photocurrent (PPC) is related to dislocation structure remains viable; however, dislocation-related mechanisms may provide only a part of the explanation of PPC.

Recommendations for future study include the following:

- Characterization efforts with topography should be continued with the aim of improving understanding of the PPC effect in semi-insulating GaAs
- Characterization of the GTE horizontal Bridgman Crystals will also be important; the effect of microgravity on solidification and crystal quality will be an important contribution
- The monochromatic topography of the interface breakdown should be further investigated
- The cause of the PPC effect in semi-insulating GaAs should be investigated.

TASK: 40

TASK TITLE: *Optical Properties of Inhomogeneous Media*

TASK OBJECTIVE: To develop the theory of the effect of conductivity, ordering, and host dielectric function upon the optical response of inhomogeneous visible and near-infrared media.

SCIENTIST: John Zetts, Ph.D.

DESCRIPTION OF WORK:

The thrust of this task was to extend the effective medium theory as an improvement of the Maxwell-Garnett (MG) theory in order to:

- Compare it to experimental data
- Determine if a simplified self-consistent algebraic version can be derived from integral formulations
- Treat the cases of zero resistivity and high resistivity
- Consider the effect of two- and three-dimensional ordering on the spectral response of inhomogeneous media.

The computational work during this task focused on the application of the general effective medium equation developed by Aspnes, and considered the Maxwell-Garnett theory, the Bruggeman self-consistent equation, and a Lorentzian absorption profile. From comparisons with the available experimental data on metal-insulator composites the original MG equation still

appears to give the best predictions in the limit of small metal volume fractions. The self-consistent equations do not give promise of an improvement to the MG equation as a better effective medium theory.

TASK: 41

TASK TITLE: Theoretical Investigation of Nonlinear Optical Material Response to Electromagnetic Waves

TASK OBJECTIVE: Formulate the problem of the nonlinear optical material response to electromagnetic waves such that the corresponding wave equations are solved analytically. Apply the results to problems in nonlinear optical phase conjugation.

SCIENTIST: David S. Moroi, Ph.D.

DESCRIPTION OF WORK:

Using a judicious choice of variable, the purpose of this task was to transform a nonlinear wave equation for electromagnetic waves in a nonlinear medium into a quasi-linear wave equation, solving the equation with standard perturbation method.

Nonlinear optical properties of barium titanate were analyzed using almost exact analysis of the polaritons on the boundary surfaces of layered material with intensity dependent dielectric functions. This resulted in an almost exact analysis of the propagation of electromagnetic waves in an optical barium titanate and a simiinfinite linear isotropic uniform medium with a plane surface boundary.

Recommendations for future work which resulted from this study include the following:

(1) Continue work on an analytical method of solution using transformation of variables and perturbation theory via quasi-linearization of the nonlinear optical wave equations.

(2) Extend the analytical method of solutions to solve the corresponding equations in the other two principal planes of the dielectric ellipsoid of barium titanate.

(3) Investigate the nonlinear optical properties of an optical system which consists of a layer of barium titanate between two semiinfinite linear isotropic uniform media.

(4) Study the nonlinear optical properties of an optical system which consists of several layers of nonlinear anisotropic optical materials surrounded by tow semi-infinite linear isotropic uniform media.

TASK: 42

TASK TITLE: Electronic Transport in the High T_c Superconductors

TASK OBJECTIVE: Prepare thin film and bulk high T_c superconducting materials; characterize their chemical, physical, and morphological features and their transport properties; relate processing conditions to optimization of transport

properties.

SCIENTIST: Izhar Bransky, Ph.D.

DESCRIPTION OF WORK:

The objective of this investigation was to use a variety of methods to prepare specimens of superconducting materials, then to characterize their properties and model their behavior.

Preparation of R-Ba-Cu-O specimens was made by calcination, sintering, and annealing in oxygen. Screening of superconducting properties was accomplished using AC susceptibility measurements, density measurements, and electrical measurements. Microstructural analysis was made by SEM to determine grain size, grain boundary structure, and porosities.

Critical transport current density measurements were carried out employing both magnetic induction and four probe techniques. The magnetic induction method resulted in J_c values 25% higher than those obtained by the four probe method; however, the four probe method tends to give lower values for I_c due to contacts heating.

TASK: 43

TASK TITLE: Laser Annealing

TASK OBJECTIVE: Laser anneal superconductor substrates such that underlying semiconductor materials are not affected by the anneal, and ohmic contacts are made to the superconductor.

SCIENTIST: Joseph Zahavi, Ph.D.

DESCRIPTION OF WORK:

The main objectives of this study were:

(1) To establish a high speed, direct, selective metallization process at ambient temperature on superconductive ceramic materials for low resistance ohmic contacts and conductive lines.

(2) To make sure of pulsed laser irradiation for metal or alloy disposition on superconductive ceramic material immersed in nonwater based plating without external power and without masking procedures.

(3) To characterize formation conditions such as mode of pulse laser operation, laser energy intensity, wavelength, number of pulses, and type of plating solution to give desired metallization patterns with desired electrical properties.

The experimental setup used in this study consisted of three basic systems: a pulsed laser system, an electroplating solution cell mounted on a computerized X-Y table, and a computer controlling the movement of the X-Y table as well as synchronizing the laser irradiation with the table movement.

Selective, direct gold deposit formation via pulse laser irradiation was carried out from nonaqueous gold plating solution without external power or lithography procedures. Gold deposit content increased with an increase in laser number of pulses, overlapping percentage values, and laser energy per pulse. Patterned metallizations of gold were deposited on superconductor ceramic substrate forming low ohmic electrical resistant contacts on the high temperature superconductor without pre- and post-surface treatment of annealing procedure.

TASK: 44

TASK TITLE: Fatigue of High Temperature Composites

TASK OBJECTIVE: To characterize the fatigue behavior of advanced composites for turbine engines.

SCIENTIST: Narayanan Jayaraman, Ph.D.

DESCRIPTION OF WORK:

The object of this investigation was to conduct experiments for the purpose of evaluating the strength and fatigue behavior of candidate ceramic matrix and metal matrix composites using fractography and electron microscopy to characterize the damage and failure mechanisms in these materials.

A detailed research program description was prepared which included a critical review of the literature and a research plan in the area of ceramic matrix composites. As a result of this activity the area of long-term micro-mechanical response of these new materials under creep-fatigue environmental conditions has been selected for concentration of effort.

In the area of residual stresses, research was accomplished in the thermal and thermo-mechanical cycling of metal matrix composites. The feasibility of determining three-dimensional-residual stresses using an x-ray diffraction technique was demonstrated.

TASK: 45

TASK TITLE: Efficient Finite Element Analysis for Micromechanics

TASK OBJECTIVE: To use finite element models to simulate failure of unidirectional composite materials under tension and compression.

SCIENTIST: Antonio Miravete, Ph.D.

DESCRIPTION OF WORK:

The purpose of this task was to analytically model the fiber/matrix and interfacial strength of a unidirectional composite as well as to develop guidelines for the performance of composite materials and to define their mechanisms of failure. The work was focused on a specific application: the optimization of composite beams and plates.

The optimization procedure implemented into the Prime and Apollo computer systems consisted of two components:

(1) The Finite Element Method - a four-node isoparametric element based on the higher order shear theory and the penalty function method.

(2) The Optimization Procedure - a fully stressed iterative procedure in which laminate thickness and fiber orientation are modified in each step and quadratic failure criterion has been applied, strength/stress ratio being constant through the beam or plate.

Graphics were built for determining the behavior of tapered composite beams and plates. Mathematical formulas and figures showing the variable thickness through the beam or plate make it possible to easily calculate the thickness and fiber orientation.

TASK: 46

TASK TITLE: NDE Signal Processing Research

TASK OBJECTIVE: Identify and/or develop improved signal processing methods for the quantitative extraction of flaw information from ultrasonic and x-ray data and images.

SCIENTIST: Prasanna Karpur, Ph.D.

DESCRIPTION OF WORK:

In this investigation the researcher compared deblurring techniques for C-Scan Images to determine improved methods for minimizing the effects of the point spread function (PSF) or the transfer function of the transducer being used for imaging.

The Marr-Hildreth operator, an edge enhancement filter, was discussed along with presentation of the equation. The Weiner filtering process was described as almost an inverse of the convolution process which produced the blurr of the image and as an object estimate rather than an edge enhancement.

Results of the study led to the following conclusions:

(1) The Weiner filtering process can be implemented by using numerically simulated Gaussian point spread functions.

(2) The results of Weiner filtering indicate that the use of an underestimated point spread function will show lower ripples and artifacts; however, the use of a larger than actual point spread function will increase the ripples and distortions in the images.

TASK: 48

TASK TITLE: Polymers

TASK OBJECTIVE: Processing of Ordered Polymers

SCIENTIST: Swapan K. Bhattacharya, Ph.D.

DESCRIPTION OF WORK:

The scientist investigated the processing conditions for spinning new ordered polymer into fibers to address their compressive strength and other mechanical properties.

A thermoplastic hexafluoro poly-p-phenylene benzobisoxazole (PBO) flexible coil polymer was synthesized for high temperature applications and fiber processing was conducted by the in-house wet spinning method. The fiber had surface undulation and the diameter was not uniform; however, when stretched to a draw ratio of 8, the drawn fiber appeared to have a very uniform diameter with negligible surface defects as viewed in the optical microscope.

Poly-p-phenylene benzobisthiazole (PBZT) end capped with a bulky poly-2,5(6)benzoxazole (ABPBO) unit was synthesized and fiber processing was conducted by in-house wet-spinning method from a polyphosphoric acid dope. Fiber processing conditions were selected based on viscosity of the polymer dope as a function of frequency at various temperatures in a Rheometer. Tensile and compressive properties of heat treated fibers were evaluated from single filament tests. Maximum tensile strength was achieved at 700 °C and highest compressive strength was achieved at between 600 and 650 °C of both PBZT end capped with ABPBO and PBZT/Fluorene systems.

The morphology of PBZT was investigated by diffusing hydrogen sulfide gas to wet fibers soaked in silver nitrate solution. The fibers were then dried and microtomed for examination by transmission electron microscopy (TEM).

A polyachrylonitrile-based carbon fiber and a pitch-based carbon fiber were studied to determine reasons for higher compressive strengths of the former. Experimentation included the following procedures:

- Ball milling using an IR Amalgamator, and subsequent scanning electron microscopy (SEM) examination of the powders suspended in alcohol
- Embedding samples in epoxy for sectioning by microtomy
- Curing and dimpling of sample
- Ion milling for examination by TEM.

TASK: 49

TASK TITLE: Polymers

TASK OBJECTIVE: Rheology and Processing of Ordered Polymers

SCIENTIST: Kung-Hwa Wei, Ph.D.

DESCRIPTION OF WORK:

The purpose of this task was to investigate the rheology and rheo-optical properties of rigid-rod polymers and their relationships with fiber spinning strength operation.

Rheology of 14 percent of PBO/PBA dopes was investigated by means of a Rheometrics Mechanic Spectrometer. Complex viscosity was studied at different temperatures and steady-state

viscosity was studied at various steady shear rates. A typical viscosity increase occurred at high temperatures, a behavior that was reversible upon cyclic heating and cooling.

Differential Scanning Calorimetry (DSC) and X-ray measurements on PBO/PBA dopes were also carried out. The DSC curves do not show any sharp peak between 220 and 300°Centigrade.

Three fibers underwent gamma ray radiation crosslinking treatment: PBT, methyl PBT, and PMT/Fluorene. They were subsequently exposed to varying levels of radiation. Of the three, methyl PBT survived best and was sent for a compressive strength test. Initial test results indicate that compressive strength of the radiated methyl PBT fiber is higher than that of thermo-treated methyl PBT fiber.

TASK: 50

TASK TITLE: Polymers

TASK OBJECTIVE: Semiempirical computations of the nonlinear optical properties of ordered polymers.

SCIENTIST: Jorge Medrano, Ph.D.

DESCRIPTION OF WORK:

The aim of this task was to develop computer software for the calculation of the polarizability and the first and second hyperpolarizability tensor of ordered polymers, using their quantum wavefunctions. A semiempirical Modified Neglect of Diatomic Overlap/Austin Model 1 (MNDO/AM1) approach was chosen for the calculation of the wavefunction; however, a finite field approach and numerical methods were used for finding the necessary derivatives. This program is now being routinely used for the prediction of nonlinear optical properties of molecules. Comparison between calculated and available experimental results is favorable.

Tensors for large molecules were calculated, providing the first theoretical prediction of these values. The effect of different substituents on a given structure and the results of doping were also studied. The polarizabilities of some oligomers as functions of the number of repeat units were calculated to assess convergence properties. Because of the required periodicity of the perturbations, calculations could not be made for infinite polymers in the same way as they are for small molecules.

Studies performed on this task resulted in preparation of papers for publication: "Nonlinear Optical Effects in Organic Polymers" and "The Materials Science and Engineering of Rigid Rod Polymers."

A new theory and bonding were developed for periodic systems such as polymers and crystals. This theory is expected to help in understanding the relationships between chemical structure and nonlinear optical properties in organic polymers.

General conclusions drawn from this research are that the theoretical predictions obtained from a MNDO/AM1 calculation coupled with the finite field procedure seem to be reliable enough to predict general trends or the effect of different perturbations on the electron density of the molecules, and substituents that change the molecules effective conjugation length very little can have an important effect on third order nonlinearities.

TASK: 51

TASK TITLE: Molecular Composite Processing

TASK OBJECTIVE: To develop innovative processing approaches to fabricate molecular composite in bulk form for structure applications.

SCIENTIST: Allan S. Crasto, Ph.D.

DESCRIPTION OF WORK:

The researcher studied the coagulation, drying, and densification steps in the formulation of molecular composites in order to assess the impact of processing conditions on the properties of the molecular composites. Interest in this investigation was precipitated by the following:

- A molecular composite is a polymeric material in which rigid-rod extended-chain molecules are homogeneously dispersed in a flexible coil matrix, analogous to a chopped fiber composite, but with reinforcement occurring at the molecular level.

- Poly(p-phenylene benzobisthiazole) (PBZT) is an aromatic heterocyclic rigid-rod polymer that has excellent mechanical properties and thermal stability.

- Molecular composites of PBZT in a variety of flexible coil polymers have been processed from solution into fibers and thin films.

- It is theorized that with thermoplastic matrix, thicker sections (as required for structural applications) may be formed by consolidating these preforms under heat and pressure.

The approach for this task was to coagulate the entire solution directly into a block which could be consolidated to the desired dimensions, thereby eliminating interfacial boundaries in the final product. Methanesulfonic acid (MSA) and sulfuric acid (SA) were employed as solvents in this process. The MSA solution was coagulated under pressure with water, which diffused in through a porous base plate of a specially designed mold. Acid diffused out and the volume shrank as coagulation proceeded, yielding a compact block. It was reported that PBZT dissolved in sulfuric acid at temperatures in excess at 100 °C. As the temperature was lowered, the solution rapidly gelled. Addition of nylon to this solution did not hinder gel formation, and this process may be used to freeze in a homogeneous dispersion of PBZT and nylon molecules from dilute solution. Addition of water to the gel promoted coagulation, producing a block free of macroscopic voids.

TASK: 52

TASK TITLE: Polymer Morphology

TASK OBJECTIVE: High Resolution Electron Microscopy of Ordered Polymers

SCIENTIST: Stephen Krause, Ph.D.

DESCRIPTION OF WORK:

The objective of this task was to research the fundamental chemical and structural nature of various types of carbon fibers to better understand the basis for the high compressive strength of particular types of carbon fibers. Application of this knowledge could then be used to improve the compressive strength of rigid-rod molecular systems. Interest in this investigation was precipitated by the following:

- Carbon fibers now dominate the field as the fiber reinforcing component for the highest performance composites due to their thermal and environmental resistance and due also to their exceptionally high specific mechanical properties including tensile modulus, tensile strength, and compressive strength.

- Limitations to the performance of the carbon fibers for certain applications include cost, conductivity, brittleness, and low toughness of some fibers.

- Other types of fibers may be used alone or incorporated with carbon fibers in hybrid composites.

- Limitations to the application of high performance organic fibers (including PPTA-poly-p-phenylene terepthalamide, PBT-poly-p-phenylene benzobisthiazole, and PBO-poly-p-phenylene benzobisoxazole) are reduced thermal resistance and low transverse and compressive strength.

- Modifications to organic fiber compressive strength have been attempted through variations in chemistry and processing, but significant improvements have not been achieved.

For this study investigators examined the structure of a high compressive strength polyacryonitrile-based carbon fiber, T300, and the structure of a high modulus pitch-based carbon fiber, P120, using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and wide-angle X-ray scattering (WAXS). SEM fracture surfaces of T300 had a granular appearance with particles 100A to 300A in diameter and 'strings' of particles 1000A to 2000A long. TEM showed that the particles were probably platelets 80A to 120A in diameter and 40A to 80A thick. The platelets appeared to be composed of 40A crystalline which evidentally had a mosaic structure with individual crystallites slightly tilted out of the plane of the platelet. The platelets may be have been connected, although slightly twisted from one another, for distances of over 300A along the fiber axis. SEM fracture surfaces of P120 fibers showed curved sheets of graphite extending along the fiber axis with dimensions of 100A to 300A in thickness, 0.1 um to 0.6 um in width, and microns in length. There was limited connectivity between adjacent sheets.

TASK: 54

TASK TITLE: Polymer Morphology

TASK OBJECTIVE: Processing Morphology Determination of Ordered Polymer Fibers

SCIENTIST: Yachin Cohen, Ph.D.

DESCRIPTION OF WORK:

The objective of this task was to determine the morphology formed during the processing of ordered polymer fibers, in order to examine the potential for influencing the compressive strength of the final fibers by process modification. The crystal structure and morphological features of PBO/PPA solutions were investigated to find out what determines the dimensions of the microfibrillar morphology. It had been postulated that dimensions of the microfibrils, formed during coagulation, are the basic structural elements responsible for the compressive properties, so that the width of the microfibrils may be a limiting factor in achieving better compressive strength. If the microfibrils form during a transition from the liquid crystalline state to the crystalline solid state, then the kinetics of the transition may play an important role, particularly the nucleation of the crystalline phase. Therefore investigators were seeking information on the unit cells of the crystal solvate phases and on the microstructure in which the solvates exist in the PBO/PPA system. This morphology could be the precursor of the structure which eventually develops in the subsequent stages of the spinning process.

Former research results which fostered interest in this topic include:

- High performance PBO/PPA fibers and films are obtained by a spinning process which induces structural transformations into the system leading to the final material.

- Extrusion through a die followed by extension in an air gap results in a uniaxially oriented nematic solution which forms a solid state when coagulated in water.

- The microstructure formed during the coagulation stage is an interconnected network of oriented microfibrils less than 100A in diameter.

- Drying and heat treatments increase the chain orientation and the size of the coherently packed crystallites which increases the tensile modulus associated with the heat treatment process.

Experimentation was performed using the following techniques:

- X-ray diffraction from the solvated PBO/PPA system
- Small angle X-ray scattering from the solvated PBO/PPA system
- Transmission Electron Microscopy (TEM)
- Differential Scanning Calorimetry (DCS)
- Molecular Modeling of the Solvated State.

Interpretation of results led to the conclusion that the PBO/PPA solvated state occurs in several crystalline forms which coexist with a disordered amorphous phase. At low moisture levels the crystallites can be characterized as being of relatively large size and having relatively large unit cell dimensions. Despite the multiphase nature of the system, no noticeable small-angle scattering is observed indicating that the density difference between the two phases is not large. This would be the case whenever the solvate crystals contain a large quantity of poly-phosphoric acid (PPA) molecules and thus have a relatively low PBO content. It is possible that at least three different crystal solvate structures exist in this highly ordered form.

Exposure to moisture by absorption of atmospheric moisture results in a less ordered crystalline form which exhibits much smaller crystalline sizes as well as a smaller dimensions of the unit cell of the chain acis projection. The sequence of events in the transformation: the more-ordered crystallites are initially of large size and contain a large amount of PPA, thus their density

is not much different than that of the amorphous phase. When moisture is absorbed, it disrupts the large crystals, extracting PA molecules into small ones which have a lower PPA content and therefore lower density, and possible smaller unit cell dimensions. The crystallites in this state have a microfibrillar structure, and possibly persist even at elevated temperatures.

TASK: 55

TASK TITLE: Polymer Morphology

TASK OBJECTIVE: Structure Analysis of Ordered Polymers

SCIENTIST: Albert V. Fratini, Ph.D.

DESCRIPTION OF WORK:

The researcher investigated the crystal structure of ordered polymer fibers PBO and PBT by X-ray diffraction techniques, and determined the unit cell packing of the polymer chains by applying the Linked Atom Least Squares (LALS) method.

The determination of accurate unit cell parameters for ordered polymeric fibers is dependent on precise measurement of d-spacings for both equatorial and nonequatorial reflections. Film methods for recording diffraction data can yield precise measurement if care is taken to reduce air scatter, minimize sample size, and correct for a number of other factors such as background.

For this task, attention was focused on several rigid-rod polymers: PBO, PBT, and di-OH-PBT. In previous research it was observed that the extent of three-dimensional order in PBO and PBT was significantly enhanced following heat treatment and that d-spacings were relatively insensitive to heat treatment temperatures. Research activities for this task involved the analysis of diffraction patterns and the measurement of experimental diffraction data required for the structure determination of rigid-rod polymers.

TASK: 56

TASK TITLE: Polymer Morphology

TASK OBJECTIVE: To investigate and characterize the compressive strength of ordered polymer fibers by small angle scattering.

SCIENTIST: David T. Grubb, Ph.D.

DESCRIPTION OF WORK:

The object of this task is to investigate the morphology of ordered polymer fibers using small angle x-ray scattering (SAXS), to examine the capabilities of the MLBP Laboratory, and to recommend improvements.

SAXS is a standard technique for the investigation of the internal structure of polymeric solids. Most ordered polymers have a fine structure on the scale suitable for SAXS study and so give a scattering pattern. In the case of ordered fibers, a common form for this pattern is a continuous streak perpendicular to the fiber direction in the equatorial plane and a pair of discrete

but diffuse reflections on the meridian, that is, in the fiber direction. However, not all fibers have this pattern. Most rigid-rod high-performance fibers do not have discrete reflections and have only the equatorial streak; others have off-axis streaks and reflections indicating higher degrees of order. Some fibers, particularly those of natural origin, have a complex SAXS pattern with many reflections indicating a well-ordered three-dimensional structure on a large spatial scale.

The morphological information most often sought by SAXS is the concentration, shape, and size of the scattering objects. These may be crystals, voids, or fibrils. In synthetic polymer systems the objects are never uniform and the size distribution may be required; their density may not be known, and the SAXS only gives a product of density difference and volume fraction, not the concentration of scatterers. In the oriented fibers, the orientation distribution of the scattering objects may also be found, if the experimental data is of sufficiently high quality.

Special requirements of SAXS to accommodate the study of high performance fibers and, in particular, for the study of their compressive strength, include smaller sample volumes and a controlled environment for the samples while the x-ray data are being collected. This could be a controlled temperature or tensile stress environment, or it could be a liquid or vapor environment for the study of precursors and swollen fibers.

The MLBP x-ray laboratory at Wright-Patterson is capable of obtaining and analyzing x-ray scattering patterns from fibers and other polymer samples due to the presence of the following:

- powerful x-ray generators fitted with monochromators and diffractometers
- an excellent system of computers for the direct control of experimental equipment and for the off-line analysis of numerical or photographically obtained x-ray data
- well maintained and well aligned commercial cameras for small angle x-ray scattering
- sophisticated ancillary equipment with the capability of producing non-standard precision x-ray apparatus.

Highest priority should be given to keeping the data collection time below one week since beyond this time other factors make the apparatus impractical: systems failures, stability problems, impatience on the part of the researcher. Recommendations for improvements to the MLBP facility include:

- obtaining beam time at a synchrotron source of x-rays
- obtaining a small scale focusing camera of the Franks type mounted on an optical bench
- acquiring one-dimensional position sensitive detectors with a precise positioner for the beam stop and a photographic test with a strong scatterer.

TASK: 57

TASK TITLE: Polymer Morphology

TASK OBJECTIVE: Morphology of Compressive Failure in Ordered Polymer Fibers

SCIENTIST: Ronald K. Eby, Ph.D.

DESCRIPTION OF WORK:

The scientist evaluated ordered polymer fibers with respect to compressive strength structure/property relationships and with consideration to microstructural perfection as assessed by x-ray diffraction.

Basic research measurements were made to provide the scientific basis for the nonlinear elasticity of fibers made from poly-p-phenylene benzobisthiazole (PBZT) in terms of the physical ultrastructure. This property and its explanations are pertinent to the basic science of the compressive properties of the fibers. Specifically, x-ray diffraction was used to measure the crystal orientation distribution within some of these fibers as a function of static tensile stress. The crystal modulus was also measured by x-ray diffraction for some of these fibers. Improved crystal orientation with increased tensile stress is one of the most important mechanisms of the nonlinear elasticity.

Interpretation of results led to the following conclusions: Fibers of PBZT exhibit nonlinear elasticity for which increasing orientation of the crystal with increasing tensile stress is a major mechanism. However, changing orientation is not the sole mechanism. Another possible mechanism could involve dislocations and shearing on the hkO planes. The nonlinearity increases with temperature. In the range of 300 to 400 °C, PBZT exhibits a mechanical relaxation which is associated with a structural change in the same range. The structural change results from rotational oscillations of the phenyl and bisthiazole moieties about their single bond connection.

TASK: 58

TASK TITLE: Molecular Beam Epitaxy of Strained Layer Superlattices

TASK OBJECTIVE: Growth of superlattice materials by molecular beam epitaxy for use in Air Force optoelectronic applications.

SCIENTIST: Ming-Yuan Yen, Ph.D.

DESCRIPTION OF WORK:

The objective of this task was to study the growth of GaAs, AlAs, and AlGaAs by MBE so as to form the basis for growing sophisticated structures and to test the performance of the Materials Laboratory's new Varian Gen II MBE system.

Molecular Beam Epitaxy (MBE) has been demonstrated in the past to be a promising technique for growing high quality single-crystal semiconductor materials. There are several advantages of this technique over others:

- a slow growth rate which makes the growth of abruption junction possible
- low growth temperature which avoids the interdiffusion of the elements during growth
- an ultra-high-vacuum environment which minimizes the impurity incorporated to a large extent
- the availability of diagnostic equipments which improve the understanding of the growth mechanism and the control of the desired structure.

Experimentation was performed on the Varian Gen II Molecular Beam Epitaxy system. Elemental Ga, Al, and As were used as the beam source materials. Investigation of results led to the following conclusions:

- High quality GaAs, AlAs, and AlGaAs compound semiconductor materials were successfully grown by MBE.

- Reflection high energy electron diffraction (RHEED) intensity oscillations have also been observed for the materials during growth, leading to the control of the growth down to the submonolayer region.

- Photoreflectance measurements show that the materials are of high purity.

TASK: 59

TASK TITLE: Development of Model Ceramic Composites

TASK OBJECTIVE: Development of a model composite system for determination of basic principles governing the behavior of brittle matrix composites.

SCIENTIST: Amit Chatterjee, Ph.D., Adtech Systems Research

DESCRIPTION OF WORK:

The objective of this task was to determine processing routes, fabricate specimens, and test composite constituent materials selected to allow variation of residual stress states in order to determine dependencies of composite properties on constituent properties.

Successful development of composites depends on the knowledge of the intrinsic properties as well as the failure characteristics of these systems. The failure of a fiber reinforced ceramic composite is a complex process occurring in several stages. During tensile loading, failure may involve multiple matrix cracking, fiber matrix debonding, fiber pullout, and fiber fracture. To fully understand this failure process, model composite systems were employed where the important parameters could be systematically varied and failure processes observed.

Experimentation consisted of unidirectional model composites being fabricated with different borosilicate glasses and silicon carbide fibers to study the effect of residual stress states on the damage progression in these composites. A specially designed straining stage was employed to study the failure modes in these materials under stepwise loading. Although both fiber and matrix cracks were observed in all specimens, the mechanisms of failure were found to be different and were related to the interfacial properties in these materials.

Unidirectional silicon carbide fiber reinforced glass matrix composites were used as model systems to study the progression of damage under tensile loading, depending on the magnitude and the sign of the thermal expansion mismatch between the fiber and the matrix, different damage states were observed. In cases where the thermal expansion coefficient was smaller than the fiber, there were random matrix and fiber cracks with extensive debonding and matrix shattering at larger stresses. In the other case, when the matrix had a thermal expansion coefficient larger than the fiber, transverse matrix cracks were observed after processing. On further loading, fiber cracking was noticed close to the matrix cracks but there was no debonding at the interfaces and no loss of integrity of the specimen. Interfacial shear strengths were

comparable from pullout and pushout experiments but theoretical models overpredict the onset of matrix cracking in these specimens.

TASK: 61

TASK TITLE: Electron Transport in Films

TASK OBJECTIVE: Model electronic transport in superconducting junctions to establish the requirements for detection of IR signals.

SCIENTIST: Paul Esposito, Ph.D.

DESCRIPTION OF WORK:

With the advent of high-temperature superconductors, Josephson junctions have taken on possibilities as devices which will contribute to high-speed, low-noise, low-power technology when used in radiation detector configurations. The purpose of this task was to model Josephson junction mechanisms in order to determine the material parameters for optimum temperature of operation and to model noise sources that limit sensitivity.

Interest in the subject has developed due to the following:

- Josephson junctions typically have very low impedances and small characteristic voltages; however, by fabricating series arrays, both may be increased to useful values.

- Arrays of tunnel junctions are difficult to fabricate, are rather fragile, have low-operating voltages, and offer low-cross sections to incident photons.

- Arrays of proximity coupled junctions are routinely fabricated, are strong, and high-operating voltages, and offer much larger cross sections to photons.

Experimentation for this task consisted of calculation and equations. Investigation of results led to the conclusion that the Josephson junction is a complicated physical system due to its inherent nonlinearity. Phase-locking is but one aspect of the nonlinear interaction between Josephson junctions. Analysis of the stability of the coherent solutions of the equations is still under study.

TASK: 62

TASK TITLE: Research in High Temperature Chemistry of Ceramic Composites

TASK OBJECTIVE: Determine temperature limitations of selected potential ceramic composite systems.

SCIENTIST: Stephen R. Jurewicz, Ph.D.

DESCRIPTION OF WORK:

The identification of useful ceramic matrix composite systems from a large list of candidate fiber/matrix combinations often involves the manufacture and testing of actual unidirectional fiber

matrix composites as the first and only evaluation step. The purpose of this task was to determine whether an organized screening process could be developed to assess whether a potential system would warrant further investigation as a true fiber/matrix composite test sample.

Experimentation began with establishing performance criteria for the successful composite. Candidate systems were selected on the basis of oxidation resistance via scale formation, availability of the fibers, and the existence of phase equilibria data for the system; included were: C/AlN, S/SiC, S/Si_3N_4, Al_2O_3/AlN, SiC/3$Al_2O_3$2SiO_2. The screening process was broken down into four categories:

(1) chemical stability calculations
(2) mechanical properties calculations
(3) chemical stability experiments
(4) mechanics "microtests."

Conclusions based on the thermodynamic chemical stability calculations included the following:

- The systems C/AlN and Al_2O_3/AlN appear to have the best chemical stability. They should both rapidly form alumina scales at high temperatures which are predicted to be resistant to rapid evaporation.

- The systems C/SiC, SiC/AlN, and SiC/mullite do not appear to be as stable as C/AlN and Al_2O_3/AlN.

- The system C/Si_3N_4 is definitely unstable slightly above established operating temperature.

The NDSANDS model was created to predict the mechanical behavior and properties of fiber-reinforced composite materials. It assumes elastic deformation and is useful for predicting the upper bounds of stresses until the initial failure of the material. For each couple being evaluated, the model was used to estimate the residual stresses resulting from the thermal expansion mismatch between the fiber and matrix during cooling from elevated temperatures. Conclusions based on interpretation of results include:

- The predictions of residual stresses appear to be in reasonable agreement with the experimentally observed failure modes; however, some systems may require a more refined analysis using more accurate values for the mechanical parameter.

- All systems under study will probably crack when cooled from the operating temperature back to room temperature. Some systems seem to indicate a higher tolerance to thermal mismatch cracking. A mechanism for crack sealing will probably be required if any of these systems are to be successful as high-temperature composite materials.

TASK: 63

TASK TITLE: Advanced Processing of Compound Semiconductors

TASK OBJECTIVE: Develop process models for molecular beam epitaxial (MBE) growths

SCIENTIST: Donald Dorsey, Ph.D.

DESCRIPTION OF WORK:

The objective of this task was to develop mathematical models which describe the growth of III-V semiconductor structures by molecular beam epitaxy (MBE) and to actually develop novel semiconductor structures which have applications in the areas of IR-detection and nonlinear optics (NLO).

At present $Hg_{1-x}Cd_xTe$ is the most widely used material for the manufacture of long wavelength IR (infrared) detectors which operate at temperatures higher than those required for doped silicon. There are many problems with the alloy, including:

- Very narrow band gaps are required which in turn require precise composition control.
- There is a lack of suitable dopants that will behave in a predictable manner.
- The required substrate fractures easily and is only available in small wafers.
- Epitaxy using any technique other than MBE typically leads to high-defect concentrations in the film.
- Abrupt heterojunctions are difficult to obtain because of alloy constituent interdiffusion.

Work performed on this task consisted of efforts by two groups to develop novel III-V semiconductor structures having applications in the areas of IR-detection (especially at long wavelength) and nonlinear optics (NLO). The first group was to grow epitaxial layers and multilayer structures by MBE with additional responsibilities in surface analysis during and after growth and in development of process control procedures for the MBE growth process. The other group was assigned identification of a potential application area, band gap engineering/structure design, optical and electrical characterization of the layers and structures, and process modeling of the MBE growth.

A Monte Carlo model describing the growth of a simple cubic crystal in the [100] direction was developed. The model accounts for adsorption of the impinging atoms and surface diffusion of the ad-atoms. Oscillations obtained in the surface step density evolution match those of previous research and correspond qualitatively to experimentally-measured reflection high energy electron diffraction (RHEED) intensities. Simulation of the specular RHEED intensity using the kinematic scattering approximation was found to be physically inadequate; a more rigorous approach is needed. The final surfaces obtained after growth were found to improve in quality with increasing temperature. Finally, it was determined that atoms do not preferentially adsorb at the highest available site (at least for this case).

TASK: 64

TASK TITLE: Electronic Transport

TASK OBJECTIVE: Optimize the magnetic susceptibility technique for evaluating high temperature superconducting ceramics (HTSC).

SCIENTIST: Iman Maartensee, Ph.D.

DESCRIPTION OF WORK:

The effects of lead substitution on the superconducting properties of bulk ceramic samples of the bismuth based compounds were studied. The diamagnetic moment of HTSC film and bulk samples was measured as a function of temperature. These measurements were related to the materials transport properties.

Interest in this subject was prompted by research by AT&T Bell Labs and the Japanese claiming that the bulk superconducting transition temperature could be raised above 100K when the lead content was set near $x = 0.3$. The lead compound in the starting mix may or may not simply act as a fluxing agent which promotes the growth of larger high-T_c grains. Better understanding the actual mechanism which is responsible for the improved material properties would allow optimizing the processing parameters for producing even better superconductors.

For this task compounds were prepared and subjected to various heat treatments. They were analyzed by means of X-ray diffraction and scanning electron microscopy. Resistivity measurements were conducted on the final samples, focusing on the magnetic properties of the materials and a tentative interpretation of their behavior.

Investigation of results led to the conclusion that the improved processing which can result from lead addition depends more on the behavior of the "flux" than on the actual formation of the desired phases. The range of sintering parameters and lead content over which beneficial results are obtained must be such that the unused components are not scattered into the grain boundaries, but remain localized in relatively large, discrete inclusions. Then the active material has a greater probability of intergranular coupling through clean grain boundaries. The presence of large grains of calcium and/or strontium plumbates identified in scanning electron microscopy (SEM) micrographs supports this type of explanation.

Recommendations for future investigations include determining the relationship between the onset temperatures of the weak-link coupling and that of the granular superconductivity when a DC field is applied.

TASK: 65

TASK TITLE: Electronic Transport

TASK OBJECTIVE: Develop a new optimized high temperature superconducting ceramics (HTSC)

SCIENTIST: William S. Harwood, Ph.D.

DESCRIPTION OF WORK:

The thrust of this investigation was to design new compositions for improved electronic transport properties, to fabricate test samples, and to analyze the electrical and magnetic properties of the test samples.

Interest in this subject was inspired by the fact that several groups have reported improvements in the properties of the 1-2-3 superconductor on addition of silver to the bulk-sintered material.

Initial work was directed toward achieving consistent uniform batches of sample. Several different furnaces were examined and the Wittenburg tube furnace was selected due to its capability of accommodating small sample geometry to minimize gradient effects. Samples of superconductor pellets were loaded into the furnace for annealing using the optimum geometry.

Results of experimentation supported the general claim that J_c is improved on addition of silver to bulk 1-2-3 superconductor. The degree of improvement is between a factor of two and five, with results suggesting a three-fold improvement in the critical current density.

Suggestions for further study include optimizing the amount of added silver and improving the processing of the composite materials.

TASK: 66

TASK TITLE: Molecular Beam Epitaxy of Strained Layer Superlattices

TASK OBJECTIVE: To grow superlattice materials by molecular beam epitaxy for use in Air Force optoelectronic applications.

SCIENTIST: Ming-Yuan Yen, Ph.D.

DESCRIPTION OF WORK:

The objective of this task was to study the electrical and optical properties of MBE grown layers and to incorporate the behavior of the Si dopant into the epitaxial layers.

Experimentation included the following activities:

- The Si dopent was introduced into the film by opening the shutter in front of the Si effusion cell.
- Hall measurement and photoluminescence were employed to characterize the electrical and optical properties of the materials.
- Residual Gas Analyzer (RGA) was utilized to determine which sources contributed to the carbon-related peak in the photoluminescense (PL) spectra.

Both undoped and Si doped GaAs and AlGaAs epitaxial layers were grown by MBE and characterized by Hall measurement and photoluminescence. Both characterization techniques confirmed that the grown materials were of very good quality. PL spectra also provided information about the Al composition and results show consistency with the RHEED oscillation analysis.

TASK: 67

TASK TITLE: Processing Science of Organic Structural Materials

TASK OBJECTIVE: To develop innovative processing approaches to fabricate molecular composite in bulk form for structural applications.

SCIENTIST: Wansoo Huh, Ph.D.

DESCRIPTION OF WORK:

The purpose of this task was formulation of rigid-rod molecules (PBT) reinforced molecular composites into acidic solutions. The coagulation, drying, and densification steps of the composites were studied to assess the impact of the processing conditions on the properties of the molecular composites.

Two different approaches have been developed for making block type molecular composite using methane sulfonic acid (MSA) or sulfuric acid (SA). The first uses MSA solvent with direct block coagulation under pressure followed by consolidation. The second is the gel formation of SA solution during the cooling process followed by the consolidation. Problems during the processing of block type composites include:

- void formation during coagulation
- phase separation of the second component
- gellation formation
- layer formation during the consolidation step.

By constructing the critical phase diagrams of the PBT/Zytel 330/MSA and PBT/Zytel 330 MSA-CSA ternary system, processing conditions were optimized. Experimentation was carried out with materials and solution processing procedures which included optical microscopy study, morphology study using scanning electron microscopy (SEM), rheological study, and gellatin analysis. Interpretation of results led to the following conclusions:

- The details of phase behavior of the PBT/Zytel 330/MSA system ca be interpreted from the ternary phase diagram.

- Optimum processing conditions can be proposed by varying polymer composition and concentration.

- From the coagulation phase diagrams of PBT/MSA with water and Zytel 330/MSA/Water systems, it was found that the control of PBT/Zytel 330 composition and polymer concentration is very important for the homogeneous coagulated structure.

- For the PBT/Zytel 330/SA system, the gelled structure formation was evaluated by varying the polymer concentration, composition, cooling rate, and solvent in order to get the homogeneous structure.

TASK: 68

TASK TITLE: Polymers

TASK OBJECTIVE: Process Morphology of Ordered Polymers

SCIENTIST: Kung-Hwa Wei, Ph.D.

DESCRIPTION OF WORK:

The rheology of poly-p-phenylene benzobisoxazole (PBO) and poly-p-phenylene benzobisthiazole (PBT) polymer solutions was studied. An on-line flow birefringence apparatus was set up to measure fiber orientation in the air gap during spinning. The apparatus consisted of a polarized laser light, photomultiplier, and camera system to record the birefringence. Flow birefringence data were obtained on PBT and PBO dopes as a function of spinning conditioning upon temperature, length of air gap, and dope concentration.

A steady-state viscosity measurement was carried out with Hastolloy C stainless parallel plates and using nitrogen gas as the heating medium in a Rheometric Dynamic Spectrometer. The following were investigated:

- Comparisons of data for the two solutions showed that the slope of the viscosity curve near the minimum viscosity point on the high temperature side was about the same for the cases of PBO and PBT dope.

- Effect of concentration was studied for the two solutions. Comparisons showed that the transition temperature is clearly affected by the concentration.

- Effect of shear rates on the viscosity was determined for the PBO dope and proved to be clearly shear-rate dependent.

- Effect of P205 content was measured on PBT polymer solutions under different concentrations and P205 content.

- Effect of oscillation frequency on dopes was measured by polarized light microscopy. At above 200 °C, the dope started to lose its birefringence, and at 270 °C there were blisters occurring in the dope.

TASK: 69

TASK TITLE: Research in Stability of Ceramic Superconductors

TASK OBJECTIVE: To identify ceramic superconductors with broader phase fields than the current materials.

SCIENTIST: Judith Bransky, Ph.D.

DESCRIPTION OF WORK:

The objective of this task was to develop a new demonstration of superconductivity, one that could demonstrate its principles and effects to the general public and require only some basic knowledge in order to understand and require only standard laboratory equipment and commercially available superconductor disks in order to perform.

The experiment was based on intercepting magnetic flux lines in a transformer core by inducing a current through a superconducting ring. The core of a simple ferrite transformer is threaded through the ring, which in its normal state has high electrical resistance and thus no effect on the transformer function. When the ring is in its superconducting state, its electrical resistance drops to zero. The alternating flux lines passing through the ring induce a current in

it. This current generates a magnetic field which completely counterbalances the flux lines in the core, thus cutting off the magnetic linkage between the secondary and primary coils of the transformer. As a consequence, the output signal of the transformer drops to zero. Input and output signals are viewed on a dual trace oscilloscope with the upper trace proportional to the input signal, while the lower trace shows the output voltage for three states of the superconducting ring:

- the normal state at room temperature
- the superconducting state at liquid nitrogen temperature (77K)
- the transition from superconducting to normal when the induced current exceeds I_c at 77K.

TASK: 70

TASK TITLE: Analysis of Patched Repair of Composite Laminates

TASK OBJECTIVE: To model a damaged composite laminate with a doubler as reinforcement.

SCIENTIST: David Chu, Ph.D.

DESCRIPTION OF WORK:

The purpose of this task was to develop a model for the repair of laminates by using a bolted doubled designed to utilize elasticity analysis coupled with a strength criterion.

A user-friendly program was completed for the Apple Macintosh computer calculating the three-dimensional elastic moduli of laminated composite materials having orthotropic plies. The program is functional and has been furnished to a number of users in the aerospace industry.

For the stress analysis of thick laminates, the model perceives the laminate as a quasi-homogeneous body with orthotropic symmetry. The models for the out-of-plane moduli are based on extensions of classical micromechanics analysis.

Additional features recommended for incorporation in the program in the future include the following:

(1) The number of plies should be increased.

(2) A version of the program should be created for DOS computers.

(3) A method for the moduli of degraded plies should be developed to accommodate the progressive failure model of a composite laminate.

TASK: 72

TASK TITLE: Nonlinear Optics

TASK OBJECTIVE: Computational modeling of the mechanical, physical, and nonlinear optical properties of ordered polymers and heterocyclic molecules.

SCIENTIST: Guru P. Das, Ph.D.

DESCRIPTION OF WORK:

Computational chemistry studies were conducted in an effort to understand and predict the compressive, tensile, and nonlinear optical properties of aerospace polymers in both single chains and bulk phase. A simplified and approximate ab-initio theory was proposed and applied to the calculation of the electrical susceptibilities of some selected organic systems and the polyenes.

The upsurge of interest in Nonlinear Optical (NLO) properties of organic substances is directly related to the expanding range of applications of laser technology. Although many substances exhibit appreciable NLO effects, they are far from adequate for practical applications. Theory can be a useful predictive tool, but the current theoretical models suffer from various levels of uncertainty. Semiempirical models are preferred over ab-initio models for economical reasons even though results are usually inferior in accuracy and in theoretical soundness. Ab-initio approaches are more accurate and more theoretically sound but expensive. This study investigates an approximate form of the ab-initio method and demonstrates the power of the method in terms of efficiency as well as ability to predict. A fragment-based ab-initio method is proposed along with a recipe for choosing the fragments.

The ab-initio viewpoint of a molecular system consists of three basic elements:

(1) The atomic functions, correct at dissociation, undergo distortion and polarization as the molecule forms; therefore, it is necessary to augment the basis set in a conventional linear combination of atomic orbitals (LCAO) treatment by requisite functions to take this into account.

(2) Owing to the strong overlap between valence orbitals, the Atomic Orbitals (AO) delocalize into Molecular Orbitals (MO) giving a framework for the "aufbau" construction of the total wavefunction.

(3) The inclusion of the electronic-correlation represents the difference of the exact energy from the Hartree-Fock value.

The methodologies were applied to the following test systems: benzene, oxazole, the cyclobutadiene ion, $C_4H_4^{++}$, and polyenes of various sizes. The emphasis was primarily on studying the efficiency and the scope of the method rather than accuracy.

The polyene calculations for all sizes, including the fragment step where the parameters are generated, took slightly more than one hour on the VAX 8650, a speed unmatched even by the semiempirical calculations. This advantage in timing is expected to persist even where the equations are fully solved.

TASK: 73

TASK TITLE: Photoconductivity Spectra of Quantum Well Superlattices

TASK OBJECTIVE: To provide theoretical modeling support for the in-house photoconductivity research.

SCIENTIST: G. Bambakidis, Ph.D.

DESCRIPTION OF WORK:

The objective of this task was the analysis of the fundamental physical processes involved in intersubband photoexcitation of carriers in quantum well superlattices, expressing photo response in terms of the photoexcited tunneling probabilities and modeling the photo response for a modulated infrared source appropriate to Fourier transform spectroscopy.

Layered heterostructures (multiple quantum wells and superlattices) of III-V superconductor compounds and alloys have been widely recognized for potential use in fabricating infrared detectors with increased sensitivity and wavelength range. Precise control of the superlattice growth parameters made possible by molecular beam epitaxy will enable the design of heterostructures for specific applications. This study considers both photoabsorption and photoconductivity for the symmetric case, and provides a starting point for incorporating effects such as photo-thermal ionization in situations where one has discrete excited levels.

The electrical dipole matrix element, absorption coefficient, and photoconductive response function were calculated for intrasubband optical transitions form the ground state to the continuum for a layered Type I superlattice. A square well potential was assumed, and overlap of the wave function in neighboring wells was ignored. The motion of the charge carriers in the plane of the layers was described by simple plane wave states. The superlattice parameters appearing in the model include the number of periods, the well and barrier widths, the band offset, and the carrier concentration in the wells. The photo response model developed previously for homogeneous bulk samples was used as a basis for calculating the photo-response in the superlattice.

Conclusions drawn from these calculations include the following:

- The shape and width of the absorption peak appear comparable to that observed experimentally, but the calculated magnitude is much less.

- The calculated photocurrent spectrum closely tracks the absorption.

- The sharp structure seen at higher energies is probably an artifact of the model.

Recommended improvements and extensions to the model include the following:

(1) Incorporate the effect of neighboring wells on the wave function.

(2) Include bound-to-bound transitions.

(3) Take into account such effects as external electric fields and strained layers by allowing the potential inside the wells to vary.

TASK: 74

TASK TITLE: Processing Maps for Moldable Raw Materials

TASK OBJECTIVE: To develop constitutive equations for the class of moldable raw materials which include liquid-to-solid metal transition.

SCIENTIST: Venkat Seetharaman, Ph.D., Universal Energy Systems

DESCRIPTION OF WORK:

The purpose of this task was to develop a Dynamic Material Model (DMM) for predicting material behavior during the solidification process (liquid-to-solid metal transition), incorporating into the model relationship between material parameters such as temperature gradients, cooling rate, and solidifying interface velocity. This model was developed in response to the need for a unified and macroscopic description of flow, fracture, and workability of complex engineering materials under hot working conditions.

The model is based on the premise that plastic deformation and fracture processes are highly irreversible and occur under conditions far from equilibrium. This leads to the application of the extremum principles of irreversible thermodynamics with the underlying assumption that nonequilibrium systems operate in such a way as to optimize the rate of production of entropy and that the rate of production of excess entropy may provide a basis for the evolution of microstructure. The dynamic material model based on the above hypotheses analyzes the stability of plastic flow and prescribes specific criteria to define the loci of all bifurcation processes which create either continuum or structural defects in the workpiece. The regions characterized by stable and continuous plastic flow in the temperature-strain rate space are considered as safe processing windows for the given material. The final result of the model is in the form of a processing map delineating stable and unstable zones with superimposed efficiency contours which relate to the ease with which the material dissipates power during processing.

Since the deformation behavior of the workpiece during hot working is considered to be both stochastic and dynamic, the operative deformation mechanisms cannot be predicted a priori. The prior thermomechanical history of the workpiece material will strongly influence its deformation behavior during processing. This model was designed to determine the constitutive behavior by the experimental approach rather than predict it from first principles. Once the flow stress data are obtained as a function of temperature, strain rate, and strain, it is relatively simple to identify the stable zones.

Although the development of the DMM model is very rigorous and requires a detailed understanding of irreversible, nonlinear thermodynamics, it appears that the stability criteria used in the model can be interpreted in a straight forward manner using simple metallurgical principles.

TASK: 75

TASK TITLE: Polymers

TASK OBJECTIVE: Synthesis of Ordered Polymers

SCIENTIST: Mark Sinsky, Ph.D.

DESCRIPTION OF WORK:

The objective of this investigation was to synthesize aromatic heterocyclic polymers to be used as components in molecular composites or in applications requiring nonlinear optical (NLO) activity. These rigid-rod heterocylics possess unique properties including high modulus, thermoxidative stability, and nonlinear optical properties. Examples of high molecular weight rigid-rod polymers include poly-p-phenylene benzobisthiazole (PBT) and poly-p-phenylene benzobisoxazole (PBO). Analogous poly benzo PBI has also been prepared, but the polymer has low molecular weight. The materials can be prepared in and processed from strong acid solvents

such as polyphosphoric acid (PPA). Fibers spun from these acidic solvents exhibit high strength and modulus. The polymers are prepared by polycondensation of terephthalic acid with an appropriate monomer.

Interest in the development of materials exhibiting NLO properties has been prompted by the following:

- Model compound studies of bisazoles have shown that these compounds exhibit high NLO activities.
- The polybenzobisimidazoles are of particular interest both as structural and NLO materials.
- Traditional methods of preparation for benzobisimidazoles by polycondensation of diacids with appropriate tetraamines give low molecular weight polymers.

Objectives of this research project included:

(1) examination of possible synthetic routes to 1,7diarylbenzo[1,2-d:4,5-d']bisimidazole-2,6-dicarboxaldehydes and similar compounds for use as monomers in polycondensation reactions.

(2) synthesis and subsequent polymerization of 2,6-di(4-carboxyphenyl)benzo-[1,2-d:4,5-d']bisimidazole.

(3) syntheses of model NLO compounds based on benzodiimidazoles, benzodithiazoles, and similar compounds containing thiophene, vinylthiophene, polythiophene, and vinylbenzene substituents.

(4) synthesis and subsequent polymerization of a series of polythiophenedicarboxylic acids.

Several materials were prepared which are presently under evaluation as NLO model compounds.

TASK: 78

TASK TITLE: Metal-High Temperature Superconducting Junctions

TASK OBJECTIVE: Develop improved metal-superconductive junctions

SCIENTIST: Spencer K. Porter, Ph.D.

DESCRIPTION OF WORK:

The purpose of this task was to investigate and characterize a variety of metal-superconductor junction systems by surface analysis techniques and low angle x-ray diffraction and to compare the data with temperature and resistivity curves, assessing the effects of junction properties on high-temperature superconductor behavior. This project was initiated due to the Air Force's interest in using thin films in the superconducting state as radiation detectors. The system chosen for study was $YBa_2Cu_3O_{7-x}$ deposited epitaxially on the (100) face of single-crystal $SrTiO_3$.

Three problems were studied during this task:

(1) Determining a reliable and reproducible method for making oriented films of the proper stoichiometry for superconductivity.

(2) Measuring the appearance of superconductivity and the extent of the Meissner effect.

(3) Making low resistance contacts to the films.

Research of the literature showed that:

(1) The oxygen contents of the perovskite-type films vary widely but making 'x' as small as possible or even a negative value (in the $YBa_2Cu_3O_{7-x}$ formula) is the key to superconductivity.

(2) At low temperatures the rate of oxygen diffusion through the solid tends to control the stoichiometry, while at high temperatures small values of 'x' become thermodynamically unstable; therefore, careful choices of deposition and annealing temperatures with attendant O_2 pressures are necessary.

(3) The best temperature for annealing is about 540°- the higher the O_2 pressure, the better.

Several excellent films were made, each oriented with the c axis perpendicular to the substrate face.

TASK: 79

TASK TITLE: Fatigue of High Temperature Composites

TASK OBJECTIVE: To obtain the failure mechanisms of glass and ceramic composites at elevated temperatures.

SCIENTIST: N. Jayaraman, Ph.D.

DESCRIPTION OF WORK:

The objective of this task was to conduct static and cyclic experiments on glass and ceramic matrix composites at elevated temperatures up to the glass transition temperature of the matrix material. Fractography and electron microscopy were utilized to determine the mode of failure and to identify the governing mechanisms of damage accumulation.

In the area of ceramic matrix composites, critical review of the literature and the research plan resulted in the group's concentration on the long-term-micromechanical response of the new materials under creep-fatigue-environmental conditions. Mechanical testing capabilities were developed in the group and actual testing was begun. Cooperative efforts between NASA-Lewis Research Center's Fracture and Fatigue group and the WL/MLLN Ceramic Matrix Composite group were initiated, an interaction which is expected to lead to establishing a research grant with the University of Cincinnati.

In the area of residual stresses in metal matrix composites, activity was carried out in support of ongoing research in Ti_3Al-SCS6, particularly the thermal and thermomechanical cycling of metal matrix composites (MMC). The residual stress state of the composite during processing and during thermal cycling was predicted by existing models. Results were found to be consistent with former research.

TASK: 80

TASK TITLE: Optimization Methods for the Forging Process

TASK OBJECTIVE: To identify opportunities for employing advanced optimization methods into the forging design process using modern analytical techniques.

SCIENTIST: Ramana V. Grandhi, Ph.D.

DESCRIPTION OF WORK:

The thrust of this research was to develop shape optimization methods for the design of forging processes using a systems engineering approach and having established these methods, to evaluate the feasibility of developing methods for selecting initial billet geometry and all the subsequent blocker forging steps required in nonlinear transient simulation methodology.

Intense competition in the manufacturing industry is forcing major changes in the product development cycle from design conception through production. Simultaneous engineering addresses both the design of the product and the design of the process. This integrated approach allows decisions that significantly affect product and process designs to be made early and intelligently.

The focus of this work was the concurrent design of the product and process. The integrated design problem was posed as finding the optimum shape of a turbine disk that yields minimum weight while meeting the strength requirements imposed on radial and circumferential stresses under centrifugal and blade forces, and process requirements imposed on forging load, forging envelope volume, die pressures, and strain rates. The process requirements affected the microstructure, die filling, equipment requirements, and manufacturing costs. The thicknesses of the hub and the rim, billet temperature, and the friction factor were assumed to have predetermined values.

This task demonstrated the feasibility of integrating product analysis, process simulation, processing maps, and sensitivity analysis procedures for a concurrent design. Using a simplified process simulation approach, the Slab method, the work identified important design issues and limitations. An optimum shape of the turbine disk that satisfies the strength requirements was obtained concurrently with an optimum shape of the forging envelope that satisfies the process requirements. The resulting shape of the turbine disk is quite smooth and practical. The disk weight increases with the increase in rotational speed in order to accommodate the increase in centrifugal forces. Component stress levels increase as the product weight decreases. Constraints imposed on strain rate, die pressure, forging load, and strain rate increase. These are conflicting design requirements, so to increase the strain rate and also keep the die pressure and the forging load within certain limits, the volume of the forging envelope had to be compromised at some point. The constraint limits and the process conditions selected were for demonstrating the approach and can be easily changed to implement a practical system.

TASK: 81

TASK TITLE: Fiber Reinforced Light Metal Composites

TASK OBJECTIVE: To investigate the structure and properties of gamma-TiAl metal matrix composites.

SCIENTIST: Simon Shong, Ph.D.

DESCRIPTION OF WORK:

The purpose of this task was to increase understanding of the interfacial reactions between powder metallurgy titanium-based matrix materials and ceramic fibers through an investigation based on diffusion couple experiments for the characterization of the microstructures of reaction zones. Critical parameters to be considered included different types of ceramic materials, fiber coating, and alloying elements in matrix.

In contrast to disordered phase alloys, consolidation of ordered intermetallic alloy powders is not a straightforward process due to poor ductility and slow atomic diffusion which may hinder successful interparticle weld. In addition, surface contamination of the powder particles may also degrade the interparticle bonding. These properties could discourage the attainment of coherent interparticle bonding of the as-consolidated materials which may contribute to intergranular fracture frequency occurring in the ordered alloys.

The high-temperature performance of intermetallics-based metal matrix composites relies heavily on the strength of reaction layer between fiber and alloy matrix which is designed to offer the continuous load transfer from matrix to fiber. This study involves the assessment of Hot Isostatic Pressing (HIP) processing parameters and their influence on the formation of defect structures with post-HIP high temperature exposure.

When intermetallic alloys are reinforced with high strength and stiffness ceramic or nonmetallic fibers, densification is even more difficult to achieve due to restricted space for alloy powder particles to creep or plastically deform around the fibers. This task focused on defining the critical temperatures and pressures required for the densification of gamma-TiAl metal matrix composites.

Microstructures including phases, porosity, and interfacial bonding between SiC and TiAl matrix were characterized using differential thermal analysis (DTA), X-ray diffraction (XRD), optical microscope (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electron microprobe (WDS). Prolonged exposure to high temperature above 1000 °C following HIP was conducted to examine the reformation and migration of large gas pores to the reaction layer through grain boundaries as a result of coalescence of micropores or vacancies present within the matrix.

Interpretation of results led to the following conclusion:

(1) Atomization solidification processing has a critical impact on the achievement of full density of TiAl metal matrix composites. Hot Isostatic Pressing of fiber with finer atomized powders produced less interfacial pores than that with larger powders because smaller particles contained less entrapped gas pores than larger ones.

(2) The gamma-TiAl metal matrix composites were densified with formation of a uniform

reaction layer at the fiber/matrix interface. After high-temperature exposure above 1000 °C, interfacial pores were found to form along the reaction layer/matrix interfaces which were not observed in the as-HIP condition.

(3) The presence of interfacial gas pores was believed to migrate from alloy matrix through grain boundaries which are low coherency boundaries to permit fast atomic diffusion to occur.

(4) Chemical analysis was conducted on both as-HIP and post-HIP heat-treated specimens. Reaction products seemed to be the same in both conditions containing two distinct reaction layers; one is enriched with Al and the other with Si and V.

TASK: 82

TASK TITLE: Polymer Research

TASK OBJECTIVE: Process Morphology of Ordered Polymers

SCIENTIST: Kung-Hwa Wei, Ph.D.

DESCRIPTION OF WORK:

The study concerned the determination of the morphology and viscosity of two rigid-rod anisotropic polymer solutions, poly-p-phenylene benzobisthiazole (PBZT) and poly-p-phenylene benzobisoxazole (PBO) in polyphosphoric acid (PPA) at various temperatures using the online flow birefringence apparatus, the Rheometric Mechanical Spectrometer (RMS), and the high-temperature X-ray diffraction system. From these ordered polymer solutions, high performance fibers and films are obtained through dry-jet wet spinning, tension-drying, and heat-treatment processes, which introduce structure transformations at each step. As a first step in choosing the optimum processing condition and obtaining the desired final properties of these materials, the structure and properties of PBZT and PBO solutions were investigated.

The steady state and complex viscosity of various concentrations of PBZT and PBO solutions were measured with parallel plates and cone-plate rheometry fixtures. The viscosities measured using cone-plates were found to be lower than that measured using parallel plates. The viscosity curves displayed a reversible behavior during heating and cooling, indicating the nature of the transition is physical rather than chemical. Strong shear-rate dependent viscosities for both 15% and at small-strain oscillation were observed, and there was a yield stress in the case of PBO solutions.

Also, polarized light microscopy was used to observe aniostropic features of the two polymer solutions from room temperature at 270 °C. The microstructure and phase behavior of these solutions were confirmed with wide-angle X-ray diffraction. At room temperature, the PBO solutions appeared to have a typical and highly oriented crystal solvate structure and the PBZT solutions appeared nematic. At high temperatures, the structure changed dramatically for both PBZT and PBO solutions, which is apparently related to the unusual viscosity increase. A construction of dynamic phase diagram for PBO and PBZT solutions from currently available data was also attempted.

TASK: 83

TASK TITLE: Polymers: "Compression Behavior of High Performance Fibers"

TASK OBJECTIVE: Process Morphology of Ordered Polymers.

SCIENTIST: Wansoo Huh, Ph.D.

DESCRIPTION OF WORK:

Compressive strength of advanced composites is a key property for many aerospace structural applications and in most cases is limited by the fibers which comprise the composite. Intermediate modulus PAN-based carbon fibers tend to have good compressive strengths while organic (polymeric) fibers have relatively poor axial compressive strengths, thus limiting their usefulness. The aim of this work was to study the compressive behavior of poly-p-phenylene benzobisthiazole (PBZT), poly-p-phenylene benzobisoxazole (PBO), and other organic fibers and make comparisons with carbon fibers.

Most existing techniques to measure the compressive strength of fibers are indirect methods and are based on certain assumptions. This investigation used the microscale compression technique (direct compression of a single fiber), optical microscopy, and scanning electron microscopy (SEM) to directly measure the compressive strengths and identify the failure mechanism of PAN-based and pitch-based carbon fibers (P75S, T-50, T-300, and GY-70) and organic fibers (Kevlar29, Kevlar49, Kevlar149, HT PBZT, AS PBZT, HT PBO, and AS PBO). The compression failure behavior of PBZT and PBO fibers with different thermal histories and processing conditions was also studied.

Experimentally, the compressive strain has been related to the number of kink bands that form upon compression. The critical compressive strain was obtained by plotting the number of kink bands per unit length as a function of strain and extrapolating to zero kink band density. For HT PBZT fiber the critical compressive strain is 0.11%, which is very consistent with reported values measured by other methods. Furthermore, the distance between kink bands of HT PBZT fibers was shown to be an inverse function of compressive strain, as given by the equation,

$$F(X) = A + BX + CX^2 + D/X + E/X^2$$

The kink band formation of HT PBZT was also shown to be irreversible. Upon recompression, the kink bands occur exactly at the same position of the initial compressed fiber and some kink bands remain after releasing the compression force. This suggests that the formation of kink bands is a plastic deformation process rather than the elastic deformation.

The effect of various compressive strain rates on HT PBZT fibers was studied using SEM. Fibers compressed up to 0.16% strain indicate that the slight buckling process occurs around the surface of the fiber, while those compressed up to 0.38% suggest a plastic deformation mechanism.

The compressive strains of PBO fibers with different thermal histories and processing conditions were also studied. The higher the coagulation water temperature the poorer the compressive strain of HT PBO fiber. Steam coagulated HT PBO fiber shows much better compressive strength. The neutralization effect of NH_4OH solutions was studied for various NH_4OH concentrations. The neutralized fiber with heat treatment shows improved compressive strain compared with other fiber. Finally, using a spin-drawing process on PBO fiber results in poor compressive strain while it might improve the tensile strength.

Interpretation of the results of this study led to the following conclusions.

1. T-300 PAN-based carbon fiber shows the highest compressive strain compared with other pitch-based carbon fibers, Kevlar fibers, PBZT, or PBO fibers.

2. The compression of HT PBZT fiber is likely a plastic deformation process.

3. The compressive strength of PBO fiber does not improve with heat treatment or by using the spin-drawing process.

4. The values of the critical compressive strain of fibers measured using the microscale compression technique are very close to those reported using other techniques.

5. The method is very reproducible compared to other techniques.

6. The compressive behavior of high performance fibers can be analyzed more effectively with this technique.

TASK: 84

TASK TITLE: Qualitative Process Discovery: "QPD Discovery System for the QPA Environment

TASK OBJECTIVE: Demonstrate a knowledge base to control and begin to perform scientific discovery upon an autoclave simulator. This work directly supports advances to the QPA environment.

SCIENTIST: Dan Wood, ThinkAlong Software, Inc.

DESCRIPTION OF WORK:

Qualitative Process Discovery (QPD) is the name of the knowledge base resulting from a research program which conjoined elements of Qualitative Process Automation (QPA) and Scientific Discovery, using ThinkAlong Software Discovery system shell, The Scholar's Companion.

The research linked a scientific discovery engine with a process control (expert system) task. QPA, as a performance engine, acts to automate the process control, but the limited understanding of the processes involved means that creation by hand of the appropriate controlling knowledge base is a difficult task. It has been proposed that a computer understand the process. This points out the need for automated scientific discovery, in the form of a computer assisting the scientist, to develop the knowledge base for the performance engine to drive the process.

The research project consisted of two stages. Stage one, the primary research objective, was the creation and demonstration of the knowledge base capable of performing process control.

This research effort demonstrates a necessary first step toward coupling a scientific discovery system to a real-world process. Specifically, a discovery engine with an expert system process control knowledge base (not a discovery knowledge base) has been coupled to a simulator of the autoclave environment.

The Scholar's Companion, ThinkAlong Software Discovery system program, is the engine of QPD and the platform for this research. The Scholar's Companion uses a nonlinear neural

network applying principles of spreading activation, several inductive and abductive tools suggested by Thagard, and principles of interaction with the environment through "sensors" and "muscles." Because of the interaction with the environment, the QPD system is classed as an open system, one eventually capable of learning from its experiences. The ability of The Scholar's Companion to control a real-time process in the fashion of QPA has been demonstrated by directly coupling a Macintosh II, running The Scholar's Companion, to an IBM-PC-compatible system, running Dr. C. William Lee's autoclave simulation program. Successful cure trials have been run, although performance improvement is possible.

The roots of stage two were only explored during this project period. The first step in this stage has been determining what is needed to allow process control with ThinkAlong's discovery engine. Other aspects studied have been the strategies for conflict resolution (the solutions to which will reside in the knowledge base itself) and issues of feedback for muscle control and perception of accomplishment.

The primary goals of stage two would be twofold:

1. To obtain an understanding of real-time discovery necessary to explore applicability of the discovery system to other domains (controlling the MBE process).

2. To allow the general knowledge in The Scholar's Companion to be used to discover the specific knowledge needed for controlling the autoclave process.

The results of this study led to the following conclusions:

1. The transition from an internal thinking discovery system to an open system (The Scholar's Companion operating in an expert system mode) has been a smooth one.

2. The application of The Scholar's Companion to the task environment outlined in the report will result in useful process control discoveries in the future.

A general outline for future research into stage two was also presented. This research would be aimed toward the coupling of a discovery system to the real world, performing discovery functions. The key tasks needed to accomplish this were discussed.

The final report also includes a draft copy of the programmer manual for The Scholar's Companion, a copy of the QPD knowledge base, and a bootable version of The Scholar's Companion.

TASK: 85

TASK TITLE: Interfacial Damage Modeling for BMC (Brittle Matrix Composites)

TASK OBJECTIVE: To develop an analytical model for BMC to relate composite effective stress-strain response to fiber-matrix interfacial damage.

SCIENTIST: Chin-Teh Sun, Ph.D.

DESCRIPTION OF WORK:

The scientist developed a finite element model to describe the fiber pull-out process

(experiment) of a unidirectional BMC. Fiber pull-out basically involves three stages of failure: failure initiation, interfacial crack propagation, and fiber slippage against the matrix. In the fiber pull-out test, the load-deflection curve of the loaded fiber provides much information about the failure process. It is conceivable that the interfacial fracture toughness of the interfacial crack can be extracted from the load-deflection curve.

The fiber pull-out problem studied was that of a SiC fiber embedded in a glass disk, the bottom of which is assumed to be bonded to a rigid surface. Both materials are assumed to be isotropic and linearly elastic and no thermal residual stress is present. Loading was applied by increasing the deflection at the free end of the fiber (stroke-controlled loading). A general purpose, commercial finite element code, MARC, was used to perform the analysis. The fiber pull-out problem is axisymmetric and, thus, can be reduced to a 2-D problem in the (r,z) plane.

A finite element-based crack-closure integral for determining strain energy release rates for two-dimensional elastostatic and elastodynamic crack problems in finite bodies was evaluated. Both the J-integral and crack-closure integral were used to obtain strain energy release rates from the finite element solution and the results from both were compared to each other and those from other methods. Details of the methods are presented in the paper "Evaluation of a Finite Element Based Crack Closure Method for Calculating Static and Dynamic Strain Energy Release Rates" attached to the report.

Three examples were used to test the methods and make comparisons. The problem of a static crack in a homogeneous isotropic medium (central crack in a tension panel) was analyzed to assess the effect of element size and examine the accuracy of the crack-closure integral and J-integral methods. The other two methods, elastodynamic analysis of a rectangular panel with a central crack under stress wave loading and self-similar crack propagation with constant velocity in a square panel (center crack that grows symmetrically and with constant velocity from an initial crack) were used to compare results for dynamic stress intensity factors.

Comparison with existing solutions showed that both methods yield very good results. However, the crack-closure integral method (1) can directly yield strain energy release rates and stress intensity factors for separate fracture modes in mixed-mode problems, (2) is simple, efficient and accurate, and (3) is very convenient to use in propagating crack problems.

Furthermore, the present method is capable of directly separating Mode I and Mode II strain energy release rates (G_I and G_{II}) and can be easily implemented into finite element programs without invoking special singular finite elements. Theoretically, only the total strain energy release rate (G) is mathematically defined. The method used to calculate G_I and G_{II} is discussed in the paper "On Strain Energy Release Rates for Interfacial Cracks in Bi-Material Media" attached to the report. In this paper G_I and G_{II} were investigated analytically and by using the finite element method for a crack lying along the interface of two dissimilar elastic media. The analytical solutions indicated that G_I and G_{II} do not converge in the form of crack-closure integrals (oscillatory terms are present) although the sum (G) is well defined. If the oscillatory terms are neglected, then $G_I = G_{II} = 0.5G$. The finite element solutions in conjunction with the crack closure method agree with the analytical solutions if the assumed crack extension is larger than the region of violent stress oscillation. Moreover, the finite element solutions also converge to $G_I = G_{II} = 0.5G$ for small crack extensions, before they start to oscillate.

The report concluded that the finite element method can be an efficient tool for analyzing fiber pull-out or push-out problems, if the objective is to calculate the strain energy release rates and to simulate the pull-out interface fracture process. From the actual load-deflection curves for the pull-out test, it is possible to extract the fracture toughness of the fiber/matrix interface. If

thermal residual stresses are included in the finite element model, the friction coefficient at the fiber/matrix interface can also be obtained.

Also, since the σ_{rr} stress is tensile in the pull-out test and compressive in the push-out test, the Mode I contributions in the two cases are different. It is conceivable that this difference may be useful in separating the fracture forces associated with Mode I and Mode II.

TASK: 86

TASK TITLE: Exact Solution for the Elastic Pull-out Problem in BMC (Brittle Matrix Composites): "Analysis of Adhesive-Bonded Cylindrical Lap Joints"

TASK OBJECTIVE: To formulate an exact elasticity solution for the axisymmetric problem of the tension loading of an elastic fiber embedded in an elastic matrix.

SCIENTIST: Shun Cheng, Ph.D.

DESCRIPTION OF WORK:

The scientist considered the stress distribution in adhesive-bonded cylindrical lap joints for which the two adherents may have different thicknesses and consist of different materials and the adhesive layer may be flexible or inflexible. Three-dimensional elasticity theory in conjunction with the principle of minimum energy (variational theorem of complimentary energy) is used to solve the axisymmetric boundary value problem. All boundary stress conditions of the joint are strictly satisfied. Since high stress intensities occur in the end zones of the joint, the stress-free end conditions of the joint must be satisfied.

The results of the analysis show no stress singularities exist in the bond joints. The present approach yields closed-form solutions. The problem of stress distribution between the fiber and matrix of composites, which is a basic problem in the study of composite materials, may also be analyzed and treated as a special case.

Numerical examples are provided to illustrate the effects of various parameters on the distributions and intensities of stresses in the joint and compared to results from other methods. In general, there is good agreement between the present solutions and those from other methods. The present method is better for predicting the intensity and distribution of the stresses in the end zones of the adhesive (i.e., the end conditions of the overlap are strictly satisfied).

TASK: 87

TASK TITLE: Research in Stability of Ceramic Superconductors: "Dependence of Transport Critical Current Density on Sample Size for Ceramic $RBa_2Cu_3O_{7-x}$ (R = Y, Ho, Gd)"

TASK OBJECTIVE: To identify ceramic superconductors with broader phase fields than the current materials.

SCIENTIST: Izhar Bransky, Ph.D.

DESCRIPTION OF WORK:

The materials $YBa_2Cu_3O_{7-x}$ (YBC), $HoBa_2Cu_3O_{7-x}$ (HoBC), $GdBa_2Cu_3O_{x-7}$ (GdBC), and YBC + Ag were prepared and evaluated using several methods. The methods and their results were:

1. Powder X-ray diffraction which showed single-phase patterns for the final superconducting powders, YBC, HoBC and GdBC.

2. AC susceptibility measurements were made to determine T_c and the superconductive properties of YBC and YBC + Ag samples prepared under different conditions. The susceptibility results showed that for all but one sample a fully-shielded condition existed at 77 K.

3. Scanning electron micrographs for the YBC-7%Ag_2O preparation showed that metallic silver is deposited in the voids between the grains.

4. Measurements of the transport critical current density, J_c, were carried out on sintered and partially melted samples of YBC, YBC + Ag, HoBC, and GdBC, using a 4-probe DC method and a contactless magnetic induction method. The latter avoids problems such as heating associated with contact resistance, often present in the 4-probe method, but its disadvantage is that the specimen must be in the shape of a ring. Results obtained by the two methods were in agreement. Sintered YBC samples have 72% - 76% of the theoretical density, whereas the partially melted samples attained 92% of the theoretical density. Differences in J_c among the sintered YBC samples were correlated with variations in sample density. YBC + Ag samples had J_c values about two times that of YBC samples.

A pronounced dependence of J_c on sample cross sectional area was observed for all samples: J_c increased with decreasing cross sectional area. Values of J_c ranging from about 30 A/cm^2 to 800 A/cm^2 were measured depending on the preparation method and sample geometry. It was concluded that in view of the cross sectional area dependence, comparison of J_c for different preparations should always be made for samples of similar geometry (dimensional parameters).

TASK: 88

TASK TITLE: Determination of Fiber Failure in Ceramic Composites

TASK OBJECTIVE: To identify means of determining fiber failure prior to composite failure.

SCIENTIST: Amit Chatterjee, Ph.D., Adtech Systems Research

DESCRIPTION OF WORK:

In the study, work was continued on the development of alternate glass matrices having a range of coefficients of thermal expansion (CTE) higher, equal, and lower than that of the SCS-6 fiber. This would allow the study of the effect of residual stresses on the failure properties in glass/silicon carbide fiber composites.

A model system consisting of CGW 7761 glass with SCS-6 fibers was fabricated and polished

to see if polish damage would crack the fibers at low stresses. An experimental plan was devised where resistance measurements would be made at the ends of the specimens and the change of resistance would indicate the cracking of fibers (the fibers conduct and the matrix does not). It was observed that there were large differences in resistance from specimen to specimen and it was difficult to establish what the change in resistance corresponded to in the tests. Further tests using this procedure are planned.

Alternate glass matrices, consisting of six different compositions (essentially potassium borosilicate) were chosen for study on the basis of their CTE's. The glasses were hot pressed to establish the optimum processing parameters (500 psi at 850°C in an argon atmosphere for 20 minutes) to give good monolithic glasses with little porosity and devitrification. The densities were measured and the longitudinal modulus was also measured using NDE techniques.

In addition, efforts were made to make use of the THETA dilatometer available at WL/MLBC to more accurately measure the CTE's. However, this proved to be unsuccessful due to unit malfunctioning. Also, various methods of conducting tensile tests on composites in both the longitudinal and transverse directions were investigated.

Further, the thermal expansion behavior of the SCS-6 fiber reinforced H-3501-6 (epoxy) matrix was studied and the results presented in the paper "Anomalous Expansion Behavior in Ceramic Fiber Reinforced Brittle Matrix Composites" published in Symposium on High Temperature Composites. Analytical modeling of the CTE of two-phase unidirectional fiber reinforced composite materials showed that the transverse coefficient of thermal expansion of the composite can be higher than that of its constituents at low fiber volume fractions. This effect is especially noticeable if the composite is fabricated with fibers of high modulus and low thermal expansion coefficient in matrices of low modulus and high thermal expansion coefficient. An experimental investigation was carried out to study this anomalous behavior in a Textron CVD SCS-6 fiber reinforced Hercules 3501-6 epoxy matrix. Numerical calculations for this system showed that increases of the order of 20% over the matrix expansion coefficient are possible for fiber volume fractions in the range of 4-5%. An experimental setup was therefore designed to make perfectly aligned unidirectional specimens using the silicon carbide monofilaments at low fiber volume fractions. The transverse coefficient of thermal expansion was measured using a thermo-mechanical analyzer. Preliminary observations seemed to be in favorable agreement with the theoretical calculations.

TASK: 89

TASK TITLE: Microstructure/Property Relationships in Rapidly Solidified Titanium Aluminide Alloys

TASK OBJECTIVE: To investigate behavior of titanium aluminide alloys exposed to rapid solidification.

SCIENTIST: Challapalli Suryanarayana, Ph.D.

DESCRIPTION OF WORK:

The main aim of the present task was to investigate the nonequilibrium behavior of materials such as aluminum, magnesium, titanium and their alloys. Extensive investigations have been carried out previously at WL on the effects of nonequilibrium processing on aluminum and

magnesium base alloys and therefore greater emphasis was placed on titanium base alloys in the present investigation.

Rapid solidification (RS) and mechanical alloying (MA) were the two prime techniques employed to produce the nonequilibrium effects. RS involves cooling of metallic melts at rates $>10^4$ k/s, while MA involves repeated welding, fracturing, and rewelding of powder particles in a dry high-energy ball charge as in a Spex mill or a Zegvari attritor. Both RS and MA can result in one or more of the following constitutional and microstructural modifications: refinement of grain size, second-phase particles, or segregation patterns; extension of solid solubility limits; formation of nonequilibrium crystalline or quasicrystalline intermediate phases; and production of metallic glasses. All these effects, either singly or in combination, can strengthen the alloy and thus contribute to the enhanced mechanical behavior of the systems.

The application of RS and/or MA techniques to light metals was investigated to produce novel alloys with better properties. The experimental techniques used to characterize the materials included: Transmission Electron Microscopy, Optical Microscopy, X-Ray Diffraction, and Differential Scanning Calorimetry/Differential Thermal Analysis. The report describes the results obtained on the nonequilibrium processing of several alloy systems.

Titanium magnesium alloys were processed using MA, due to the fact that the whole operation could take place in the solid state. Among other things, there was evidence for recrystallization in the particles and X-ray diffraction clearly revealed that at high temperatures the alloy separated into elemental titanium and magnesium.

Intermetallic phases, especially those based on titanium, have potential for high-temperature applications. Thus a Ti_3Al - base intermetallic, with the nominal composition Ti-14Al-20Nb-2Mo-3V-2Er (at.%) was subjected to mechanical alloying. The results suggested that MA can be a better processing method than RS for achieving a homogeneous distribution of the dispersoids.

The possibility of producing the equiatomic TiAl intermetallic compound through MA of a mixture of Al_3Ti and TiH_2 powders was explored. The results showed that MA appears to be a novel way of producing the TiAl compound.

A new gamma alloy with a composition of Ti-48Al-2Nb-0.3Ta (at.%) was characterized after being subjected to six different conditions. In all cases, the grain size of the gamma phase is about $5\mu m$ and a small quantity of the α_2 phase also is present. EDS analysis showed these particles to be very rich in aluminum (as high as 98 at.%) and that the Nb content in the gamma phase was nearly 7 at.% (instead of the nominal composition of only 2 at.%).

Attempts were made to produce an amorphous phase in (1) pure Nb, (2) Nb-Si alloys and (3) Ti-Si alloys using mechanical alloying. X-ray diffraction patterns showed the presence of broad peaks indicating the formation of amorphous phases, but more analysis needs to be done to assure that MA does produce these phases.

Finally, MA was also used in an attempt to synthesize the quasicrystalline phases in Al-Mn alloys. As to date, this has proved to be unsuccessful, producing only metastable phases.

TASK: 90

TASK TITLE: Research in High Temperature Chemistry of Ceramic Composites

TASK OBJECTIVE: Determine temperature limitations and mechanical compatibility of selected potential ceramic composite systems.

SCIENTIST: Stephen R. Jurewicz, Ph.D.

DESCRIPTION OF WORK:

During this task research was performed to evaluate chemical interactions between, and mechanical compatibility of, potential constituents in high temperature composite systems. This included the identification of potential systems, fabrication of specimens, evaluation of stability, mechanics molding, and fabrication and evaluation of sample composites.

The first step in developing new composite materials is finding fiber and matrix constituents which have "the necessary" mechanical and chemical properties. Generally, the most important properties are assumed to be (1) a close match in thermal expansion coefficients between the fiber and matrix, (2) a high Young's modulus (particularly for the fiber), (3) a "weak" fiber-matrix interface, and (4) chemical stability throughout the use temperature range. In addition, for each application the composite must survive a specific duration of exposure to the maximum use temperature and an expected environment type (oxidizing or reducing).

The next step in designing a new composite is to collect a list of potential fiber and matrix candidate combinations based on the above considerations. Subsequently, experiments are performed to screen out the fiber-matrix combinations that are most promising.

The main purpose of the investigation was to determine if an organized screening process consisting of calculations and simple tests is sufficient to assess if a potential fiber-matrix combination warrants further investigation as a unidirectional composite test sample. The philosophy behind the project was first to select a likely group of potential fiber and matrix combinations and then to run them through a series of "tests" which evaluate some of the critical properties mentioned above. In fact, since the screening process was itself being evaluated, the effectiveness of the tests used was also under study.

Six fiber/matrix combinations were initially considered, C/SiC, C/AlN, C/Si_3N_4, SiC/AlN, Al_2O_3/AlN, and SiC/mullite. These systems were chosen either because they had already been proved to be viable composite systems or one of the components of the system as some or all of the desired composite properties.

The selection process (tests) was broken into four categories: thermodynamic (chemical) stability calculations(using free energies of formation from the JANAF tables), residual stress calculations (using the NDSANDS model), oxidation couple experiments (using the embedded pellet or chopped fiber techniques), and interface strength "microtests" (using the block shear test method). Both calculations and experiments were included in the screening process to provide some level of redundancy in order to minimize the chance of eliminating a worthwhile system. The oxidation couple experiments verified the results of the thermodynamic calculations of phase stability for most hot-pressing conditions. The results from the oxidation and the interface strength microtest experiments were used to check the results of the residual stress calculations. The effects of the oxidation experiments on the composite systems were determined by using reflected light methods, scanning electron microscopy (SEM), X-ray diffraction, and EPMA (electron probe microanalysis for chemical composition).

The results of the study led the author to several conclusions. Based on the screening techniques used in the study, the C/SiC composite has the best potential of the systems studied

to be a useful ceramic matrix composite (CMC), with a maximum use temperature of 1400 °C. The only other system determined to have high CMC potential is SiC/Mullite, but it definitely requires a weak interfacial coating to make it useful. However, it is apparent that the entire system screening process is dependent on the criteria selected as critical to a successful composite. While the categories used in the study were important, other parameters, such a creep resistance and fracture toughness of the component materials, should be included in a more thorough study.

TASK: 91

TASK TITLE: Analysis and Design of Tapered Beams and Plates

TASK OBJECTIVE: To establish an analytical model for the optimum tapering of composite structures subjected to realistic loads and boundary conditions.

SCIENTIST: Antonio Miravete, Ph.D.

DESCRIPTION OF WORK:

Composite materials have been increasingly used during the last decades to make light-weight structures. Two steps are essential in the process of taking advantage of these kinds of materials: design and optimization.

Optimization (tapering or ply drop) of composite structures is a recent issue, since both optimization techniques and composite structures have only been developed during the last few decades and therefore, the conjunction of both is even more recent. Composite materials are an expensive but efficient way to obtain minimum weight structures and it is logical to attempt to find how to design properly optimum-laminated composite plates with no reduction in their strength. Many kinds of ground and air vehicles have rectangular plates as a common structural element, thus resulting in an increasing demand for improved structural efficiency in such applications. Composite materials offer a number of advantages other than their high stiffness to density values, such as their capability of being tailored by adequate orientation of the filaments in the various layers in order to optimize the desired structural behavior.

The interest of the optimization of laminated composite plates is focused on three different fields: in-plane loads, transverse loads, and buckling. The present report includes a fairly extensive literature review of the problem and it is evident that the problem dealing with in-plane loads has already been studied, and a number of technical publications and software packages can be found.

Also in the study, the optimization of rectangular laminated composite plates subjected to transverse and buckling loads was investigated. First, an analytical formulation was derived for transverse loads. Laminate thickness and fiber orientation were treated as design variables, the thickness of the laminate being variable along the plate. A fully stressed iterative procedure and a quadratic failure criterion were applied in order to get the minimum weight plate using strength as a design criterion.

Once the analytical formulation for transverse loads was completed the problem of a one-dimensional plate with variable thickness was studied by means of a 2-D plane-strain finite element model (accounting for in-plane and interlaminar stresses). Two-dimensional laminated composite plates were analyzed using a more general model based on a higher order shear theory. The method proved to be both efficient and accurate and the results from the shear deformation theory and the 2-D plane-strain model were very close.

Through-thickness stress distributions were determined for different cases, and the influence of geometric parameters and the applied load on the strength of the plate were also analyzed. The failure mechanisms reported on experimental testings were then described. Finally, verification of the theoretical model by means of a number of experimental testings was carried out. Results for optimum configurations of one- and two-dimensional plates of variable thickness, and sandwich panels (subjected to uniformly distributed and point loads), and angles of orientation of the fibers, were presented considering different boundary conditions.

From the results of the study on transverse loads the following conclusions were made:

1. The variable thickness effect has a remarkable influence on the behavior of a tapered laminated composite plate. The distributions of through-thickness stresses are very sensitive to the thickness ratio and the angle of variation of thickness. Especially, the interlaminar shear stress reaches very high values in the areas of change of thickness. The peak value can be controlled by modifying some parameters: thickness ratio, angle of variation of thickness, type of loading, etc. The distributions of interlaminar stresses vary as a function of the sign of the bending moment.

2. The failure mechanisms for variable-thickness composite plates can be grouped in three general modes:

   a. Interlaminar shear mode (stresses): It appears in the tapered surfaces when the change of thickness is sharp (high angles of variation of thickness). In thick plates, it can also appear in the midplane.

   b. Bending modes (stresses): These modes are usually found in thin plates, with very low angles of variation of thickness and low thickness ratios. They are the typical failure modes in thin untapered plates.

   c. Mixed modes: A compression-interlaminar normal mode was found in the area of application of the load in the fatigue testing. This mode does not appear in the 4-point bending test.

3. Very high weight savings were also obtained for both the uniformly distributed and point loads.

For buckling loads a similar procedure was followed, except that the optimization (design) criterion was the critical compressive force. The same finite element used for transverse loads was used in this case. Results for plates subjected to buckling loads were presented for uniform uniaxial compressive loads (1-D plates) and uniform uniaxial and biaxial compressive, shear and combined loads (2-D plates), using different boundary conditions and types of loading.

For 1-D plates, optimal configurations and critical compressive forces were presented. Also, different variable-thickness solutions were depicted, and their weight savings given (between 15 and 66%).

For 2-D plates, optimal angles of orientation of fibers and critical compressive and shear forces were presented for all cases. Relative weights with respect to aluminum and the quasi-isotropic configuration were also reported. The highest weight savings were found for low aspect ratios.

TASK: 92

TASK TITLE: Molecular Beam Epitaxy of Strained Layer Superlattices

TASK OBJECTIVE: Growth of Superlattice materials by molecular beam epitaxy (MBE) for use in Air Force optoelectronic applications.

SCIENTIST: Ming-Yuan Yen, Ph.D.

DESCRIPTION OF WORK:

The objective of this task was two-fold: to study the uniformity and reproducibility of GaAs materials grown by MBE and to study the quantum Hall effect.

The samples used in the study were as follows:

1. Two samples were Si-doped GaAs epitaxial layers grown on 3-inch (100) GaAs substrates with the intent to have 10^{16} cm^{-3} carrier concentration in the thin films.

2. Two samples were GaAs/AlGaAs multiple quantum well (MQW) structures with different GaAs well thickness.

Several methods were used to check the uniformity and reproducibility of the samples. Hall and C-V measurements on the first two samples indicated that the materials were very uniform across the 3-inch wafers and could be fabricated quite reproducibly. Depth profiles measured at several positions across the wafer were virtually identical and the barrier height for the Hg/GaAs interface was reproducible within acceptable limits. DLTS showed that no deep traps were detected in the material.

The results of photoluminescence (PL) spectra from the first two samples demonstrated uniform and reproducible optical properties. PLS for GaAs/AlGaAs MQW structures showed similar results.

All the results consistently showed the uniformity and reproducibility achieved by MBE growth. The materials were also shown to be of high quality.

TASK: 93

TASK TITLE: Analytical Material Process Modeling: "The Extrusion of IN100, an Investigation of the Ring Test, and a Performance Evaluation of ALPID"

TASK OBJECTIVE: To develop, improve, and implement analytical methods for simulating material flow and heat transfer in a variety of processes.

SCIENTIST: Robert L. Goetz, M.S.

DESCRIPTION OF WORK:

The development of the finite element method and its application to material deformation processes (forging, extrusion, rolling) has made it possible to avoid costly and time consuming trial

and error methods. This is especially useful when new alloys of interest to the Air Force are considered. The finite element program ALPID (Analysis of Large Plastic Incremental Deformation) is a computer program which can model deformation processes and provide useful insight into material flow, strain, strain rate, state of stress, and temperature distributions throughout the workpiece at any given time in the process. Defects can be predicted, and the combination of strain, strain rate, and temperature contours can be used to predict the microstructure throughout the product.

This project dealt with three areas of interest: the use of ALPID to simulate deformation processes, experimental validation of ALPID simulations, and performance evaluation of ALPID. Three versions of ALPID (MME-ALPID(2.1), MME-ALPID(2.2), and ALPID(2.3)) were employed in this study.

The isothermal extrusion of the superalloy IN100 was first simulated using MME-ALPID(2.1) and the results correlated well with load predictions from the slab and upper bound methods.

The nonisothermal extrusion of IN100 in a 304 stainless steel can (a two-material billet) was also simulated using MME-ALPID(2.1). The results brought to light a problem with ALPID in that it does not allow slip at the interface between core and can (i.e., there cannot be any relative motion at the interface, which is possible in an actual extrusion). The strain and strain rate distributions and effective stress contours showed similar results to those of the isothermal simulations. The FEM grid distortion represents the deformed interface between the IN100 core and 304 S.S. nose cap and can be compared to the experimental extrusion as a validation of the simulation. It also indicates that the inner radii flow faster than the outer radii. The interface was originally perpendicular to the centerline, and is ~45°to the centerline after deformation.

Four experimental extrusions of IN100 were performed (three with IN100 only and one with IN100 in a 304 S.S. can with a 1/4-inch can thickness) using a 700-ton horizontal Lombard extrusion press. The extrusions were used in conjunction with the earlier ALPID simulations to provide more insight into the extrusion process. However, the ALPID simulations were done for a powder metallurgy Pratt-Whiney extruded alloy, PWA 1056, while the extrusion experiments used cast billets. The difference between the two is significant and comparisons of the simulation and experimental data were difficult.

In addition, ALPID simulations for the compression of a ring between two flat dies (ring test) were performed to develop friction factor calibration curves for Al 2024-O, Ti-48Al-1V, and Ti-6Al-4V. The results indicated that strain-rate sensitivity affects the curves dramatically for friction factors greater than 0.15. Also, two lubricants, G-n Paste with MoS_2 and Unimoly R30 Metallic, were evaluated with Al 2024 rings at 425°C. Results showed that friction factors of ~ 0.15 and 1.0 can be expected with Unimoly and MoS_2, respectively. The simulations were also used to examine the volume change of the workpiece as a function of die displacement. The results showed that the volume change is linked to the magnitude of a material flow stress. Details of the study can be found in the paper, "Effects of Material and Processing Conditions Upon Ring-Calibration Curves" attached to the report.

Finally, the three versions of ALPID were evaluated and compared. The execution times of the MME-ALPID versions were evaluated by simulating the extrusion of IN100. Version 2.1 was ~32 times slower than version 2.2. Also, the load-stroke curve from version 2.2 was slightly higher. Identical results for the volume change of the workpiece were obtained for both MME-ALPID(2.1) and ALPID(2.3).

TASK: 94

TASK TITLE: Advanced Processing of Compound Semiconductors

TASK OBJECTIVE: Develop advanced process models for molecular beam epitaxial (MBE) growths.

SCIENTIST: Donald L. Dorsey, Ph.D.

DESCRIPTION OF WORK:

The objective of this task was to develop a process model for molecular beam epitaxy (MBE) of III-V semiconductor thin films and ultrastructures. Theoretical predictions indicate these new materials would make excellent IR-detectors, with cut-off wavelength as high as 25 μm. The purpose of the process model is to assist in developing new processes to produce these materials, and to provide part of the database required for an artificial-intelligence-based process control algorithm for MBE.

The research was a continuation of a previous task in which a preliminary growth model, using the Monte Carlo technique to simulate thin film growth of a simple cubic crystal in the [100] direction, was developed. The solid on solid (SOS) approximation was used (an atom can only occupy a lattice site if the lattice site directly below it is occupied, i.e., no vacancies or overhangs).

The primary work performed in this study was modeling growth of a zinc blend structure crystal. The model developed describes low temperature deposition (i.e., surface diffusion was not accounted for) of a face-centered-cubic (fcc) structured crystal in the (111) direction. The advantage of the model is that it has an analytical solution, and can therefore be used to check the results of a more physically rigorous Monte Carlo model for the case of low-temperature deposition. This is the limiting case for (111) growth of GaAs, and can be used to test more sophisticated models for MBE growth of GaAs.

The model is based on two assumptions:

1. The gallium arsenide growth surface is considered to be arsenic-stabilized at all times during growth (i.e., there are never any exposed Ga atoms on the surface; it reacts with excess As in the gas phase as soon as it is deposited).

2. Gallium atoms are deposited randomly at available adsorption sites and diffusion across the surface is not allowed (i.e., case of deposition at a low substrate temperature). This deposition rule results in no vacancies or overhangs in the lattice. Also, the deposition rate is taken to be proportional to the concentration of available sites.

The model was used to obtain several results and conclusions:

1. The deposition rate is determined by the product of the impingement rate times the number of available sites on the surface. A system of equations was developed that completely describes the rate at which any number of deposited layers form and can be solved using a fourth-order Runge Kutta technique.

2. The growth is far from layer-by-layer mode because the first layer nears completion only as growth of the fourth layer commences. The number of atoms deposited in four-time steps is only equal to as many atoms are required to fill ~2.4 layers.

3. The specular reflection high energy electron diffraction (RHEED) intensity, as calculated using the kinematical scattering approximation, rapidly decreases initially to zero, and then rises to a small peak as the first layer nears completion, indicating that the growth surface is rough. The oscillations for this case are strongly dampened, which is consistent with low-temperature growth where the deposition is random and no evaporation or surface diffusion occur.

TASK: 95

TASK TITLE: Feature-Based Reasoning about Geometric Dimensioning & Tolerancing

TASK OBJECTIVE: Demonstrate how tolerances can be incorporated within the framework of a system for feature-based design and inspections planning, so the same constraints can be reasoned about both symbolically and with particular values.

SCIENTIST: Leon Sterling, Ph.D.

DESCRIPTION OF WORK:

The scientist performed work involving the development of a prototype system for reasoning about tolerances expressed in a form compatible with the Geometric Dimensioning and Tolerancing standards. A consistent, coherent framework was established for reasoning symbolically, and was applied to reasoning about parts for manufacturing. The framework is based on constraint logic programming. While the paper emphasizes the importance of symbolic reasoning, in fact the work was more general. A unique feature of the approach is that the same code can often be used both for symbolic and numeric values. The flexibility stems from using a logic programming language which evaluates constraints if there are actual values, but treats them symbolically if there are symbolic values. The part description being reasoned about can contain any combination of symbolic and numeric values.

The paper describes several examples of reasoning with symbolic representations. Examples are described of defining generic and toleranced parts, incorporating features in the style of feature-based design as developed in the RDS ("rapid design system") project, defining whether a specific part meets its tolerances (reasoning about dimensioning and tolerance information), checking a part using design rules, performing boolean operations on underspecified parts, and drawing underspedified part descriptions on a terminal screen or hardcopy device.

The experiments were done using the logic programming languages Prolog and CLP(ℜ). The parts tested were simple two- and three-dimensional examples. The results lead to several conclusions. Constraint logic programming is a promising paradigm for reasoning about parts in the context of computer-aided design tools. The representation scheme has excellent expressive power to describe relationships between features in complicated parts. Effective inference engines implementing constraint logic programming need to efficiently solve large collections of constraints. There is a good potential for building a robust system but it remains to be determined whether current constraint-solving techniques are adequate, or whether new methods need to be developed. Further research is needed to ascertain the practicality of constraint logic programming for designing complex parts. Further research is also needed on systems for solving symbolic constraints and embedding such solvers into a logical reasoning system.

TASK: 96

TASK TITLE: Theory of Electromagnetic Waves Propagating in Nonlinear Anisotropic Optical Materials

TASK OBJECTIVE: To model the behavior of electromagnetic waves in nonlinear optical materials arranged in geometries appropriate for integrated optics.

SCIENTIST: David S. Moroi, Ph.D.

DESCRIPTION OF WORK:

The objective of the study was to obtain the accurate solution, in analytical form, to Maxwell's equations for an arbitrary optical system which consists of nonlinear optical materials, such as barium titanate ($BaTiO_3$) or strontium barium niobate [$Sr_{0.6}Ba_{0.4}Nb_2O_6$(SBN:60)] and linear optical materials such as air or any metal with plane boundaries. The solutions of the nonlinear wave equation resulting from the Maxwell equations reveal the response of the materials to electromagnetic waves and provide information on their nonlinear optical properties, such as dispersion, reflection, refraction (transmission), and optical activities. The results of the calculation can be applied to various problems in nonlinear optical phase conjugation including aberration compensation, pointing and tracking, etc., as well as amplitude-modulation, self-focusing, etc. In the present work, a general formalism for obtaining the plane wave solutions, including the surface P-waves on the plane boundaries, was reported.

TASK: 97

TASK TITLE: Engineering Analysis of Stresses in Composites: "Residual Stresses in Thermoplastic Matrix Composites During Processing"

TASK OBJECTIVE: To perform engineering and experimental analyses on the stresses in composites resulting from the manufacturing/fabrication processes.

SCIENTIST: Shing-Chung Yen, Ph.D.

DESCRIPTION OF WORK:

Perhaps, the most difficult task that one may face in the analysis of the residual stress development is the continuing change of viscoelastic material properties due to the change of molecular and chemical state (e.g., crystal-morphology, degree of cure, etc.) during cooling. In particular, for a thermoplastic composite material (carbon/PEEK), the coefficient of thermal expansion (CTE), the degree of crystallinity, and crystal-morphology of the matrix changes continuously with temperature and cooling rate. This implies that at least several sets of master curves and shift factors related to the viscoelastic properties for different states of crystallinity and crystal-morphology must be established in order to determine the state of stress of composite after being cured. The time integration using the Boltzman-type formulation to determine the residual stress must be carefully conducted.

In the study, engineering analyses were performed to quantify the residual stresses in fiber reinforced composites resulting from the manufacturing/fabrication processes (time, temperature and pressure) required to produce structural grade composite material. Parameters considered included resin-type (thermoset/thermoplastic), fiber-type (carbon/glass), fiber orientation, and ply

stack up orientation. An analytical procedure to determine the curing residual stress development of the thermoplastic composite structures was developed.

The approach used in the research was primarily based on mechanics of materials, micromechanics for compsites, lamination theory, and theory of viscoelasticity. The mechanics of materials was used to establish the stress development in both the fiber and matrix undergoing a continuous deformation process. The micromechanics were used to establish the orthotropic properties of a composite laminate. The lamination theory was used to determine the time-delay responses related to the thermal history of a cooling process. The viscoelasticity was introduced in the analyses involving the properties of the matrix material.

Several assumptions were made in order to narrow the scope of the problem studied in the project. First of all, the fiber material was considered as elastic while the matrix material was assumed to be viscoelastic. The fiber and matrix were considered to be isotropic and their properties were considered to be temperature dependent (fit using second order polynomials). It was further assumed that the matrix properties are dependent upon the coupling effect of time, instantaneous temperature, cooling rate, and degree of crystallinity. Another important parameter incorporated in the project was the volumetric straining during the cooling procedure. It was assumed that the volumetric straining of the matrix material is related to the coefficient of thermal expansion (CTE). That is the CTE for the matrix material can be determined from the relation between the volumetric straining and temperature. One thing not accounted for was the rate-dependent volumetric straining. It has been shown previously that the volumetric straining vs. temperature relation varied with different cooling rates. This means that the CTE of the matrix material should be a function of both temperature and rate of temperature decrease. It was also pointed out that CTE is related to the amount of thermal loading developed in a laminate.

The scientist developed several equations for basic material properties and developed a fiber matrix interaction model in an attempt to determine the axial stress in the fiber and matrix due to the thermo-viscoelastic condition generated by the cooling process. Equations were also derived for cases when different constraints are introduced into the system. Three examples were given: the calculation of the axial stress developed in the fiber and matrix of a layer under a partical constraint, the residual stress transverse to the fiber direction due to a total constraint condition (against the thermal expansion), and the shear stress under a total constraint condition.

A basic emphasis of the project was to model the residual stress problem using the properties of the constituents of the composite (a micromechanics approach). The micromechanics equations, rule of mixture (for modeling the modulus and CTE in the fiber direction and the Poisson's ration), Halpin-Tsai equation (for modeling the transverse and shear moduli), and the Schapery equation (for modeling the CTE transverse to the fiber direction) were used to model the viscoelastic orthotropic material properties. The material properties determined using the equations developed can be used to determine the stiffness matrix of an orthotropic lamina.

Also developed was a viscoelastic stress-strain relation for a unidirectional composite layer (orthotropic lamina) based on the Boltzman principle (integral) and viscoelastic stress-strain relation under a given thermal history for an off-axis lamina. Since a closed form expression for the resulting integrals is almost impossible to obtain, a numerical procedure using a small incremental time step was used.

A similar procedure was used to determine the residual stresses in composite laminates. The Boltzman integral was introduced, along with lamination theory for the viscoelastic response of composite laminates. The same incremental time-step approach was also used for the integrations. From the resulting equations, the deformation (midplane straining and curvature) profile of a

composite laminate can be performed.

Finally, the analytical equations can easily be converted into a numerical procedure. A recommended algorithm is given for the development of a computational procedure as a part of an expert system for a process control module for residual stress.

TASK: 98

TASK TITLE: Polymer Research

TASK OBJECTIVE: Computational Analysis of Ordered Polymer Mechanical Properties.

SCIENTIST: Douglas A. Smith, Ph.D.

DESCRIPTION OF WORK:

The broad objective of this research was the computational analysis of ordered polymer mechanical properties. The specific work to be done included the use of computational chemistry methods to predict and explain mechanical and physical properties of ordered polymers, for use in future aircraft and space systems. The group which performed the work is currently involved in basic research studies of small organic and oligomeric systems to determine (1) nonlinear optical (NLO) properties of these systems, in particular the parameters alpha (polarizability), beta (first hyperpolarizability), and gamma (second hyperpolarizability); (2) the necessary and sufficient level of theory to accurately calculate these properties; and (3) the underlying physico-chemical basis for the calculated (and experimentally observed) nonlinear optical parameters.

The initial work performed was the evaluation of two similar semiempirical molecular orbital computational methods and packages, AMPAC 3.1 modified to include a routine for calculating NLO properties and MOPAC 5.0 with the routine POLAR, and the merging of them into a single, optimally functionalized package. This includes printouts of the polarizability tensors and solving for the hyperpolarizabilities both as a function of the energy and the dipole. In addition, modifications were added to allow one to plot the molecular orbitals, using the programs Density and Draw. This allows the chemist to view the changes in the orbitals involved in NLO effects as a function of applied electric field.

Studies on the effect of the magnitude of the electric field and of the SCF criteria on calculated NLO parameters were also performed. It was found that the electric field must be set to a value of at least 0.005 for convergence to be observed.

Two major projects were undertaken, using MOPAC 5.0 with the Polar routine modified as stated above, and are considered to be nearly completed. The first was a systematic study of substituted ethylenes. Optimized geometries and NLO parameters for 25 compounds derived from ethylene were calculated. Calculations of molecular and fragment volumes were done using MacroModel 2.5, a molecular mechanics package. No clear trends or rules have been determined as of yet, although correlations with molecular volume, functional group volume, and electron density of the functional group are being investigated.

In the second study minimum energy conformations and NLO parameters for linear polyenes were calculated. In the first part of this work, compounds containing from one to eleven ethylene units in an all-trans, completely extended, conformation were studied. Calculated values of gamma are reported, along with available experimental values and previously calculated results from ab

initio studies. The results showed that the repeat unit average value for gamma had not yet begun to level off to a constant value, as would be expected for a polymer of infinite length.

The second part of this study investigated the effect of conformation of the polyene chain on NLO parameters. For butadiene and hexatriene systems the heat of formation was used to obtain a Boltzmann distribution of the various conformers and therefore the NLO values for the equilibrium system.

For butadiene the results showed:

1. The transoid (extended) form has higher values of alpha and gamma.
2. At 25 °C the cisoid to transoid ratio is 21.392:78.608.
3. The equilibrium value of gamma = 1.814×10^{-36} esu.

The results for the trans form of hexatriene showed:

1. The Boltzmann distribution at 25 °C for the transoid-trans-transoid, cisoid-trans-transoid, and cisoid-trans-cisoid conformations is 74.864:20.134:5.002.
2. The equilibrium value of gamma = 12.886×10^{-36} esu.

TASK: 99

TASK TITLE: Processing Science of Organic Structural Materials: "Polyimide In Situ Molecular Composites Processing"

TASK OBJECTIVE: To develop innovative processing approaches to fabricate molecular composites and rigid-rod polymers for structural and nonstructural applications.

SCIENTIST: Yih-Fang Chen, Ph.D., Adtech Systems Research

DESCRIPTION OF WORK:

Rigid-rod molecules (PBT/PBO) reinforced molecular composites and their derivatives were formulated in acidic solutions. The processing conditions of the fibers and films were studied to assess their impact on the material properties.

Polyimides are high-temperature-application resins, which are widely used in composite, adhesive and electronic industries. These polymers are mostly derived from poly(amic acid), poly(amic ester), or poly(amic amide) (PAA). The poly(amic acid) and poly(amic ester) systems have one inherent problem, the removal of the condensation by-product, water or alcohol. The Materials Laboratory uses the poly(amic amide) system and has developed a general synthesis method of high molecular weight poly(amic dialkyl amide) via poly(isoimide).

The advantages of using poly(amic amide) precursor include: it can make high molecular weight polymers and by careful design, the leaving group, i.e., the amine, can be used as a thermosetting matrix resulting in so-called in situ molecular composites. This study investigated the processing of in situ molecular composite for poly(amic dialkyl amide) systems.

The imidization was evaluated by monitoring the film by FTIR in situ. The rheology of the polymers upon reaction was studied by Torsion Impregnated Cloth Analysis (TICA), a technique similar to Torsional Braid Analysis (TBA).

Two different series of poly(amic dialkyl amide) systems were studied. The first was poly(amic amide)/DNI-3A polymers, with different molecular weights, made via adjusting the PMDA (pyromellitic dianhydride) and TMB (tetramethyl benzidine) monomer ratio. The resultant polymers have intrinsic viscosities between 0.34 and 3.90 dl/g. The TICA experiments for this series of polymers showed several results. The moduli and tan delta curves are similar to one another (since the chemical behavior of the polymers is the same). However, different polymers exhibited slight variations in transition temperature onset, in the range 190-210 °C. The moduli returned to their maximum values in the range 290-300 °C and then immediately dropped above 300 °C. TBA data showed that the polymer lost weight gradually when heated up after 240 °C. Compared to PAA/dodecyl, which exhibited a sudden weight loss in the 270 °C range then leveled off, PAA/DNI polymers suffered from degradation of thermoset units resulting in decreases in the moduli.

The poly(amic amide) polymers with different alkyl groups (so-called leaving group since it leaves the polymer backbone when the imidization occurs) have a PMDA/TMB ratio of unity. Although these polymers have similar chemical structures their intrinsic viscosities varied from 1.41 to 3.60 dl/g, probably due to the fact the polymers were not synthesized from the same batch of polyimide and thus their molecular weights varied. The TICA results indicated for linear alphilic group polymers, the larger the group the earlier the polymer began to soften. At the Tg transition the drop in the rigidity value (G') for PAA/decyl was two times that for PAA/octyl or PAA/dodecyl. The PAA with linear alphilic groups began to soften in the 170-190 °C range and leveled off in the 290-310 °C range.

It was also noted that PAA/DPI-3A (poly(amic amide)/di-phthalicimide-3A) had the highest transition temperature because its leaving groups are aromatic rings. This was also observed for the PAA/DNI polymer with a viscosity of 3.90 dl/g (similar to that for PAA/DPI-3A).

When the polymers were heated up their moduli decreased due to thermodynamic effects. The moduli dropped rapidly at the moment the materials defrost from the glassy state to the leathery state. Consequent temperature increases initiated chemical reactions, which determined the polymer's rigidity. The rigid product can be either a thermoset network like in the epoxy process or a rigid thermoplastic structure like the formation of rigid rods from coil polymers (as is the case for polymers without the DNI-3A leaving group).

Also, after complete reaction at elevated temperature, polymers with linear alphilic leaving groups exhibited higher G' values, close to those of unreacted polymers at 0 °C, than polymers with aromatic leaving groups. The alphilic leaving group served as a better plasticizer, which helped the system to increase the chain mobility for easier rigid-rod formation.

The results of the research lead to the following conclusions:

1. The poly(amic amide) systems have different behaviors due to the different leaving groups.

2. They can be used as candidates of in situ molecular composites by carefully designing the leaving groups.

3. The FTIR and TICA data both demonstrated that the imidization of the PAA/DNI-3A systems is a two-staged first-order reaction process.

TASK: 100

TASK TITLE: Polymers: "Synthesis of Thiophene Dicarboxaldehyde Monomers for Novel Poly(Schiff Bases) Which Exhibit Nonlinear Optical Properties"

TASK OBJECTIVE: To synthesize novel poly(schiff bases) which exhibit nonlinear optical properties.

SCIENTIST: James J. Kane, Ph.D.

DESCRIPTION OF WORK:

The Materials Directorate (MLBP) is directing certain of its research efforts toward the development of new materials possessing optimal nonlinear optical (NLO) properties. This property is primarily concerned with the response of a dielectric material to a strong electromagnetic field. Thus, MLBP is compiling an NLO model compound database in order to uncover molecular structure - NLO property relationships. These data will then serve as a guide for the design and the synthesis of organic polymeric materials predicted to exhibit optimal NLO properties. Structures which have been included in the database to date are based on benzodiimidazole and benzodithiazole model compounds containing phenyl, vinylbenzene, thiophene, vinylthiophene and polythiophene segments as part of the extended conjugated pi-electron system.

Preliminary data collected for the model compound systems mentioned above indicate that the thiophene nucleus is effective in enhancing NLO properties. This observed trend, together with the fact that relatively little NLO data is available for the class of conjugated poly(schiff bases) or the polyazomethines prompted this study of the synthesis of several thiophene dicarboxaldehyde monomers for conversion into a series of azomethine model compounds and polyazomethines for subsequent evaluation of their level of NLO activity. Specifically, the nomomeric dialdehydes 3,4-didecyloxy-2,5-thiophenedicarboxaldehyde (I) and 3,3' - (3,4-didecyloxy)thiophene-2,5-di-yl bis-propenal (II) were sought and I was successfully produced. The condensation products of I and II with aromatic monoamines or diamines will provide model compounds. Incorporation of the decyloxy substituents in the thiophenes is intended to enhance the solubility of the final polyazomethines which are known to have very low solubility.

The most convenient route to monomer I starts with the readily available diethyl-3,4-dihydroxy-2,5-thiophenedicarboxylate. Several attractive routes are available for conversion of the diester to the desired dialdehyde, I. Three approaches were selected for evaluation in the current project.

McFadyen Stevens Reaction Sequence

The above diester was first converted to a bisbenzenesulfonylhydrazide. This was subjected to the McFadyen Stevens reaction procedure (ethylene glycol, sodium carbonate, and heat) to produce a red oil which, according to thin layer chromatography (TLC), appeared to be a mixture of six to eight components. The FTIR spectrum showed an OH stretch absorption and a carbonyl absorption. This reaction scheme was not pursued further due to the complexity of the product mixture, the anticipated difficulty of removing ethylene glycol from the desired product and the probable need for considerable experimentation to evaluate a variety of solvents, temperatures and reaction times.

Lithium Aluminum Hydride Reduction of the Diester

This procedure used $LiAlH_4$, diethyl amine, and the diester in heptane at room temperature. TLC showed enough components to account for all conceivable reaction products, thus this scheme was also abandoned.

Reduction of Diester to Dialcohol and Subsequent Oxidation to the Dialdehyde

Four different reaction schemes were employed for this reaction sequence. The only reaction scheme to have any success was oxidation of the diol, 3,4-dedceyloxy-2,5-dihydroxymethylthiophene, (created by reduction of the above diester) using four equivalents of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) per mole of diol in diethyl ether resulting in an 83% yield of dialdehyde.

TASK: 101

TASK TITLE: Advance Intermetallic Microstructure/Property Relationships

TASK OBJECTIVE: To provide basic understanding of microstructure/properties relationships in advanced intermetallic materials.

SCIENTIST: Vijay K. Vasudevan, Ph.D.

DESCRIPTION OF WORK:

The purpose of this work was to determine the fundamental mechanisms governing the plastic deformation behavior of intermetallic alloys based on TiAl. Electron microscopy and mechanical testing techniques were used to study the structure and mechanical behaviors. Major emphasis was placed on alloy compositions (in at.%) Ti-46 Al, Ti-48 Al, Ti-50 Al and Ti-52 Al. Compositions in the range of 46 to 50Al are two-phase TiAl + Ti_3Al alloys, whereas the 52Al alloy is single-phase TiAl. The investigation consisted of the five parts described below.

The Effect of Purity

The effect of purity, interstitial O, C and N, on the deformation behavior of polycrystalline TiAl and TiAl + Ti_3Al was divided into two parts. In the first, erbium (Er) was added to purify the alloy by gettering O, C, and N from the TiAl matrix and forming particles of erbia (Er_2O_3 containing C and N). Alloys of the compositions Ti-51.48Al-1Er (TAE1), Ti-49.5Al-1Er (TAE2) and Ti-47.52Al-1Er (TAE3) were prepared by electric-arc melting of commercially pure Ti, four nines pure Al and Er. An appropriate homogenization procedure was determined by subjecting specimens to two types of heat treatment and then studying the microstructures of the alloys in both as-cast and heat-treated conditions by optical and transmission electron microscopy (TEM). For complete homogenization the following heat-treatment procedure was necessary: 1300 °C, 25h + 1150 °C, 50h + 1050 °C, 2h + air cooling. The results also showed the addition of Er had a significant effect on the solidification microstructure. A bimodal distribution of erbia particles consisting of large, homogeneously distributed particles and finer particles (appearing within pools of Ti_3Al, indicating they may have formed by internal oxidation in the solid state) in the interdendritic regions, was observed.

In the second part of the purity effects study, highly pure binary TiAl alloys were prepared from highly pure starting elements (Ti with an O content of about 156 ppm and five nines pure

Al) using arc-melting. An initial sample of Ti-52 Al showed an O content of about 140 ppm, comparable to that in the initial Ti material. Subsequently, Ti-52 Al, Ti-50 Al and Ti-48 Al alloys were prepared. Deformation and ductility studies are currently being performed.

The Effect of Grain Size on the Yield Stress

The effect of grain size on the yield stress and the temperature dependence of the yield stress of TiAl and TiAl + Ti_3Al, homogenized and forged samples of Ti-52 Al, Ti-48 Al and Ti-50 Al alloys were used. The optical microstructure of the Ti-48 Al alloy showed elongated grains which were heavily deformed and contained numerous deformation bands and twins. Some regions showed dynamically recrystallized grains. Further testing of the three alloys is presently underway.

Interface Structure and Geometry of the Ti_3Al + TiAl Lamellar Structure

The two-phase alloys are characterized by a microstructure consisting of alternate lamellae of Ti_3Al and TiAl. The presence of this structure has important effects on the mechanical properties, so effort was directed to determine their structure and the mechanisms involved in their development. Ti-48 Al and Ti-46 Al alloys were heat treated to produce the lamellar structure and characterized by TEM. The orientation relationship between TiAl and Ti_3Al was observed to be (111) TiAl // (0001) Ti_3Al and $[0\bar{1}1]$ // $[s\bar{1}\bar{1}20]$ Ti_3Al. The TiAl regions in contact with any given Ti_3Al lamella occurred not only with a twin relationship (i.e., related by a shear along a [112] direction on a common {111} plane), but also as orientational variants, whose structure and geometry was examined by electron diffraction. The results showed simultaneously a [110] pattern in one and a [101] pattern in the adjacent region. The results of tilting experiments showed that the unit cells of these regions were oriented with the c-axis at 90° to each other. The formation of TiAl lamellae with this orientation could be rationalized on the basis of a reduction in elastic strains.

Deformation Behavior of TiAl Single Crystals

Single crystals of Ti-48 Al, Ti-50 Al, Ti-52 Al and Ti-54 Al alloys were examined by optical metallography. The microstructures revealed that all alloys appeared to be polycrystalline and contain Ti_3Al. Large areas of single crystal material were present, as judged by the response of the polished and etched surfaces to polarized light. TEM revealed that while the ingots were not fully single crystal, the growth direction or the crystal axis is by and large near a [110] direction. Deformation studies are still in progress.

Study of Quartenary TiAl alloy, G2, and Binary Al-Ta alloys

The microstructures of extruded and heat treated samples of the quartenary TiAl alloy, G2, were characterized by TEM and the results correlated with the optical microstructure.

The crystal structure and symmetry of a new intermetallic compound "AlTa" were determined by TEM. Both conventional and convergent beam electron diffraction showed that the unit cell of this compound was face centered cubic, with space group Fm3m and lattice parameter of 18.6 Angstroms and contained approximately 386 atoms.

TASK: 102

TASK TITLE: Polymers

TASK OBJECTIVE: Computational Predictions of Structure in Ordered Polymers.

SCIENTIST: Barry L. Farmer, Ph.D.

DESCRIPTION OF WORK:

Computational chemistry methods were used to study rigid-rod and pendant-substituted rigid-rod polymers. Part of the effort undertaken represented a continuation of previous research reported last year. The effort, in large part, centered on bringing several items to publishable completion and submitting a manuscript to Polymer (which was also submitted with this report). The results of this effort included:

1. Preparation of publication-quality figures of the conformational energy maps and molecular structures

2. AM1 calculations on PPBI to verify the planar geometry of the amine nitrogen of the heterocycle

3. Completion of the study of hydrogen bonding effects in hydroxy-substituted poly-p-phenylene benzobisoxazole (PBO) and poly-p-phenylene benzobisthiazole (PBZT), and comparison with structural data on a model compounds

4. Quantitative comparison of the conformational energy curves and maps by calculation of the conformational entropy associated with the different rigid-rod polymers and various substituents on PBZT and PBO.

An additional topic addressed was further analysis of the molecular trajectories of rigid-rod polymers. Previously reported results were subject to considerable uncertainty in the measured angles because of the manner in which the molecules were constructed by Chem-X.

To assure the proper geometry of the molecules and to avoid out-of-plane displacements for the phenyl and heterocylcic rings and deviations in the angles measured between the para connections across a phenyl ring, the following procedure was used. The geometries for each component ring were first optimized using molecular mechanics and this unit was then oriented such that its atoms lay in the xy plane, and the z coordinate of each atom was set to zero. The planarized components were then used to construct representative polymers with chain lengths on the order of 25 to 30 Angstroms, corresponding to three repeat units of PBZT and PBO polymers, and five units of the poly-BZ and poly-BO polymers.

The trajectories of the rigid-rod polymers were obtained by measuring the distances between the same atom in neighboring and next-neighboring repeat units of the polymer. For most of the polymers considered, the trajectories are dependent on the orientations of the repeat units (i.e., on the torsion angles along the backbone). Conformations at the two extremes were reported. In most cases, the conformations that were examined had all the rings of the polymer coplanar to the extent allowed by the molecular topology. In all cases, the sequence of torsion angles was such that the planes of alternating rings along the chain were parallel or coplanar.

For homopolymers, the results ranged from the syn form of cis-BZ, which became nearly circular after about 10 repeat units, to many other structures which were quite linear. Usually, for structures reasonable in the context of roughly linear trajectories, most angles are in the range of 170°to 180°. For fibers of these materials, property improvement upon annealing may correlate with the redistribution of ring orientations to give the most linear geometry available. Further, the

slight misorientation (~10°) between the bonding directions and the molecular axis may provide a relatively "soft" deformation mode which would dictate the initial moduli of the polymers.

Trajectory data for the alternating BZT-Fluorene polymer and for PBZT containing a single fluorene unit as a defect were reported. By virtue of the 156° angle between the connecting bonds of the fluorene unit, substantial nonlinearity is introduced to the polymer chain, thus significantly influencing the trajectories.

The results of this research lead to the following conclusions:

1. The introduction of one or a series of fluorene units has a dramatic effect on the trajectory of the polymer molecule.

2. Some molecules can make lateral excursions of up to 25 Angstroms (from the path a PBZT homopolymer segment would take) before the next occurrence of a fluorene unit.

3. Alternatively, adjustments of orientation of the repeat units could produce a molecule having less than a 10-Angstrom excursion.

4. Such excursions at the molecular level, coupled with the conforming influence of intermolecular interactions, could account for the higher degree of interweaving observed in scanning electron micrographs of fractured PBZT-Fluorene fibers.

5. Perfection of conformality or minimization of the excursions may also be correlated with improved fiber properties attained after annealing.

TASK: 103

TASK TITLE: Assessment of Fiber Coating Options for Oxide Fibers

TASK OBJECTIVE: To identify viable options for stable coatings on oxide fibers for use in ceramic composites.

SCIENTIST: Amit Chatterjee, Ph.D., Adtech Systems Research

DESCRIPTION OF WORK:

The scientist was to identify potential coatings for oxide fibers, with particular attention to mullitebased compositions, which would be compatible with selected oxide matrices. In addition he was to devise and perform tests to evaluate the most promising coating.

The major effort of the study was the development of a test technique which minimizes bending strains in ceramic composites containing oxide fibers. Since the loads to failure for the SDS-6 fiber reinforced glasses was expected to be small (around 15-25 lbs), it was felt that epoxy grips would be strong enough. Different combinations of epoxy and pneumatic grips were tried but the only method which worked was to have epoxy at the top and at the bottom.

The test technique was first performed on a brass plate strain gauged on either side. It exhibited minimal bending strains. A CGW 7761 glass composite was tested in the transverse direction for measurement of properties. The volume fraction in this composite was around 16% fibers. The Young's modulus was 10 MSi and the stress at nonlinearity was 0.4KSi. A single crack

formed right under the gauge. This was considered a valid test.

Overall, this test technique seems to work. Efforts are being made to fabricate specimens with the six-matrix combinations for further testing.

TASK: 104

TASK TITLE: Synthesis and Characterization of Crown Ethers and Other Macromolecular Complexes of the Lanthanide and Transition Metal Ions

TASK OBJECTIVE: To investigate several entirely new classes of potentially optically active compounds. In this investigation an attempt will be made to synthesize new compounds and to modify existing compounds and to correlate their chemical structure and their optical characteristics.

SCIENTIST: Shyama P. Sinha, Ph.D., University of Dayton Research Institute

DESCRIPTION OF WORK:

The objective of the study was to investigate several new classes of potentially active compounds for their optical nonlinearity responses. The main thrust of the research was directed towards the synthesis and characterization of crown ether complexes of the lanthanides and the study of their optical nonlinear properties.

The scientist was able to synthesize the 18,6-crown ether complexes of the general composition $[M(NO_3)_3]_4[(18\text{-crown-}6)]_3$, where M(III) is one of the following lanthanides: Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, and Y. In total, 12 different new complexes were prepared and their optical spectra investigated.

Spectral studies of these complexes involved the scanning of the UV, VIS, and near infrared (NIR) region (190-900 nm) of the optical spectrum. Characteristic peaks, slightly modified due to complexation, were detected and identified. In addition several other studies were performed, the results of which were presented in three papers, attached to the report.

"Time Resolved Fluorescence Spectra and Lifetimes of $Eu(NO_3)_3$ Complexed with 18-Crown-6 Ether in the Solid Phase and in Aprotic Solvent."

Two complexes of composition $Eu(18,6\text{-crown})(NO_3)_3$ were synthesized, each having very different crystal morphology (as detected from infrared and X-ray analysis) and exhibiting different values of the excited state (5_{D_0}) lifetime under monochromatic excitation (using a Pulsed Spectrofluorometer). The solid complexes are dichroic in nature. The 5_{D_0} lifetimes (at ~620 nm) of the solid 4:3 Eu(III)-complexes were in general very high, 1640 and 1860 μs. The complexes in acetonitrile (CH_3CN) solutions also possessed relatively high lifetimes (1350 μs for both), compared to 275, 185, and 110 μs for $Eu(NO_3)_3\ 6H_2O$ in CH_3CN, $Eu(NO_3)_3\ 6H_2O$ (solid), and Eu(III) aquo ion, respectively. Considerable increase in the lifetime of the 5_{D_0} level of Eu(III) in the crown ether complexes may be viewed as due to the protective action of the crown ether (18,6) during complexation and the absence of water to hydration in these complexes.

"Third Order Hyperpolarizability of Nd(III)-18-Crown-6-Tris-Nitrate Complex in Aprotic Solvent"

Aprotic solutions of $Nd(18,6\text{-crown})(NO_3)_3$ complex were tested for their nonlinear responses

using a degenerate four-wave mixing experiment ($\lambda = 532$ nm). Values of hyperpolarizability, $\chi^{(3)}$, obtained from plots of reflectivity vs. probe energy were : 0.13×10^{-12}, 0.09×10^{-12}, and 2.85×10^{-12} esu for Nd(18,6-crown) nitrate, CH_3CN, and CS_2 (standard liquid), respectively. The $\chi^{(3)}$ values of the complex are both concentration and probe-energy dependent.

"MNDO Calculation of Dipole Moments and Hyperpolarizabilities of Some Inorganic and Organic Solvents and Molecules Having Nonlinear Optical Responses"

Molecular orbital calculations for a number of organic ligands used in complexation and various inorganic and organic solvents commonly used in laser and nonlinear optical spectroscopy were performed using the molecular orbital package MOPAC at the MNDO level. The dipole moments (μ), second (β) and third (γ) order hyperpolarizabilities were determined and compared with the standard (NLO) liquid CS_2.

TASK: 106

TASK TITLE: Molecular Beam Epitaxy of Strained Layer Superlattices: "Molecular Beam Epitaxial Growth of Undoped and Si-Doped GaAs and AlGaAs Compound Semiconductor Materials"

TASK OBJECTIVE: Growth of superlattice materials by molecular beam epitaxy for use in Air Force optoelectronic applications.

SCIENTIST: Ming-Yuan Yen, Ph.D.

DESCRIPTION OF WORK:

The objective of this task was to study the MBE growth of GaAs and AlGaAs and their properties so as to have the foundation for further study of other materials. High energy electron diffraction was used as a tool to quantify optimum growth conditions and the results were compared with surface analytic techniques.

An AlGaAs sample with an Al composition of ~8% was grown by MBE and delivered to Materials Directorate Electronic & Optical Materials Branch (MLPO) to study the DX center. This measurement is still under way. The sample was also examined by photoluminescence and Hall measurements. The PL spectrum at 4K gave an Al composition of 12.51%, as measured from the bound excitation peak at 1.700 eV for the AlGaAs layer. It was postulated that the broad peak at 1.565 eV might be due to the electrons transferred from AlGaAs to GaAs. Hall measurements indicated that the carrier concentration is $\sim 1.5 \times 10^{17}$ cm^{-3}.

DLTS measurements were also performed on several MBE grown samples. EL2 was not detected in any of the GaAs layers. However, when GaAs was grown on 3 μm AlGaAs, it did show the presence of a deep level at about Ec-0.40 eV. The concentration was shown to be greatest near the interface of GaAs and AlGaAs and virtually zero near the GaAs surface. It was postulated that this deep level is due to Al tracking the growth front as GaAs is deposited on the AlGaAs layer.

A lightly Si-doped GaAs layer was also grown to examine the quality of the material after opening and bakeout of the system. The mobility from Hall measurement, for a carrier concentration of 2.26×10^{15} cm^{-3}, was found to be 5670 cm^2/v-sec at room temperature and 26,950 cm^2/v-sec at 78K. These results indicated that the material was of high quality.

The results of this study led to the conclusion that high-quality GaAs and AlGaAs compound semiconductor materials can be successfully and reproducibly grown by MBE.

TASK: 107

TASK TITLE: Superconducting Detector Arrays

TASK OBJECTIVE: Model phase locking in arrays of Josephson junctions when exposed to infrared radiation.

SCIENTIST: Paul Esposito, Ph.D.

DESCRIPTION OF WORK:

The primary goal of the study was to model the performance of single SNS Josephson junctions and regular arrays of junctions in the presence of coherent and incoherent electromagnetic (EM) radiation. However, along the way many things needed to be investigated; aside from the difficult questions of fabrication, there are new aspects of the normal-superconductor transition, impedance matching problems, sensitivity and coherence effects, the formulation of performance criteria and figures of merit, interface problems, to name just a few. In the report the scientist discusses several aspects of high temperature superconductors that have immediate importance to the main goal of infrared detection by Josephson junction arrays. The main items discussed were (1) the correlation length, (2) Landau-Ginzburg theory, (3) Kosterlitz-Thouless transition, and (4) flux flow and flux creep.

High temperature superconductors are extreme cases of type-2 superconductors; the correlation length (fundamental length scale) which describes the physics of these superconductors is very short, usually about the size of a few unit cells. Thus, local conditions (local variations in stoichiometry, defects, twinning planes, etc.) and fluctuations significantly affect the properties of the superconductors. The effect of high T_c, the Kosterlitz-Thouless transition temperature, is to make the correlation length smaller. These materials also are highly anistropic, have low carrier concentration and a low Fermi velocity.

In the configurations that the scientist is mainly involved with, the I-V characteristics of films or 2-D arrays are of fundamental interest. Since the arrays will be operated at temperatures well above absolute zero, there will always be some quasi-particles present. The current carried by these quasi-particles will be normal; they will produce a voltage drop. The phase transition between the nromal state and the superconducting state must be carefully considered. For bulk materials, this has been well studied and characterized. The transition from normal behavior to superconductor in 2-D is more complicated than for bulk materials. This transition is known as the Kosterlitz-Thouless transition.

In order for high temperature superconducting devices to be useful in connection with ordinary electronics, the high temperature materials must have a high critical current. For low power loss, those features of the high temperature materials that lead to the appearance of voltages must be minimized. A well established theory for low temperature superconductors is the Landau-Ginzburg. This theory describes, in terms of a correlation length, the resistive-superconducting transition in terms of the Kosterlitz-Thouless transition in which voltages are due to flux-flow.

The question of flux-flow in high temperature superconductors is of vital importance to device

applications (its effects on the performance of Josephson junction arrays as infrared detectors are discussed in the report). The report states that a new Landau-Ginzburg theory must be formulated which incorporates a very short correlation length and anisotropy.

Also investigated were the effects of fluctuations on the diamagnetism of superconductors. The short correlation length in high temperature superconductors has the additional effect of making the wave function of the superconducting pairs of electrons small in extent: (i.e., there is not a very great overlap of the wave function of distinct pairs). Therefore, the coherent phase locking is susceptible to fluctuations and in general, the shorter the correlation length, the more fluctuations count. A rather lengthy calculation on the effects of fluctuating diamagnetism is presently being pursued.

Finally, the transport properties of high T_c materials are among the most important aspects in providing a clue as to the nature of the superconductivity. The report discusses the results of zero magnetic field resistivity measurements of metals, low and high T_c materials in the normal state and semiconductors. Also discussed are measurements of the thermal conductivity and specific heat. From the results it appears that the temperature dependence of the resistivity of high T_c oxide superconductors is the same as for a metal (linear). The conclusion drawn from the results was that the temperature dependence of the resistivity of high T_c superconductors is the same as that produced in ordinary metals by electron-phonon scattering and that the large magnitudes found are the result of a small carrier concentration and a large effective mass.

TASK: 108

TASK TITLE: Analytical Modeling of Thick Composite Laminates

TASK OBJECTIVE: To develop a post-processor for the strength analysis of thick composite laminates. This processor must convert the ply-by-ply strains into strength ratios for delamination.

SCIENTIST: Jose L. Perez, M.S.

DESCRIPTION OF WORK:

The research focussed on the development of a three-dimensional, linear, static finite element (FEM) program intended for the analysis of fiber directional (orthotropic) materials. The model is based on a 24 degree-of-freedom isoparametric element, which uses linear, Lagrangian polynomials for shape functions. Given a sufficiently refined mesh, this element produces optimal results for three-dimensional analysis. Following the completion of the finite element code several steps were performed that resulted in a complete design tool:

1. Partial verification with existing 3-D elasticity solutions.
2. Pre-processor development for automatic input file generation (mesh generation) for a composite plate with hole.
3. Post-processor development for analysis of FEM program output.
4. Study of in-plane and out-of-plane stresses and strains for several lay-ups.
5. Study of stress concentration factors for several lay-ups and geometries.

Validation

Validation was performed by comparing calculated and exact elasticity solutions for

longitudinal, in-plane stresses for a short, straight beam under sinusoidally loading (cylindrical bending). For linear, isoparametric elements the correlation of the exact solution is a rigorous test.

Mesh Generation Program

A computer program capable of generating the mesh data for any geometric configuration of a composite plate with an open hole (taking into account symmetry, lay-up, stacking sequence, etc.) was developed. The input to this program consists of several parameters: radius, plate width, number, and direction of plies, and number of elements. The output becomes the input to the FEM code: control parameters, coordinates, connectivity data, material properties, etc.

Numerical Test Case (Verification of Plate Problem)

The programs were run for a simple case with a simplified geometry (thin plate) and the results were compared to those predicted by a two-dimensional finite element analysis. The small difference between the two approaches indicated that in the limit, the three-dimensional theory agrees with existing more simplified approaches. Even with thin structures, the analysis was able to identify some classical behavior of composite materials, like edge effects.

Post-processor Development: Graphics Tool

Given the extensive amount of information generated by the FEM program, geometry, displacements (in three directions), strains, stresses (six components), and strength ratios (in virtually thousands of points), the need for a powerful graphics tool was evident. Since commercial graphics programs poorly accommodate composites, particularly this application, one was developed as part of this research effort.

The graphics program was developed using the PostScript language from Adobe Systems (an industry standard used by many professional printers). A FORTRAN computer program was written (1) to automatically read the finite element output data file and (2) to create a file containing PostScript commands and generate information to plot graphics on an Apple Laserwriter printer. The graphics results can also be visualized on an Apple Macintosh by using the commercially available PostShow program. Examples presented show: geometry plotting, node and element numbering, deformed geometry with respect to the original, and gray mapping of strength ratios.

TASK: 110

TASK TITLE: Research in Chemical Vapor Deposition in Ceramic Composites

TASK OBJECTIVE: Determine effective fiber coating chemistries, morphologies and CVD process parameters for obtaining desirable mechanical properties in ceramic composite systems.

SCIENTIST: Jason Guth, Ph.D.

DESCRIPTION OF WORK:

The objective of this task was to design and assemble an apparatus to coat fibers using chemical vapor deposition. The resulting apparatus was tested to determine what deposition conditions could be obtained.

The design of this system, as with any chemical vapor deposition (CVD) system, required five main components. These are: source gas control and delivery, substrate heating source, substrate holder, vacuum generation and control, exhaust gas treatment. The specific design of some components of the system was in part dictated by the available materials and what could be fabricated in the machine shop.

The main ingredient for growing materials by CVD is source material(s) in the gas phase. Compressed gases, or liquids and solids with sufficient vapor pressures, are used to supply reactants to the system. Pressure control of the compressed gases is achieved using gas regulators and flow control of gases is achieved by using thermal mass flow measurement devices coupled with proportioning valves. Power supply, set point, and readout are performed with a solid state controller consisting of six controllers with flow ranges of 50 to 500 sccm and two four-channel controllers. For liquid source delivery, a 1000 ml dip tube bubbler is used, as a container only, to deliver chlorosilanes by heating the liquid and passing the vaporized material through a mass flow controller.

The substrate heating source is a resistively heated tube furnace. Temperature control of the furnace is achieved using a solid state pid controller with input from one type S thermocouple.

The substrate (fiber) holding assembly consists of a mounting device and a 1" OD vitreous silica process tube held on both ends by O-ring seals. The end flanges holding the tube also provide for gas inlets and outlets. Typically, fiber(s) is suspended from the top end flange by sticking the end of the fiber(s) into a rubber septum which also provides a gas tight seal. The fiber can be spooled continuously through the reactor to coat long lengths.

Vacuum generation and control are accomplished with a rotary vane pump, capacitance manometer, proportioning valve, and controlling/readout device. Pressure control is achieved with a capacitance manometer and a proportioning valve in the exhaust line. A set point/readout controller runs the valve to balance the set point and measured system pressure.

Many of the gases used and their by-products are corrosive, toxic, and/or flammable so they must be neutralized before being discharged into the atmosphere. To accomplish this, two devices are used. The first is a scrubber which consists of a resin, designed to adsorb and neutralize toxic and acid gases, supported on beads. The second device is a burner to safely and controllably burn an hydrogen carrier gas to prevent explosions in the lab.

The system is configured to allow for the greatest flexibility in the use and control of different source materials and coating processes. Up to six gases can be used at any given time and introduced into either of two gas inlets at the bottom of the process tube. The gas flow can also be inverted so that the flow direction is down. All gas flow is conducted through stainless steel tubing or PVC hose in the case of exhaust flow.

The system was tested to determine if any desired processing windows can be achieved. In general any temperature (up to 1600 °C) and pressure (down to about 10 torr) can be achieved at any desired flow rates up to the limit of the mass flow controllers. Carbon has been successfully deposited onto fibers at atmospheric pressure.

TASK: 111

TASK TITLE: NDE Signal Processing Research

TASK OBJECTIVE: Identify and/or develop improved signal processing methods for the quantitative extraction of flaw information from ultrasonic and X-ray CT images.

SCIENTIST: P.K. Bhagat, Ph.D.

DESCRIPTION OF WORK:

The aim of the research was the determination of the extent to which it is possible to extend existing signal processing routines for the extraction of flaw information from ultrasonic and X-ray CT image data generated in a noisy environment. Also, algorithms which are least sensitive to this noise and are still capable of providing good defect resolution were to be identified.

Image reconstruction from projections is the process of developing an image of a two-dimensional disbribution (of a physical property) from measurements of its line integrals along a finite number of predefined lines. In computerized tomography, cross sectional images of objects under study are produced from the attenuation data of X-ray/ultrasound along a large number of lines through the cross-section. With ultrasound, the problem of image reconstruction gets more involved due to mode conversion refraction effects.

Currently, the standard technique for image reconstruction is that of filtered convolution back projection. This procedure requires that the projection data be convolved with a user defined filter prior to back projection. The study used an alternative approach, the direct Fourier inversion method based on the Fourier slice theorem. This theorem states that the one dimensional Fourier transform of a parallel projection is equal to a slice of the two-dimensional Fourier transform of the original object (or object function). The study showed, that given the projection data, it is possible to estimate the object by simply performing a two-dimensional inverse Fourier transform and that the resulting equation for the object can be readily implemented using a fast Fourier transform (FFT) algorithm. The results also imply that values of the 2-D Fourier transform along radial lines can be determined via Fourier transformation of the projections of an object at different angles. Since in practice only a finite number of projections of an object are taken, interpolation is necessary to define the needed Fourier transform data.

The success of reconstruction of the data depends on interpolation that must be performed in the frequency domain. From the projection theorem, the Fourier transform of the object is known at sample points along radial lines going through the origin in the frequency domain. However, in order to use the inverse 2-D FFT method, the samples need to be distributed on a Cartesian grid rather than on a polar grid. Therefore, the job of the interpolator is to approximate samples on a Cartesian grid in the frequency domain and the better the approximation, the more the reconstructed image will look like the original. In general there are two types of interpolation: local and global. For reconstruction purposes, the simpler the technique used for interpolation, the faster the reconstruction (at the expense of greater approximation errors). Local interpolation procedures are often implemented as "finite element" methods. The report discusses several interpolation methods: the nearest neighbor interpolation, bilinear interpolation, and the Mersereau and Oppenheim method (concentric squares raster method).

Finally, the effects of noise in the projection data of a reconstructed image were considered. Errors introduced via aliasing artifacts which are caused by insufficiency of data and noise due to electrical noise and/or round off errors were ignored (the latter can be modeled as additive noise). The reconstruction from the measured projection data is obtained by first filtering the projection by using a smoothing (filter) function which depends on a user defined trade off between image distortion and variance.

The results led to several conclusions. From the noise analysis it was apparent that very little improvement can be obtained in the use of a back projection algorithm, in a trade off between image quality and noise variance. In CT systems an attempt to improve resolution implies an increase in noise variance and the element-to-element noise is highly correlated due to the convolution kernel. The study also points out that the additive noise component due to scattering decreases the SNR of each measurement. It was recommended that optimum filter design be considered as a possible alternative study area to further the aims of this research.

TASK: 112

TASK TITLE: Role of Hydrogen in Titanium Aluminides

TASK OBJECTIVE: To establish a basic understanding of the role that hydrogen has on mechanical behavior of Titanium Aluminides.

SCIENTIST: Dan Eliezer, Ph.D.

DESCRIPTION OF WORK:

In recent years, increasingly demanding design requirements for advanced aerospace structures have initiated the development of new materials with improved mechanical property combinations. This demand has led to examination of the potential of the titanium-aluminides Ti_3Al and TiAl and their alloys as structural materials, as well as their use in hydrogen-rich environments at elevated temperatures.

Stoichiometric Ti_3Al and TiAl are brittle at room temperature, but they are ductile at elevated temperatures. One way of improving the room temperature properties of titanium aluminides is by adding elements such as Mo, Nb, V, and W, which stabilize the high temperature body-centered cubic (bcc) form of titanium (beta) at low temperature, resulting in alloys with aluminide + beta structures, which have adequate low temperature ductility. In these alloys it is possible to produce a B2 (CsCl) type structure over a wide range of alloy compositions.

Hydrogen embrittlement of titanium alloys, although most often associated with a single form of degradation (hydride formation), can be very complex, and very little understanding presently exists of the hydrogen interaction with the titanium-aluminide phases.

The report presents a preliminary study of the effects of hydrogen on the microstructure and fracture behavior of Ti_3Al alloys, as evaluated by various electron optical methods. Specifically, work was conducted on hydrogen induced cracking of Ti-24Al-11Nb and Ti-25Al-10Nb-3V-1Mo alloys (in at.%) using: transmission electron microscopy (TEM), scanning electron microscopy, selected area electron diffraction (SAD), and X-ray diffraction. The following conclusions were obtained from the results of the study:

Ti-24Al-11Nb Alloy

1. Selected area electron diffraction patterns and X-ray studies of the uncharged alloy revealed the existence of a hexagonal phase, with lattice parameters close to the alpha-2 phase and the existence of a new ordered phase that can be produced by a small distortion of the alpha-2 phase.

2. The results of the cathodic hydrogen charging process revealed the formation of a hydride

phase, probably based on the (TiNb)H composition.

3. Hydrogen induced cracking as a result of the cathodic hydrogen charging in the absence of any externally applied stress revealed the formation of hydrogen induced: main transgranular cracks running across the acicular microstructure, microcracks among the needles of the acicular microstructure, and fine microcracks, appearing mostly parallel to the long axes of the needles.

4. Hydrogen induced room temperature brittleness can be attributed to either some form of lattice bond interactions or the result of localized, strain-induced, hydride formation in front of the crack tip, which decomposes after fracture.

5. In cathodically charged Ti-24Al-11Nb alloy, transformation of the $AlTi_3$ matrix is probably due to $AlTi_3$-H hydride and depends on the particular hydrogen distribution after the charging and during outgassing.

6. The fraction of $AlTi_3$-H drops from about 70% on the surface to zero at a depth of 2 μm for samples which were charged for 24 h and aged for 4 h. The weight fraction of the $AlTi_3$-H hydride in the surface decreased after a long period of aging (7 days) to about 64%.

Ti-25Al-10Nb-3V-1Mo Alloy

1. The Ti-25Al-10Nb-3V-1Mo alloy is subjected to ductility loss when hydrogen charged. The cracks induced by cathodic hydrogen charging exhibited small crack angles and lack of plastic zone.

2. The directions of the perpendicular microcracks are probably parallel to the $\bar{g}$ (110) and g (1$\bar{1}$0) vectors, in an area having B2 (CsCl) structure.

3. Hydrogen induced cracking as a result of the cathodic hydrogen charging in the absence of any externally applied stress revealed the formation of hydrogen induced: main transgranular cracks having ridged or step-like crack flanks, fine microcracking along favorable crystallographic slip planes, and microcracks along the interface matrix/precipitate.

4. Hydrogen induced room temperature brittleness can be attributed to either some form of lattice bond interactions or the result of localized, strain-induced, hydride formation in front of the crack tip, which decomposes after fracture.

TASK: 113

TASK TITLE: Polymers: "The Synthesis of Bithiophene and Terthiophene Dicarboxylic Acid Monomers and the Synthesis of Polybenzothiazoles Prepared From These Monomers"

TASK OBJECTIVE: To synthesize novel aromatic-heterocyclic polymers for molecular composites and/or nonlinear optical applications.

SCIENTIST: Ronald C. Tomlinson, B.S.

DESCRIPTION OF WORK:

Materials which may exhibit nonlinear optical (NLO) properties, such as polybenzobisthiazole (PBT) and polybenzobisimidazole (PBI), are currently being investigated at WL/MLBP (Polymer Branch). The majority of the research effort at MLBP is focused on the synthesis and NLO evaluation of model compounds (those containing the PBX heterocyclic ring system) in order to accumulate a data base of structure versis NLO property relationships. Preliminary data indicated that the extension of the conjugated π electrons will enhance the NLO response. This was demonstrated with benzodiimidazole and benzodithiazole model compounds containing phenyl, vinylbenzene, thiophene and vinylthiophene pendants.

Recently, it was shown that poly-2,5-thiophene exhibits large NLO activity. The goal of the present investigation was the synthesis of several aromatic-heterocyclic thiophene containing compounds in order to support the NLO data base and reveal if there is a direct comparison of the NLO properties of model compound versus that of a polymer containing the same moieties. Several carboxylic acids (2,2'-bithiophene-5-carboxylic acid, 2,2'-bithiophene-5,5'-dicarboxylic acid, 2,2':5',2"-terthiophene-5-carboxylic acid, and 2,2':5',2"-terthiophene-5,5"-dicarboxylic acid) and the corresponding dicarbonyl chloride derivatives, a PBT polymer containing a polythiophene segment, andthreemodelcompounds(5,5'-di(2-benzothiazolyl)-2,2'-bithiophene,5,5"-di(2-benzothiazolyl)-2,2' :5,5'-terthiophene, and 2,6di[5-(2,2'-bithiophene)]benzo[1,2-d:4,5-d']-bisthioazole) were prepared and characterized using FTIR, NMR, UV, elemental analysis, mass spectroscopy, and melting points.

The bithiophene and terthiophene model compounds were prepared in quantitative yield from the respective dicarbonyl chloride compounds by condensation with o-aminothiophenol in poly phosphoric acid (PPA). The bisthioazole model compound was prepared in 92% yield from the condensation of the corresponding carboxylic acid and 2,5-diamino-1,4-benzenedithiol dihycrochloride in a solution of 1,2-dichlorobenzene containing PPSE and tributylamine. The maximum UV absorption (in MSA), λmax, for the model compounds is given as 460.9, 497.8, and 511.5 nm for the bithiophene, terthiophene, and bisthioazole, respectively.

The PBT polymer derivative poly[(benzo[1,2-d:4,5-d']bisthiazole-2,6-diyl)-5,5'-(2,2'-bithiophene)] was prepared in 98% yield from the condensation of 2,2'-bithiophene-5,5'-dicarbonyl chloride with 2,5-diamino-1,4-benzenedithiol dihydrochloride in 83% PPA by the P_2O_5 adjustment method. The polymerization was performed at 8, 10 and 12 percent polymer concentrations and the intrinsic viscosities of the polymers were determined to be 2.9, 4.7, and 2.4 dL/g, respectively. The UV λ max for the 10% polymer concentration was 571.9 nm.

The results demonstrated that 2,2'-bithiophene-5,5'-dicarbonyl chloride is stable under the PPA polymerization conditions based on the quantitative yields for the corresponding model compound and the intrinsic viscosity of the polythiophene PBT polymer. This is in contrast to a recent report by Sinsky that states the monomer decomposes in PPA. The model compounds and the polymer have been submitted for NLO evaluation.

TASK: 114

TASK TITLE: Polymer Morphology

TASK OBJECTIVE: Morphology of Compression Failure in Fibers.

SCIENTIST: Ronald K. Eby, Ph.D. and Mary Becker, M.S.

DESCRIPTION OF WORK:

The scientists performed a comparative study of compressive failure mechanisms of a series of organic and carbon fibers, particularly concentrating on the results from X-ray diffraction measurements of the crystal size, perfection, orientation and modulus. PAN-based carbon fibers were measured and the results compared with earlier results obtained for pitch-based fibers in order to determine the relative effects of the PAN and pitch precursors. Fibroin fibers were measured in order to examine the effects of a "two-phase" fiber in contrast to the "single-phase" carbon fibers. A few measurements were made on one pitch-based fiber in order to confirm some earlier observations.

The results for pitch-based and PAN-based fibers suggest that they achieve the same macroscopic modulus by different mechanisms. The crystals for the former have a lower modulus but a better alignment. The crystals for the latter have a higher modulus but a poorer alignment. These effects compensate to yield approximately the same macroscopic modulus for the two fibers.

The results for a "two-phase" fiber, fibroin, suggest the presence of a relaxation mechanism. It is most likely located in the amorphous component of the "two-phase" fiber. This presents questions concerning the fine-scale details of the morphology and also raises questions about the use of the uniform stress assumption for the fiber. Further questions arise from the lack of change in crystal orientation with stress and the subsequently published work of the others.

TASK: 115

TASK TITLE: Polymer Morphology: "Structure of Ordered Polymer Fibers"

TASK OBJECTIVE: The structure analysis of ordered polymer fibers.

SCIENTIST: Albert V. Fratini, Ph.D.

DESCRIPTION OF WORK:

The structures of poly(p-phenylene benzobisthiazole) (PBZT) and poly(p-phenylene benzobisoxazole) (PBO) have been of interest for the past decade. Based on diffraction patterns which show molecular transform scattering on layer lines and diffuse (biaxial) reflections along the equator, the as-spun polymer is viewed as a nematic solid with a high degree of orientational order but with axial translational disorder. Heat treatment induces crystallization of the chains, as seen by axial bright field lattice imaging. The crystallization process is reported to be more extensive for PBO than for PBZT; thus a considerable amount of axial disorder is expected in the final structure of PBZT.

In the study, the crystal structure of ordered polymer fibers, especially PBO and PBZT, was investigated using several experimental techniques: X-ray diffraction patterns using Weissenberg, Buerger precession and 57.3 mm radius vacuum cylindrical cameras, diffractometer scans (equatorial and meridional) using a four-circle diffractometer modified for modulus studies, and microdensitometer scans of fiber rotation photographs to obtain integrated intensities of equatorial and off-axis reflections, corrected for background and L_p factors.

Strong equatorial and multiple meridional reflections are general features of the diffraction patterns of both polymers. Heat-treated fibers show a limited number of off-axis (hkl) reflections, indicating the presence of 3-D order. The measured monofilament fiber densities for both as-spun

and heat-treated PBZT and PBO fibers are 1.57 and 1.50 g/cm^3, respectively.

D-spacings, obtained by least-squares, were satisfactorily indexed using both primitive and nonprimitive unit cells. Best-fit lattice parameters (cell constants) for both primitive and nonprimitive unit cells for PBZT and PBO were obtained by minimizing the sum of the squares of the differences between observed and calculated d-spacings. The calculated and observed d-spacings show good agreement. Also, the calculated densities of 1.70 and 1.66 g/cm^3 (same for nonprimitive and primitive unit cells) for PBZT and PBO, respectively, also show fairly good agreement with the observed values.

The basic structure for both polymers was determined from the experimental results. The chain direction in both polymers is parallel to the fiber axis (c-axis). The length of the c-axis corresponds to the repeat distance of a single polymer unit, which is comprised of a bisbenzazole and attached p-phenylene segment. The b-axis is roughly the perpendicular distance between the faces of two overlapping heterocyclic rings, while the a-axis is the approximate distance between equivalent edges of side-by-side heterocyclic rings. The structure and cell parameters of PBO are similar to those of PBZT, except that the a- and c-axis in PBZT are slightly larger, probably due to conformational differences between chains and the larger size of the sulfur atom.

The linked-atom least-squares (LALS) method was employed to refine the unit cells and obtain the final structures of PBZT and PBO. This involved reducing the number of variables by constraining most of the bond lengths and bond angles to values obtained from model compound studies. A scale factor, one torsion angle per polymer repeat unit, and three angles which define the orientation of chains in the unit cell were refined. The final fractional atomic coordinates of the repeat units were presented in the report.

Analysis of the packing of molecules in primitive cells and closer examination of the X-ray photographs revealed some serious shortcomings. Thus, further refinement of primitive cells was discontinued.

The problems encountered with the primitive cells was virtually eliminated with nonprimitive unit cells ($Z = 2$), constructed by doubling the length of the a-axis of the primitive cells. This permits a second chain to be added which can have a different azimuthal orientation relative to the first chain thus allowing the overall structure to have additional lateral disorder. A c-axis view of the molecular packing is shown for both polymers.

Both PBZT and PBO adopt a nonplanar conformation with mean torsion angles of 46 and 13°, respectively. For PBO this contrasts with the planar conformation observed in the crystal structures of model compounds. The final X, Y, Z orientation angles are -40.8, -92.7, and 9.3°, respectively, for PBZT and 90.3, -91.3, and 158.1°, respectively, for PBO. The R index for PBZT is 12.0% (based on 8 Bragg maxima) while that for PBO is 11.4% (based on 11 Bragg Maxima). The observed and calculated structure factor amplitudes are also given.

TASK: 116

TASK TITLE: Polymer Processing: "Investigation of the Role of Phase Separation/Gelation in Rigid Rod Polymers"

TASK OBJECTIVE: Phase equilibria of ordered polymers.

SCIENTIST: Paul S. Russo, Ph.D.

DESCRIPTION OF WORK:

The primary objective of the study was exploration of microscopic phase separation of poly(p-phenylenebenzobisthiazole), PBT, expecially in the context of production of polymer composite systems and the investigation of the phase equilibria of ordered polymers in solution form, in comparison with molecular composite solutions and bulk forms. A secondary objective was to exchange ideas about the possible role of microphase separation in other applications, such as nonlinear optical materials. Since WL/MLBP (Polymer Branch) and Louisiana State University (LSU) have distinctly different capabilities and objectives, a third objective was technology transfer between both laboratories.

A preliminary investigation into the gelation behavior of hairy PBT (HPBT) was performed, expecially with an eye towards differences between this polymer and ordinary, linear PBT. Hairy PBT has a PBT backbone with poly(ehterketone) sidechains, or pendants, of unspecified and unequal length. The polymer's reported intrinsic viscosity was 8 dl/g and it dissolved easily in 96.3% H_2SO_4 and in methane sulfonic acid (MSA). This system did not have the integrity of typical PBT gels.

Experiments were conducted to determine whether gelation was more likely at higher water content and/or higher polymer contents. It was discovered that the polymer would dissolve, with some difficulty, in 78% H_2SO_4 at 135 °C. This material did not have the integrity of PBT/H_2SO_4 gels and the "rubbery" character of gels made from high molecular weight PBT was decidedly absent. Rather, the HPBT gel had the consistency and appearance of axle grease.

The scientist also repeated some of Dr. Hoe Chuah's experiments on the production of pure PBT bulk solids and studied some of his samples. The samples were molded after extracting the acid, but not the water, and found to have a brittleness similar to slate rock and were suprisingly hard. Some foam samples were found to have densities between 0.38 - 0.75 g/cm^3. The results lead to the conclusions that gel-processed rodlike polymers may find useful application, though not as high-strength materials. Metal-coated polished foams could make lightweight mirrors which at the same time provide thermal insulation. Finally, gel-processed PBT may be the best form for resale (since the problems inherent in shipping and storing PBT in PPA would not be present). If dried gel redissolves to give the original properties of the polymer, great cost savings in shipment and storage might be realized, as well as expanding processing options. Work should be continued in this area.

Also, preliminary studies into PBT/Teflon and PBT/poly(styrene) systems were begun. It was hoped that a PBT/poly(styrene) mixture form a bicontinuous composite material. However, there was an aggregation problem, probably due to the use of carboxylate-modified latex particles. The experiments were to be continued at LSU using amino-functionalized latex spheres.

A PBT/poly(tetrafluoroethylene) (PBT/Teflon or PBT/PTFE) system was made by dispersing PTFE in pre-made gel and then processing. The result was a PBT/Teflon material which, qualitatively, had good consolidation. The PBT content was just 30%, so the material appeared to have more Teflon-like properties. There did seem to be some improvement in hardness.

Finally, suggestions for opening new and productive avenues of research on PBT and nonlinear optical model compounds were given. The new research would use techniques such as plasma desorption time of flight mass spectroscopy (PDMS), light scattering, video optical microscopy (using a confocal tandem scanning optical microscope), and mobility measurement methods (Fluorescence Photobleaching Recovery, FPR, and Pulsed Field Gradient NMR, PFGNMR). A few technical suggestions are also given.

TASK: 117

TASK TITLE: Polymer Morphology: "Crystal Transformations in Solutions of Rigid Polymers"

TASK OBJECTIVE: Ordered Polymer Crystal Solvates.

SCIENTIST: Yachin Cohen, Ph.D.

DESCRIPTION OF WORK:

Fibers and films exhibiting high modulus and strength are fabricated from solutions of rigid polymers by a spinning process. Typically, the polymer solution is in the liquid crystalline state. Because of their inherent rigidity, such polymers are soluble only in strongly interacting solvents, such as protonating acids, and water is commonly used as the coagulant. Solubility is thus a consequence of electrostatic repulsion between the protonated rodlike molecules, and solidification during coagulation is due to deprotonation of the polymer by the coagulant leading to crystallization of the uncharged polymer.

In the spinning process, the phase transition in the coagulation stage is from the liquid crystal to the solid polymer crystal state. However, it has recently come to focus that other crystalline phases can occur in solutions of rigid polymers. These are the so-called crystal-solvate phases, in which the rigid polymer co-crystallizes with its solvent. It is possible that some crystal solvates be considered as salts of the protonated polymer polycation and the anions of the solvent acid.

Crystal solvate phases have been observed in solutions of both PBZT and PBO in PPA. Two forms of the solvate phases have been identified, depending on the extent of exposure to the coagulant (moisture). Form I appears at low moisture levels and is characterized by several sharp equatorial reflections in the wide angle X-ray diffraction pattern. Form II occurs at higher moisture levels and its X-ray diffraction pattern shows broad equatorial reflections, as in the as-spun crystalline polymer state, but at different spacings.

The crystallization which occurs during the coagulation stage in the spinning process results in formation of the solid polymer microstructure which is responsible for its properties. The motivation for this work stemmed from the hypothesis that there is a direct connection between the nature and kinetics of the phase transition during coagulation and the microstructure and properties of the final materials. It is thus conceivable that the crystal solvate phases may serve as intermediate stages in the solidification process, by which control may be exserted on the kinetics of crystallization and hence on the resulting morphology and properties.

Very little is known about the transitions between the liquid crystal, crystal solvates and polymer crystal phases. Thus an investigation of the formation, temperature and moisture dependence, and structure of the polymer crystal solvates was studied by means of the high intensity X-ray synchrotron source at DESY (Hamburg, W. Germany). Several results were obtained. In the form I crystal solvate two reversible transitions were observed. Dissolution of the crystal solvate to the liquid crystalline phase occurs up to about 70°C. This is interpreted as dissolution of the "salt" of the protonated polymer polycation and the PPA anions. At elevated temperatures, above about 250°C, another reversible transition is observed: formation of the polymer crystal phase. This is interpreted as aggregation of the polymer chains following their thermal deprotonation. At higher moisture levels (~5%), the form II crystal solvate appears. It does not melt to the liquid crystal phase, and transforms irreversibly at elevated temperature (above ~250°C) to the crystalline polymer phase.

TASK: 120

TASK TITLE: Fatigue of High Temperature Composites

TASK OBJECTIVE: To evaluate the failure mechanisms of glass and ceramic composites at elevated temperatures under fatigue.

SCIENTIST: Narayanana Jayaraman, Ph.D.

DESCRIPTION OF WORK:

This study consisted of mainly two research activities, one in the area of "Ceramic Matrix Composites" and the other in the area of "Residual Stresses in Metal Matrix Composites."

Ceramic Matrix Composites

A critical review of the literature and research plan was performed. As a result of this activity, it was decided that further work should concentrate on the long-term micro-mechanical response of these new materials under creep-fatigue-environmental conditions. Mechanical testing capabilities were developed and testing was started. Results from the creep tests on the Amercom Materials (SiC-SiC composites) are still being evaluated.

Residual Stresses in Metal Matrix Composites

In this area, the residual stress activity was carried out in support of on-going research work in Ti_3Al-SCS6, particularly the thermal and thermo-mechanical cycling of MMC's. The residual stress state of the composite during processing and during thermal cycling was predicted by existing models. The results were found to be consistent with those published by General Electric and University of Dayton Research Institute (UDRI).

TASK: 121

TASK TITLE: Synthesis of crown ethers and other macromolecular complexes of the lanthanide and transition metal ions: "Synthesis, Characterization and Testing of Inorganic and Organic Materials for NonLinear Optical Applications"

TASK OBJECTIVE: Investigate several entirely new classes of potentially optically active compounds. In this investigation an attempt will be made to synthesize new compounds and to modify existing compounds and to correlate their chemical structure and their optical characteristics.

SCIENTIST: L. V. Natarajan, Ph.D.

DESCRIPTION OF WORK:

As part of the task of developing new nonlinear optical materials, the synthesis and characterization of lanthanide crown ethers and related complexes and organic materials were performed. The effects of structure and composition on nonlinear optical properties were also studied.

The lanthanide complexes, Neodymium(III) salicylate, Neodymium(III)-18-6-crown ether, and Gadolinium-18-6-crown ether were synthesized and characterized by elemental analysis and UV-Visible spectroscopy. A luminescence study of Europium complexes formed between Europium nitrate and thioindigo dye was performed. Luminescence of solid Europium(III) nitrate was compared with that of a solution of Europium(III) nitrate and crown ether. Luminescence lifetimes of the systems were determined. In addition, a solution of Neodymium with 18-6 crown ether was tested for third-order nonlinear optical response.

Various organic materials (anthraquinones, diphenyl polyenes, liquid crystals and liquid crystal polymers) were also tested for nonlinear optical applications. The anthraquinones and diphenyl polyenes were tested for nonlinearity by power in and power out experiments using a Nd:Yag laser at 532 nm. The transmission and optical density as a function of incident energy were calculated from the measured incident and transmitted pulse energies.

The anthraquinones, 1-aminoanthraquinone, 2-aminoanthraquinone, and 2-pyrrolidino anthraquinone, were tested as optical limiters. The dyes were incorporated in polymers; (e.g., polymethyl-methacrylate) and the optical nonlinear behavior was observed around pulse energies of 1 μJ to 10 μJ. The change of transmittance was large, as high as 500 to 600% of the initial transmittance.

The diphenyl polyenes, cis-stilbene, trans-stilbene, 1,4-diphenylbutadiene, diphenyl hexatriene, diphenyl octatetraene, were dissolved in chloroform and tested for optical nonlinearity. The results were compared with CS_2 as a reference. The performance of the diphenyl polyenes was very impressive when compared to CS_2. The onset of nonlinearity was at much lower fluences and the optical density changes were large. A value as low as 1 μJ energy was observed for diphenyl octatetraene at a concentration of 0.01 molar. A systematic variation of the concentration of trans-stilbene showed the onset of nonlinearity change from a fluence value of 90 J/cm^2 to 11 J/cm^2 for concentrations from 4 x 10^{-4} to 0.1 molar, respectively. For different polyenes at the same concentration, the best nonlinear behavior in terms of low threshold value was shown by diphenyl octatetraene. A relationship was shown to exist between the number of conjugated double bonds and optical limiting. The efficiency increases up to 10 double bonds and seems to level off for higher saturation of the effect of conjugation around 12 double bonds. Another interesting observation was that the nonlinear behavior, as seen from optical limiting, of cis-stilbene was much less efficient compared to its molecular isomer, trans-stilbene. A possible explanation given was that the nonplanar spatial conformation of cis-stilbene affects the delocalization of the pi electrons of the two phenyl rings, while the nearly planar trans-stilbene has efficient conjugation.

Finally, the nonlinear behavior of the liquid crystal E7 was tested. A very low value of 800 nJ energy was seen for optical limiting with the direction of alignment parallel to the laser polarization. For perpendicular alignment with the laser polarization, a much higher value for nonlinear threshold was observed. Also, the optical density changes for E7 were very sharp and very large.

TASK: 122

TASK TITLE: Processing Science of Organic Structural Materials

TASK OBJECTIVE: To develop innovative processing approaches to fabricate optical quality specimens using rigid-rod polymers for nonlinear optical applications.

SCIENTIST: Rajeev Mehta, M.S., Adtech Systems Research

DESCRIPTION OF WORK:

During the study, work was done on three related projects: development of the processing technology of optical quality specimens of rigid-rod polymer fibers and films, using 6F-PBO as a base material; upgrading the processing equipment; and studying the feasibility of epoxy bonded nonlinear optical (NLO) films. The two main objectives were to generate data for third-order nonlinear optical properties versus different kinds of extruded films and to improve the quality of the extruded films.

The 6F-PBO extruded film is not water-white transparent like the 6F-PBO cast film. In order to be able to extrude 6F-PBO with different polymers having high NLO activity, it was imperative that a water-white transparent 6F-PBO film be able to be extruded. During the study three types of films were extruded: 20%Zytel 330, 1 PBT/MSA (four films), 3% PBT/Zytel 330, and 2% PBT/Zytel 330, 5/6F-PBO/MSA. The samples for these films, as well as for some other films, were prepared by four different drying methods: ring mounted samples, film sandwiched between two microscopic slides, film enclosed between a microscopic slide and a Teflon coated microscopic slide and film enclosed between a microscopic slide and a metal plate with a window. The samples were sent elsewhere for determination of their NLO properties and the results were not completed at the time the report was written.

A detailed film defects analysis of the samples was also performed using optical microscopy and scanning electron microscopy (SEM). The presence of inhomogeneities and surface nonuniformities in the film is an important problem. If the film is to be used as a medium for electromagnetic wave transmission (i.e., an NLO film), it is imperative that the film be free of all defects. Four kinds of defects were recognized in the extruded films: presence of bubbles, solid particles, lines in the transverse direction, and lines in the machine direction. The characterization of the defects and the steps taken to eliminate them are discussed in detail in the report. In addition, problems with necking down (leading to a thickening of the film), necking-in and uneven necking-in (resulting from the entrapment of an air layer between the film and the drum) are discussed.

Finally, the development of the technique for epoxy bonded film (to a microscopic slide) is in its initial phase. Basically, the objective is to bond a film to a grated slide through a spectrally transparent epoxy. The basic procedure developed to date is discussed in the report.

TASK: 123

TASK TITLE: Processing Maps for Moldable Raw Materials

TASK OBJECTIVE: To develop constitutive equations for the class of moldable raw materials which include liquid-to-solid-metal transition.

SCIENTIST: Venkat Seetharaman, Ph.D., Universal Energy Systems

DESCRIPTION OF WORK:

The scientist developed constitutive equations derived from a dynamic material model in order to predict the material behavior during the solidification process (liquid-to-solid-metal transition). The relationships between material parameters, such as temperature gradient, cooling rate, and

solidifying interface velocity were incorporated into the model. Specific constitutive equations included: the flow stress (σ), at any plastic strain, as a function of the strain rate for various temperatures, and also as a function of temperature for various strain rates (both in terms of a quadratic equation); the strain rate sensitivity parameter (m) as a function of test temperature and strain rate; the temperature sensitivity parameter (s) at constain strain and strain rate (essentially a temperature gradient of the flow stress); the peak flow stress (σ_p) as a function of the test temperature for various strain rates; the temperature dependence of the secondary creep rate ($\dot{\varepsilon}$); the thermally activated deformation at constaint strain rates; the grain boundary mobility (μ); the temperature compensated strain rate (Z), which combines the effects of temperature and strain rates; and the strain localization parameter (α), for axisymmetric, uniaxial compression (related to the stress and strain). These equations were used to determine the plastic flow behavior of the Ti-48Al-1V alloy and the plastic deformation behavior and microstructural evolution of the G-2 TiAl alloy.

Ti-48Al-1V Alloy

Flow stress data for a cast and hot isostatically pressed sample were analyzed in detail in order to determine the strain rate and temperature dependence. The microstructure consisted of equiaxed γ grains and lamellar aggregates of γ and α_2 phases. Several results were observed from the analysis.

All the flow curves exhibit nonmontonic behavior; i.e., the flow stress initially increases with true plastic strain, reaches a maximum, and then decreases gradually. The flow stress, at any plastic strain level, increases steeply with strain rate and decreases with increasing temperature. In general the strain rate sensitivity parameter, m, decreases with an increase in strain rate and the modulus of the variation of m with the strain rate (at constant temperature and strain) increases as the temperature decreases. The values determined for the temperature sensitivity parameter, s, indicate that the alloy may have a strong propensity for undergoing dynamic recrystallization (thought to be the cause of the pronounced flow softening) at all the temperatures and strain rates studied. Futhermore, this is confirmed by the temperature and strain rate dependence of the peak strain.

Also, the mean activation energy for grain boundary diffusion was determined to be 74.4 kcal/mol, which is approximately twice that expected from the grain boundary migration activation energy (estimated by a different study). It is apparent from the results that the activation energy obtained from the analysis cannot be associated with a specific mechanism, but is instead due to several processes. The results for the temperature compensated strain rate, Z, tend to support the activation energy data determined in the present study.

Finally, the pronounced strain softening observed in all the flow curves suggests that the alloy is prone to strain localization. The values for the strain localization parameter, α, at 1175 °C and a strain rate of 10^{-3} s^{-1} are low. Also, the macrographs of longitudinal sections of the compressed specimens reveal that sever strain localization occurs at 1000 °C at all strain rates, while specimens deformed at 1150 °C show that the strain localization becomes very diffuse, particularly at low strain rates.

G-2 TiAl Alloy

The metallographic analysis of the transverse sections of a cast and hot isostatically pressed ingot of the alloy revealed a nearly uniform microstructure consisting of equiaxed γ-grains and isolated platelets of the α_2 phase. Tests performed at 1200 °C on specimens with different diameters indicated very little sensitivity of flow stress to specimen size and location. Subsequent

tests were carried out in the temperature range 1000-1400 °C and for strain rates in the range 0.001-10.0 s^{-1}.

The variation of flow stress with temperature and strain rate (flow curves) exhibit nonmonotonic behavior. At low strain rates and at high temperatures, the flow stress approaches a steady-state value asymptotically. The peak strain is strongly dependent on the test conditions and increases with the imposed strain rate at constant temperature for the lowest temperatures studied. At higher temperatures the peak strain is nearly independent of the strain rate.

The values of the strain rate sensitivity parameter, m, were obtained and found to be negative for $\dot{\epsilon} \geq 1.0\ s^{-1}$, which are ascribed to the formation of both micro- and macro-cracks at high plastic strain levels. The metallographic study of the G-2 alloy revealed the presence of several cracks in specimens deformed at high strain rates up to a strain of 0.7.

Transmission electron microscopy showed that specimens deformed in the temperature range 1000-1200 °C contained only the equiaxed γ phase grains. Deformation at temperatures corresponding to the $\alpha + \gamma$ (1300 °C) or α (1400 °C) phase fields led to the room temperature microstructures consisting of γ and α_2 phases. The volume fraction of lamellar structures increases progressively with temperatures above 1300 °C.

Finally, the mean grain size of the γ grains was determined as a function of the strain rate at 1000 and 1200 °C as the specimens were cooled slowly and compared to previous data in which the specimens were quickly cooled by gas. The data show a pronounced decrease in the grain size with an increase in the strain rate and a decrease in the temperature. However, the grain sizes of the slow cooled specimens are nearly four times higher than those of the gas quenched specimens. Furthermore, the grain size curves of the slow cooled specimens exhibit an apparent saturation at high strain rates.

TASK: 124

TASK TITLE: Polymer Computational Chemistry: "Band Gaps of Model Polymers from Semi-empirical Crystal Orbital Method"

TASK OBJECTIVE: NLO property computations.

SCIENTIST: Tahir Cagin, Ph.D.

DESCRIPTION OF WORK:

In polymers, just as in the three dimensional crystalline solids, the interaction of polymer unit cell with all the other neighboring unit cells leads to the formation of electronic bands. The highest occupied electronic levels constitute the valence band (VB) and the lowest unoccupied electronic level the conduction band (CB). The difference between the conduction band and the valence band, the band gap (E_g), determines the intrinsic electronic properties of the polymer (such as its electrical conductivity). Saturated polymers are typically insulators, while conjugated polymers are generally expected to be semiconductors.

Experimental efforts for synthesizing highly conductive polymers have grown enormously. Computational chemistry can play an important role in this field by (1) attempting to explain the questions concerning the electrical conductivity phenomenon in polymers, and (2) identifying the polymers which may have the suitable intrinsic properties; i.e., very narrow band gaps.

In this study semiempirical quantum molecular/crystal orbital methods were applied, using the program MOSOL at the AM1 and MNDO levels, to obtain the optimized geometries, total energies, heats of formation, and energy band gaps of conjugated polymers. The specific polymers studied were:

1. The polyacetylene (PA) isomers, trans-PA, cis-transoid PA, trans-cisoid PA, trans-regular PA, and cis-regular PA,
2. The 4, 5, or 6 membered ring PA derivative polymers, polycyclobutadienylene (PCB), polyfulvalene (PF), and polyparaphenylene (PPP),
3. The PF derivative polymers formed by (a) adding sp^2 carbons between the rings of PF, (b) benzennation of PF and its sp^2 derivatives, and (c) heteroatom (N, NH, and S) replacement of a carbon atom in the 5-membered rings of PF and its derivatives,
4. The PPP derivative polymers formed by (a) adding sp^2 carbons or S atoms between phenyl rings and (b) forming S-, O-, and NH-bridges between phenyl rings,
5. Polyacene and multi-ladder structures obtained from polyacene,
6. The polymers, poly-p-phenylene benzobisthiazole (PBT), poly-p-phenylene benzobisoxazole (PBO) and poly benzobisimidazole (PBI).

The results of the study lead to the following conclusions:

1. The calculated band gaps for pure conjugated polymers were all in the semiconducting region.
2. Regular cis-PA and trans-PA showed lower E_g values, by about 1.5 eV.
3. The E_g values for PCB, PF, and PPP were between 6 to 8 eV and in the order PCB > PPP > PF.
4. Adding sp^2 carbons to PF raised E_g, while benzennation tended to lower E_g.
5. Heteroatom replacement in PF increased E_g, while for PF-sp^2 polymers E_g decreased.
6. Heteroatom replacement in bezennated PF decreased E_g, substantially in some cases. Polyisothionaphthene has the lowest E_g (~4.1 eV) of all heteroatom polymers (1.5 eV below that of its precursor).
7. For PPP heteroatom and sp^2 derivatives the E_g was comparable to that for PPP, except for the fully bridged sulfur derivative which showed an ~1 eV lowering in E_g.
8. The ordered polymers, PBT, PBO, and PBI, have comparably large E_g's (~7 eV).
9. Polyacene ribbons show considerably lower E_g's than the other polymers studied. The larger the polyacene ribbon, the lower the band gap (0.56 eV for the largest structure).
10. The MNDO and AM1 methods gave comparable results for all properties. The E_g's from MNDO were always larger than those from AM1.

TASK: 125

TASK TITLE: Thermal/Mechanical Fatigue of High Temperature Composites

TASK OBJECTIVE: To evaluate the roles of residual stresses and environment on the fatigue of ceramic composites subjected to thermal and mechanical cycling and elevated temperature exposure.

SCIENTIST: Robert C. Wetherhold, Ph.D.

DESCRIPTION OF WORK:

The goal of the study was to determine the rate and extent of oxygen embrittlement of Nicalon fiber/aluminosilicate glass matrix (CMC) composites by subjecting them to combinations of mechanical and thermal cycling and exposure to high temperatures. A damage amelioration scheme was also investigated.

All the NDE methods used to detect damage (ultrasonic wave speed and attenuation, electrical resistance and capacitance, infrared transmissibility, and eddy current) did not prove useful. A vibration analysis to determine changes in damping will be carried out in future work.

The damage amelioration scheme was investigated by using high temperature treatments (including tempering) of the CMC to decrease the paths available for oxygen infiltration from the surface. This was very successful, as the samples demonstrated decreased sensitivity to thermal exposure after the treatment. Tests also determined that the thermal treatments were effective for specimens exposed under load. An unexpected experimental result was that precracking of the matrix by tensile loading had no effect on the embrittlement process during subsequent thermal exposure. Results from 80 mm flexural tests were tabulated.

Plates produced under different conditions all experienced oxygen embrittlement, the degree and speed of the process being due to several variables. Fabrication conditions for optimum strength were quantified and presented. The eventual goal is to be able to control the degree of embrittlement, or to reproducibly fabricate plates of different types at will.

TASK: 126

TASK TITLE: Micromechanical Failure Model for BMC (Brittle Matrix Composites)

TASK OBJECTIVE: To develop a micromechanical model to predict the failure initiation and growth in a unidirectional BMC. The model shall be based on an extension of the capabilities of the computer model called NDSANDS.

SCIENTIST: Gyaneshwar P. Tandon, Ph.D., Adtech Systems Research

DESCRIPTION OF WORK:

A micromechanical failure simulation model was proposed in the study to predict the complete stress-strain curve of a unidirectional brittle matrix composite (BMC). The experimental stress-strain curve under transverse tension showed three distinct regions: (1) linear stress strain region (characterized by slope E_i) which is a result of continuous bonding between the constituents; (2) the onset of non-linearity which signifies either initiation of interface debonding or matrix cracking depending on the strength of the interfacial bond and the residual stresses; and (3) a second linear region, characterized by slope E_f, which corresponds to complete debonding of fiber from the matrix. Depending on the magnitude and sign of the residual stresses, the boundaries between the tree regions may occur at different stress levels. Also, regions II and III may not be present in all specimens as ultimate failure of the composite can occur before these stages are reached.

First Linear Region (Perfect Bonding)

Analysis of the composite behavior in the initial linear region was done by Pagano and Tandon using a composite circular cylinder assemblage subjected to prescribed displacement or traction on its boundary to yield bounding solutions for the composite effective moduli. The model assumed

ideal elasticity and perfect bonding between the constituents. The interphase region(s) between the fiber and the matrix was (were) modeled as coating layer(s). The behavior of the stress-strain curve in the initial region prior to occurrence of any damage can be effectively predicted from their analysis.

Second Linear Region (Complete Debonding)

The work in this part of the study was aimed at evaluating the effective thermoelastic moduli of continuous fiber reinforced brittle matrix composite systems in which debonding and slipping between the constituents occurs. Among the issues addressed was the fact that several definitions of composite strain may be used in the computation of effective moduli. The effective modulus theory relates the averages of the stress and strain tensors over a representative volume element through the effective elastic constants. Physical measurement of composite strain, however, is done by the use of strain gages which report the values on the lateral surfaces. Under perfect bonding, both the mathematical and physical definitions of composite strains are equivalent if the body is subjected to prescribed displacements that would lead to constant strain in a homogeneous medium. However, under imperfect bonding conditions at the interface, it was shown that the two definitions do not necessarily lead to the same value of composite strain and hence the effective moduli. This difference was critically examined under conditions leading to fiber slipping and complete interfacial separation. It was further shown that the composite effective stiffness tensor becomes unsymmetric under certain interfacial conditions. These facts call into question the applicability of effective modulus theory as it is now practiced. The fiber-matrix (debonding) separation problem was also modeled as a matrix weakened by cylindrical voids in place of the fiber, where the strain field within the void region does not vanish, in an attempt to provide a more realistic solution for this problem. In order to conduct the study, some preliminary groundwork was also done to develop new theorems for composite stress and strain in the presence of two-dimensional stress fields under arbitrary interface boundary conditions. The results of the study are discussed in the paper "Modeling of Imperfect Bonding in Fiber Reinforced Brittle Matrix Composites" published in the journal Mechanics of Materials and attached to the final report.

Work still in progress includes:

1. Efforts aimed at modeling the second region (partial debonding) of the stress-strain curve of a unidirectional composite when the fiber-matrix debonding is not complete.
2. A damage model in which the damaged material is represented as a coating layer of reduced elastic modulus. An iterative algorithm is being investigated to predict ultimate composite failure, which will then be appended to the existing computer code NDSANDS so that the complete stress-strain curve of a unidirectional brittle matrix composite can be predicted.

TASK: 127

TASK TITLE: Experimental Verification of ALPID Finite Element Code

TASK OBJECTIVE: To determine heat transfer coefficients and friction factors which are required for simulating deformation processing of titanium aluminide materials.

SCIENTIST: Vinod K. Jain, Ph.D.

DESCRIPTION OF WORK:

The research on this task was concerned with the development of a methodology and determining the contact heat transfer coefficient and shear friction factor between die and workpiece for the forging of high temperature materials, such as super alloys, titanium aluminides, etc. Both parameters depend upon the physical and chemical properties of the lubricant and the die/workpiece interface and their surface roughness. Knowledge of the shear friction factor is important and necessary for the analytical simulation, using ALPID, of both isothermal and non-isothermal forgings.

The contact heat transfer coefficient is used for the ALPID (FEM) simulation of nonisothermal forgings. It is a measure of the heat loss from workpiece to die at high pressure during forging.

A literature search and experimental work were directed on both the determination of shear friction factor and heat transfer coefficient. The results are presented in two published papers (attached to the final report), discussed below.

Heat-Transfer Coefficient

The paper "Determination of Heat-Transfer Coefficient for Forging Applications" in the Journal of Material Shaping Technology discusses a setup for measuring the contact heat-transfer coefficient between a tool-steel die, and a specimen was designed, developed, and fabricated. Tests were conducted under dry and lubricated (MoS_2 as lubricant) conditions at different temperatures and pressures on four aluminum alloys, 2024-T4, 2024-O, 6061-0, and 1100-0. Results indicated that the heat-transfer coefficient increases with pressure and decreases with specimen yield strength. Variation in heat-transfer coefficient with temperature is due to chemical changes which occur in the lubricant at the test temperature. The heat-transfer coefficient was an order of magnitude greater at high pressures than at nominally zero pressure.

Work on the determination of the heat transfer coefficient was extended since the publication of the above paper. A new set up was developed in which the specimen is heated to high temperatures (up to 2000°F) using an induction unit. The die is heated by cartridge heaters. A new set of oscillator tubes was acquired to heat the Ti-Al specimens up to 2500°F. The unit is currently being used to determine the heat transfer coefficient for IN 718 specimens.

Ring-Calibration Curves

The ring test has been established as a method of determining the shear friction factor (m) at the die-workpiece interface. It has been reported that ring-calibration curves are dependent upon the strain, strain-rate, thermal, and mechanical characteristics of the material as well as ring geometry. The paper "Effects of Material and Processing Conditions Upon Ring-Calibration Curves" presents results of the study of the effects these variables have on ring-calibration curves using the rigid-viscoplastic finite-element program ALPID and experimental data. Three materials were studied, Al 2024, Ti-6Al-4V, and Ti-48Al-1V. ALPID analysis indicated that the calibration curves are dependent upon the ring geometry and strain-rate sensitivity of the material. The inner-surface profile of compressed rings is dependent upon the ring geometry, percent reduction in height, and shear friction factor. Compression tests on Al 2024 rings of 6:3:1 and 6:3:2 geometry were conducted to evaluate two lubricants using the ALPID results.

TASK: 129

TASK TITLE: Polymers: "Preparation of Electrically Conducting Polybenzazoles"

TASK OBJECTIVE: Synthesis of ordered polymers.

SCIENTIST: Jom Pin J. Chen, Ph.D.

DESCRIPTION OF WORK:

The objective of the research was the synthesis of rod-like conducting polymers, such as polybenzazole (PBZ) and its derivatives, especially polybenzothiazole (PBT) and polybenzoxazole (PBO). As polymers, polybenzazoles have received an extensive interest for their excellent tensile strength and modulus, chemical and thermal stability, and environmental resistance. A conducting polybenzazole is expected to have similar properties as PBZ, and be able to be used as advanced conducting materials in aircraft, instrumentation, and civilian industries.

Most polymers which have successfully produced conducting fibers have three basic characteristics: a conjugated π-orbital system (as found in PBZ), an ordered linear structure (PBZ forms an anisotropic solution in polyphosphoric acid, PPA, and can be fabricated into highly ordered fibers by dry-jet wet spinning method), and potential for ionization. In order to gain conductive properties, polybenzazoles must be modified to be capable of ionization. Two approaches for the modification of PBZ were taken in the study:

1. The synthesis and study of self-protonated PBZ, which is PBZ with a pendent containing a strong acidic proton capable of protonating the nitrogen in the polymer backbone.

2. The synthesis and study of hydroxy-PBZ, PBZ with a pendent hydroxy group which can undergo ionization in base by removal of the proton on the hydroxy group.

The results and conclusions of the study are:

1. An anisotropic dope of poly-(4,4'-(1,1'-biphenyl-2,2'-diyl-hydrogen phosphate)benzobisthiazole) (BPP-PBT) in PPA at a concentration of 10.2% was prepared from 4,4'-dicarboxy-2,2'-dihydroxybiphenyl and diaminodithiophenol. The intrinsic viscosity of the polymer was found to be 9.7 dl/g (MSA, 30°). The anisotropic dope of BPP-PBT has the potential to be spun into ordered fiber.
2. TGA analysis showed that the thermostability of BPP-PBT is similar to that of PBT
3. The model compounds, 1,1'-biphenyl-2,2'-diyl-hydrogen phosphate and 4,4'-(1,1'-biphenyl-2,2-diyl-hydrogen phosphate)benzobisthiazole resist hydrolysis in acid and base suggesting that BPP-PBT is a very stable polymer.
4. The BPP-PBT fiber may have improved compressive strength, since there is strong intermolecular hydrogen bonding between the phosphoric acid diesters or between phosphoric acid diester and benzothiazole's nitrogen.
5. BPP-PBT has the potential for ionization and can likely be converted into conducting fiber.

TASK: 130

TASK TITLE: Polymers

TASK OBJECTIVE: Synthesis of ordered polymers.

SCIENTIST: Dale H. Hill, Ph.D.

DESCRIPTION OF WORK:

The purpose of this research was the investigation of the synthesis of novel rigid-rod polymers to be used as multifunctional polymeric structures. The effort included the synthesis of the requisite monomers as well as the study of polycondensation conditions.

Molecular composites have recently become an important area of research. A molecular composite is a composite material consisting of a rigid-rod polymer which is dispersed on the molecular level in a flexible coil polymeric matrix. A true molecular composite has higher modulus and greater strength than a conventional macroscopic composite because of the high aspect ratio (length/diameter) which is achieved from a single rigid-rod polymer molecule. The primary approach taken thus far, for fabricating molecular composites, has been the physical blending of rigid-rod polymers with coil polymers. The problem with this approach is that the rigid-rod molecules often aggregate in solution. As a result of the incomplete dispersion of the rigid-rod polymer on a molecular level, the aspect ratio is greatly reduced. Consequently, the modulus and strength of the materials are greatly reduced. The goal of the research conducted under this contract was to develop synthetic methodology which allows the synthesis of molecular composites which have no detectable phase separation.

The approach explored was two fold. First, a rigid-rod precursor polymer and flexible coil polymer were chemically connected to form a block copolymer. At this point the rigid-rod precursor is molecularly dispersed in the coil matrix. Second, the rigid-rod precursor is thermally converted into a rigid-rod polymer. Thus, the rigid-rod polymer was formed "in situ." It is already molecularly dispersed because the precursor is less prone to aggregation in the matrix. The chemical connection of the rigid-rod precursor (and subsequent rigid-rod) to the coil polymer also inhibits aggregation.

Prior to the initiation of the synthesis of the polymers, several preliminary experiments were performed which would help in optimizing the reaction conditions used for the synthesis of the "in situ" generated block copolymer containing the rigid-rod and coil segments. First, a series of polymerization reactions of 4,4'-oxydiphthalic anhydride and 1,3-bis(3-aminophenoxy)benzene were performed at varying ratios. The resulting polymers have an intrinsic viscosity $[\eta]$ in the range, 0.158 - 0.685 and Tg values in the range, 170.69 - 176.54.

Next, a series of polymerization reactions involving 3,3',5,5'-tetramethyl-4,4'-amino diphenyl and 1,2,4,5-benzenetetarcarboxylic dianydride were also performed. The $[\eta]$ values for the resulting polymers is in the range, 1.44 - 2.62.

TASK: 131

TASK TITLE: Statistical Process Control and Self-Directed Process Control

TASK OBJECTIVE: Research the merits and adaptations of statistical process control and self-directed process control.

SCIENTIST: Thomas E. Sharp, M.S.

DESCRIPTION OF WORK:

The objective of this task was to develop an automated system that will optimize a

manufacturing process, based on quantitative changes in the process, with minimal interaction from human experts. Ideas from Evolutionary Operation (EVOP), Statistical Process Control (SPC), and Genichi Taguchi have been combined to develop an on-line automated optimization system that will interface to QPAL. This system is a Self-Directed Optimizer (SDO) or Self-Directed Process Control (SDPC). SDO is a software package, written in HyperTalk, that will run on any Apple computer that supports HyperCard, and is meant to be used with QPAL.

SDO is meant to be used during the manufacturing of a product to direct the process so that the process will provide both product and knowledge at the same time. The system combines concepts from the three sources mentioned above, EVOP, SPC, and Taguchi.

Evolutionary operation is the basis for the automated optimization system that was developed. The main idea behind EVOP is that a process should be made to evolve towards the optimum conditions during the manufacturing of product and is accomplished by continuously performing experiments on the process, thus exploring the small area around the current working process.

SPC techniques were used to monitor the process and provide a signal to show when the process is out-of-statistical control. SPC performs the role of maintaining a level of quality once it is achieved. Tools are provided which help the operator determine if the out-of-control situation is caused by the SDO system or by some outside cause. ANOVA tools allow the operator to determine the significance of the changes made to the different process parameters.

Two of Genichi Taguchi's ideas were included in SDO. SDO's cost function supports terms with the form of his quadratic loss function, where the loss is proportional to the square of the distance the characteristic is from its target value. SDO also uses Taguchi's approach to removing process variation by selecting the setting of the process parameters that reduce the process sensitivity to noise (by using a term in the cost function of the form of the quadratic loss).

The system was tested with a simple model of a process to determine the effects of noise and the other parameters on the rate at which it converges to the minimum solution. The optimization algorithm was analyzed and an equation was determined that predicted the expected rate at which the SDO system would converge on the minimum value. The equation was tested against runs of the SDO system and predicted the actual results rather well. Based on the experimental and analytical results, three SDO parameters were found to have an affect on the rate at which the system converges: the number of replicants (which had a negative effect on the convergence rate, thus only one replicant should be used), the significance level (best value of which was found to be one standard deviation of response), and the step size for the process parameters (which should be set at the largest value that can be used and still have the quality of the end product not significantly affected).

The main benefit of SDO is that it will allow a process to be optimized with little interaction from experts. The simulations run to date show that the simple algorithm used works as predicted, even with a large amount of noise present.

TASK: 132

TASK TITLE: NDE Signal Processing Research

TASK OBJECTIVE: Identify and/or develop improved signal processing methods for the quantitative extraction of flaw information from ultrasonic and X-ray CT images.

SCIENTIST: T. Raju Damarla, Ph.D.

DESCRIPTION OF WORK:

Classification of faults from ultrasonic signals obtained for various materials using neural networks was performed. Among many neural network algorithms and architectures the existing Backpropagation algorithm was identified as most suitable for the task. The Backpropagation network works in two modes; namely, (1) supervised learning mode and (2) application mode.

Necessary software for the Backpropagation algorithm suitable for classification of NDE signals was developed on a VAX machine. Signals from the materials with and without impact damage were used for training the neural network. Only seven good and bad (impact damage) signals were used for training purposes. The trained network was used to classify 200 signals as impact damaged or no-impact damaged. It was found that the trained network classified the signals with a 92% success rate.

TASK: 133

TASK TITLE: A Qualitative Process Discovery System

TASK OBJECTIVE: Continue project to build a knowledge base capable of performing scientific discovery using an autoclave simulator. This work directly supports advances to the QPA environment.

SCIENTIST: Dan Wood, ThinkAlong Software, Inc.

DESCRIPTION OF WORK:

The research report discusses progress in work on the science of Qualitative Process Discovery (QPD), the activity of performing discovery upon a process control domain. It focuses on a discovery knowledge base called Qualitative Process Discovery, written for the explicit purpose of building models of domain events by means of both hand entry of knowledge and by discovery.

The progress supports the hypothesis that a discovery system which is endowed with a knowledge base of elements of process models gleaned from the physical sciences can be constructed and applied to an interesting task domain. The system, while operating in a real or simulated process environment, can learn to control the particular process it is tasked to control. At the same time, the discovery system learns how to explain the process it is observing and controlling. Finally, the system may discover something about the process (through its search and conjecture mechanisms) which is not directly explainable by the prior knowledge provided.

The purpose of the report was twofold: to discuss the actual discovery results gained thus far in the qualitative process domain from the research, and to animate and illuminate aspects of the discovery systems (both generally and in the domain discussed in the paper).

The progress reported derives from earlier work with a qualitative reasoning system for closed-loop process control in real-world, noisy environments. It also draws from work with learning mechanisms for applied aritificial intelligence in the field of discovery and theory formation. From experience with the Qualitative Process Automation (QPA) qualitative reasoning system discussed in the report, it is known that autoclaves can cure chemical compounds, such as

polymers, with a cure protocol derived solely from the cure in progress. However, a more complete understanding of the details of some of the many processes involved in the cure and its proper protocol will contribute to improved polymer-based products.

Understanding in any domain derives from experience gained from experimental trials combined with prior knowledge. The project is based on the notions that experience can be gained from trials, that prior knowledge may be applied to the learning, and that this learning process can be accomplished by a computer program. It is argued that the project combines much of the most appropriate prior exercises in machine learning with a computational architecture designed specifically to perform machine learning and discovery tasks. The architecture is coupled with an external world, a polymer curing simulator (autoclave), with which the computer system can conduct trials.

It is also argued that, central to any process control protocol, a theory of the process itself is an appropriate starting point. It is the discovery of that theory (more particularly, a portion of the development of a knowledge base for the discovery of such a theory) that is the focus of the report. Work in progress is reported, as well as the early success of the system, to draw on limited prior knowledge of polymers to achieve satisfactory results in early trials on the simulator. Also, a prototype of the QPD process-oriented discovery knowledge base was built and tested and its strengths and weaknesses of the knowledge base are discussed.

The report is divided into six main sections. First, the prototypical application problem at hand in the QPD domain, that of curing polymers in an autoclave, is presented. A discussion on the polymer curing problem introduces many of the issues that are of potential interest as topics for scientific discovery.

QPA is introduced in the next section as the first attempts at the understanding and controlling of polymer curing with qualitative reasoning tools. A review of the research work done to date precedes a discussion of some open issues yet to be understood and the potential areas for discovery.

The third section introduces scientific discovery by machines and explores some related issues. A review of the work previously done in the scientific discovery field and a review of the important terms and tenets of a discovery system are presented.

A discussion of ThinkAlong Software's own architecture for a discovery system, The Scholar's Companion, is presented in the fourth section. Its component features, such as a neural network, memory, interaction with the environment, and directed graph performance engine, are summarized. Detailed discussions on the system ontology are also given.

The next section demonstrates the application of the tools to the science by examining the QPD algorithm developed in the research. A knowledge base, described in the report, resides as a layer on the discovery system tool and attempts to learn and improve its abilities to control a curing autoclave.

Finally, the last section describes the results of the application of the QPD knowledge base to the polymer curing problem, summarized the findings, and discusses the future of the work. It is argued that the QPD knowledge base, with continued development, will be a robust discovery tool capable of application to process-oriented protocol development in a variety of application domains.

TASK: 134

TASK TITLE: Polymers

TASK OBJECTIVE: Investigate packing of ordered polymers by computational methods.

SCIENTIST: Barry L. Farmer, Ph.D.

DESCRIPTION OF WORK:

As an outgrowth of a previous study of the trajectories of the rigid-rod polymers poly-p-phenylene benzobisthiazole (PBZT) and poly-p-phenylene benzobisoxazole (PBO), a preliminary study of the molecular dynamics of those polymers was carried out. In addition, semi-empirical molecular orbital calculations were performed on a single repeat unit of PBZT protonated on both the nitrogen atoms of the heterocyclic ring.

The calculations were made using the SYBYL molecular modeling package on a MicroVax II computer. Molecular mechanical energy minimizations and molecular dynamics studies were carried out entirely within SYBYL. In addition, SYBYL served as the interface to the MOPAC molecular orbital program, allowing utilization of the graphical display capabilities of the SYBYL package.

Molecular mechanics and dynamics calculations were made using the same force field. The parameters were those of the SYBYL force field, modified slightly to provide better agreement with the results of X-ray structure analysis on PBZT and PBO compounds, and the results of molecular orbital calculations. The molecular dynamics calculations were made on chain segments consisting of five (usually) and seven repeat units of the polymer chains. The repeat units were connected so the inter-unit single bond had the same length as the intra-unit single bond.

The dynamics program uses the Verlet method to calculate atom velocities and positions at alternate half-time steps. All atoms of the molecules were considered in the dynamics; i.e., the Shake algorithm was not employed to eliminate consideration of CH stretching vibrations. Electrostatic contributions to the energy were not considered. The dynamics simulation was done without solvent or periodic boundary conditions.

MOPAC calculations used the AM1 (Austin Model 1) method and MNDO (modified neglect of diatomic overlap) sulfur parameters. Molecular mechanics minimum energy geometries were taken as the starting geometries for the molecular orbital calculations. For both PBO and PBZT, both nitrogen atoms of the heterocycle were protonated (+2 charge on the molecules). In both cases, the energy minimization resulted in planar nitrogen atoms with the protons in the plane of the heterocycle.

Qualitatively, the results for PBZT and PBO are much the same except for the torsion angle plots. PBO shows an oscillation about the backbone single bond, while PBZT shows a full rotation. The angle used to measure the linearity of a single repeat unit varies over a 10° range. For both PBO and PBZT, the most striking feature is the oscillations in the end-to-end distance values. The magnitudes of the changes in the end-to-end length were large, as much as 8-12%, indicating that the molecules have developed substantial bends.

Much of the deformation that leads to the nonlinear molecular trajectories can be attributed to out-of-plane bending occurring at the atoms at either end of the backbone single bond and at the midplane of the heterocycle. This provides unexpected flexibility to the polymer molecules.

The results point out that the molecular geometry itself has this inherently softer deformation mode. Also, the results provide a basis for understanding the high resolution electron microscopy results of Martin and Thomas, where assemblages of molecules are seen to make substantial jogs and bends.

Calculations on protonated PBZT and PBO were made to evaluate the energy barrier to torsion about the backbone single bond. The results showed a loss in delocalization as the rings are rotated from coplanarity, which leads to a larger energy barrier in the diprotonated molecule. The change in delocalization with bond rotation also could be seen in the distribution of charge among the atoms of the molecule.

The results of the study suggest that a substantial portion of the rigid-rod character of PBZT and PBO may be due to the protonation effects of the strong acids in which they dissolve. The molecular dynamics studies of the neutral molecules indicated a surprising degree of flexibility, attributable mostly to out-of-plane bending deformations of the molecules. Even assuming this bending mode of deformation will not be influenced by protonation, the MOPAC data indicate that protonation will at least tend to confine the dynamic contortions of the molecular backbone to a plane. More likely, the resistance to out-of-plane bending will also be increased by protonation, giving a much stiffer and more linear molecule than would be supposed from the molecular dynamics and other calculations on the neutral molecule. Another implication of these results was that the molecules would be weakened upon precipitation should neutralization occur during that process. The solid-state form of these polymers may well be more flexible than the solution form.

TASK: 135

TASK TITLE: Polymers: "Compressive Strength Study of Ordered Polymers"

TASK OBJECTIVE: Compressive Strength Study of Ordered Polymers.

SCIENTIST: Satish Kumar, Ph.D.

DESCRIPTION OF WORK:

This study examined the nature of compressive failure in fibers and fiber composites, both from literature and from possible experimental approaches.

Most single fiber compressive strength tests measure the compressive strength indirectly and significant discrepancy remains between the results obtained from single fiber compression tests and from composite tests. Recoil test data for polymeric fibers are close to the composite data, while carbon fiber recoil data are consistently lower than composite data. Research work has been done to further refine this technique, where the fiber is coated with a nonstructural grease, according to an idea developed by Allan Crasto of the University of Dayton Research Institute (UDRI). Several properties of various fibers obtained from this modified technique are reported.

To better understand PAN-based carbon fiber morphology and correlate the HR-SEM results with SAXS, HR-SEM work was performed on S- and E- glass fibers. The results of this work gave a fibrillar radius 0.4 to 1.0 μm for PBZT and PBO fibers. Compressive strain, kink band density, and kink band angles were also determined. However, these values were not reported as yet since it was felt that further statistical work needed to be done to understand the relative importance of these parameters.

TASK: 136

TASK TITLE: Deformation Processing Studies of TiAl Base Materials

TASK OBJECTIVE: To determine the optimum processing conditions for rolling and extruding various gamma Titanium Aluminide alloys.

SCIENTIST: S. L. Semiatin, Ph.D. and Mr. Soo-Ik Oh, Ph.D., Battelle Memorial Institute

DESCRIPTION OF WORK:

The overall objective of this work was to assist the Air Force in short- and long-term efforts to establish optimum processing conditions for rolling, extrusion, etc. of gamma titanium aluminides and other advanced intermetallic alloys. This objective was to be met by (1) the review and interpretation of prior Air Force and contractor programs on the processing of titanium aluminides and (2) assistance in the design and conduct of a research and development plan incorporating an appropriate combination of material property characterization studies, determinations of interface effects, process models, and process model validations. To this end, the following specific tasks were conducted:

1. A prior Battelle review of the effect of processing parameters on microstructure and workability of near-gamma and gamma titanium aluminides was updated and distributed to Air Force personnel.

2. Microsegregation in ingot metallurgy, multicomponent near-gamma and gamma titanium aluminides, which can play a major role in final product properties, was documented for a wide range of compositions. The results of this effort revealed that the magnitude of the segregation for multicomponent alloys is very similar to that found for binary titanium aluminum alloys, except for materials containing additions of high-melting-point elements such as tantalum. These latter materials tend to exhibit substantially greater degrees of microsegregation.

3. Homogenization treatments for a typical ingot metallurgy near-gamma titanium aluminide were developed. The metallurgical mechanism underlying the homogenization process was defined.

4. Ingot breakdown of a model intermetallic alloy, Ti-24Al-11Nb (a/o), was investigated using the isothermal hot compression test. Results were interpreted in terms of the behavior of conventional (disordered) titanium alloys as well as the wrought version of Ti-24Al-11Nb.

5. Simulation of the nominally isothermal hot compression test, incorporating heat transfer between the dies and workpiece as well as frictional effects, was conducted using flow stress data for a typical near-gamma titanium aluminide. Results indicate that workpiece heat generation and subsequent heat transfer between the dies and workpiece have a small but nonnegligible effect on the deformation field. In addition, the average pressure-height reduction curve from such tests, when corrected for deformation heating effects, is within 5 percent of the actual true stress-strain curve of the material.

6. Technical assistance on a number of other in-house projects was provided. These projects included ongoing work on processing of binary gamma titanium aluminides, input to the development of a scope of work for processing studies/process modeling for gamma alloy

G2, and initiation of a project on the modeling of the casting of gamma titanium aluminides.

TASK: 137

TASK TITLE: Shubnikov-de Haas and Quantum Hall Effects in Type II Superlattices: "Magnetotransport Studies in Strained Type II Superlattices"

TASK OBJECTIVE: To determine the band structure of GaInSb/InAs Type II Superlattices, to optimize their applications, by analysis of the Shubnikov-de Haas effect.

SCIENTIST: Ikai Lo, Ph.D.

DESCRIPTION OF WORK:

The Type II superlattice, InAs-GaSb, has the property that the energy of the conduction band edge of InAs is lower than that of the valence band edge of GaSb. Electrons, which transfer from the GaSb valance band to the InAs conduction band leaving holes behind, produce a dipole layer consisting of two-dimensional electron and hole gases at the heterointerface. The band structure of InAs-GaSb superlattice is strongly dependent on the period of layers. The semiconducting energy gap decreases with increasing period, resulting in a semiconductor-to-semimetal transition. Aside from the novel electronic properties, the strained Type II superlattices, InAs-GaInSb, have been proposed for infrared detector applications. The energy gap can be adjusted by changing the layer thickness or alloy composition, and hence superlattices can be engineered to optimize their optical properties.

In order to engineer these superlattices, the knowledge of actual band structure is necessary. The Quantum Hall Effect (QHE) and Shubnikov-de Haas (SdH) effects were used to determine the band structure of Type II superlattice. An experimental setup was designed and assembled to study these effects on semiconductor thin film. The computer program for the data acquisition and analysis was also done. The system was tested for the AC modulation QHE and SdH effects measurements on a GaAs/AlGaAs sample.

Since the Type II superlattice was not yet available, High-Electronic-Mobility-Transistors (HEMTs) samples were used to study the electronic properties of two-dimensional electron gases. QHE and SdH measurements were performed at low temperatures and with different magnetic field orientations. The amplitude of SdH oscillations decreased with increasing angle between the magnetic field and sample surface and the frequency of SdH oscillations changed as well. The results showed the typical behavior of a two-dimensional electron-gas in the semiconductor samples.

Furthermore, the second subband Shubnikov-de Haas oscillations in AlGaAs/GaAs heterostructure were observed by using the Persistent Photoconductivity (PPC) effect, which flashes a light on the sample at low temperatures to pump electrons from deep-donors to the conduction band. It was found that using the PPC effect causes the electron concentration to increase and populates the second subband.

TASK: 139

TASK TITLE: Mechanics of Natural Composites

TASK OBJECTIVE: To analyze the structural response of natural composites for the purpose of ascertaining their potential effect on the optimization of synthetic composite materials.

SCIENTIST: Joseph E. Saliba, Ph.D., University of Dayton Research Institute

DESCRIPTION OF WORK:

Composite materials have been used for many years in a wide variety of structural applications. Fiber-reinforced composite materials consist of high-strength fibers embedded in a continuous phase called the matrix. The fibers are typically discontinuous and are usually stiffer and stronger than the continuous matrix phase.

Both fiber and matrix have significantly different physical properties, yet together they produce a combination of properties that cannot be attained with either of the constituents alone. The composite properties are strongly affected by the properties of their component materials and may be as simple as the sum of the volume fraction of their constituent properties, or they could be quite complex providing the composite with properties that neither component has alone. Fibers are generally considered to be the primary load-carrying members, while the binding matrix is credited for keeping the fiber in place and in the preferred location and orientation. The binding matrix also acts as the load transferor and protector against environmental damages such as humidity, temperature, etc.

The drift from the development of simple isotropic structural material to an orthotropic or anisotropic composite requires more sophisticated analysis and design methods. While such analysis and design methodologies for composite materials are based on older methods used for metals, new problems and criterion are unique to composites alone. Such unique problems appear in determining the complex stress state present on the microscopic scale.

Two different approaches are commonly used in the mechanics of fiber-reinforced composites, macromechanics and micromechanics. Macromechanics is concerned with the overall response of a composite laminate to mechanical and thermal loads. It uses classical elasticity approaches and methods to compute stresses, strains, and deflection in the laminate. Micromechanics is concerned with the interaction of the constituent materials on a microscopic scale and attempts to mathematically describe such characteristics as matrix yielding, crack initiation, and thermal and elastic behavior at the local scale.

The finite element method is currently the most commonly used method for existing micromechanics analysis. The finite element approaches rely on the isotropic material properties of the constituents to predict the microstress and microstrain distributions inside of the typical model. A general state of strain is typically assumed, mainly because of simplicity and lower computer time and memory needed if three-dimensional finite element modeling is ideally used.

The report presents a fairly extensive critical literature review of the three dominant theoretical methods used to compute single-ply strengths from constituent properties: strength-of-materials, statistical, and advanced methods. Several different models using each method are discussed.

The strength-of-materials methods includes the rule-of-mixtures for predicting the longitudinal tensile strength (S_{L11T}) and microbuckling and constituent debonding at the interface for predicting the longitudinal compressive strength (S_{L11c}), the matrix-strain magnification factors and stress-concentration factors for predicting the transverse compressive and tensile strengths

S_{L22c} and S_{L22t} respectively, and the shear strength S_{L12s}, as well as, the semiempirical method for predicting all five uniaxial strengths. Thus, the strength-of-materials method is founded on the assumptions that the total load is divided between constituents based on their relative stiffness and the ply is in a state of constant stress-strain, in an average sense.

The statistical methods are based on two assumptions: the fact that the fiber strength is length- dependent, and that the final fracture of a ply occurs when a critical number of cracks have occurred at some section along the axis of ply. If the fiber strength is mildly length-dependent, then the statistical model simplifies to that of the rule-of-mixtures model.

The advanced methods are primarily classical solid mechanics methods of analysis, such as finite difference, point-matching, or finite element. These methods are mainly used for analyses like obtaining the stress-strain state in the matrix or fiber, rather than for strength prediction. It is common to see the advanced methods used for predicting the ply transverse tensile (S_{L22}), transverse compression (S_{L22c}), and intralaminar shear strengths (S_{L12s}). Once the principal stresses are computed by the advanced method, they are then compared with a suitable failure criterion (usually the maximum distortion energy) for combined stress to predict if failure has occurred.

TASK: 140

TASK TITLE: Computational Mechanics of Composite Materials

TASK OBJECTIVE: To develop a fast computational methodology to solve critical problems in micro- and macro-mechanics analysis of composite materials.

SCIENTIST: Seng Tan, Ph.D., Adtech Systems Re

DESCRIPTION OF WORK:

From the study of the currently existing compression test methods for composite laminates, one finds that the compressive strengths of unidirectional composites measured by different test methods vary significantly. This diversity suggests the need for analyzing these test methods carefully.

There are two standard ASTM (American Society for Testing and Materials) test procedures for compression tests of composite materials: Test Method for Compressive Properties of Rigid Plastics (ASTM D 695-89) and Test Method for Compressive Properties of Unidirectional or Crossply Fiber-Resin Composites (ASTM D 3410-87). The latter includes the Celanese and Illinois Institute of Technology Research Institute (IITRI) test methods. The difference between these two methods is the grip design. The Celanese test method utilizes conical wedge grips (which limit the overall tabbed specimen thickness to around 3.99 mm) whereas IITRI accommodates trapezoidal wedge grips (which allows the overall tabbed specimen thickness to vary from 1.5 to 12.7 mm). To the scientist's knowledge, there is no analysis of the Celanese and IITRI test methods available in the literature. Therefore, the objective of the study was to analyze and evaluate the two test methods.

A quadrilateral isoparametric finite element method (and resulting computer program), based on two-dimensional constitutive relations for stresses of an orthotropic laminate, was utilized to analyze the Celanese and IITRI compression specimens. Strain-displacement relations of elastic-materials were utilized to obtain the element strains in terms of nodal displacements.

Uniform displacements and stresses boundary conditions were both applied to formulate the problem. The stress distributions along the mid-planes, the outer surface and around the tab tip region of these specimens were illustrated. The stress concentrations obtained by the uniform displacements are worse than those under uniform stresses boundary conditions.

In order to make this computer program as easy to use as an analytical solution, a finite element mesh generator, MESH, was developed. The user of the program only needs to input the geometry of the specimen and the number of divisions desired along the thickness and the length of the specimen. The boundary conditions are specified by simply inputting the magnitudes of the total forces or displacements. An example is illustrated by specifying 15 elements from the middle of the specimen to the tip of the end tab, 37 divisions for the remaining length of the specimen, 8 elements along the thickness direction of the laminate and 3 divisions through the thickness of the adhesive layer, to produce a mesh which contains 971 elements and 1047 nodes.

An experimental study was also performed to examine the theoretical analysis and to aid in understanding why the Celanese-measured compressive strength is lower than those measured by other test methods. The laminate material was graphite/epoxy AS4/3502 and the end tab was glass/epoxy. The mechanical properties of the laminates and the adhesive are summarized in the report.

Parametric studies were performed to show the effect of the distributions of the stresses and displacements due to the thickness of the adhesive layer, the laminate thickness and the tab material. The results of these studies showed that: the thickness of the adhesive layer has no remarkable effect on the stress distributions of the laminate, the laminate thickness has significant effect on the stress distributions, and a more compliant tab material can help to reduce the stress concentrations around the tab tip area of the specimen. Results using the Celanese test method lead to the following conclusions:

1. The fracture of the specimen was triggered by global buckling.

2. The longitudinal compressive modulus of a unidirectional laminate can be evaluated with this method.

3. The measured apparent strength of a unidirectional graphite/epoxy laminate is much lower than the value measured by other testing methods and the true compressive strength. Therefore, the Celanese test method is not recommended for measuring the compressive strength of these types of materials.

For IITRI specimens, global buckling could be eliminated if the thickness of the specimens is increased. However, the small ratio of the gage length to the laminate thickness creates nonuniformity of the stress distributions through the thickness of the entire laminate. The apparent modulus must be interpreted appropriately to acquire the true moduli. The apparent compressive strength will be lower than the true compressive strength because of the large value of stress concentrations near the tab tip of the specimen.

TASK: 141

TASK TITLE: Polymer Morphology

TASK OBJECTIVE: Scanning Electron Microscopy of Fibers.

SCIENTIST: Deborah L. Vezie, M.S.

DESCRIPTION OF WORK:

The scientist studied the microstructure of Cortaulds polyacrylonitrile-(PAN) based carbon fibers and Amoco pitch-based carbon fibers using low voltage, high resolution scanning electron microscopy (HRSEM). A Hitachi S-900 field emission SEM was used.

The Cortaulds PAN-based fibers were proprietary samples in various stages of processing. The samples were tensile fractured by hand in liquid nitrogen, coated with Au-Pd and then the transverse fracture surfaces were imaged. The partially and fully oxidized fibers looked like other PAN-based fibers examined previously; the fracture surfaces appeared granular with possibly two phases present. Also, no sheet-like structures were seen in the fibers. Over 100 micrographs of the samples were left at WL/MLBP (Polymer Branch) for further analysis.

The mesophase pitch-based fibers studied were from the commercially available Amoco P-series: P-25, P-55s, P-75s, P-100, and P-120. The fibers were tensile fractured by hand at room temperature and imaged uncoated. Stereopairs of the transverse fracture surfaces were taken for the purpose of studying the three-dimensional nature of the sheet-like structures in the fibers. About 25 black and white slides of P-100 stereopairs (transverse fracture surfaces) were left at WL/MLBP.

Several figures showing stereopairs of the fracture surfaces were presented. The P-55s fiber showed long sheets that are somewhat wavy along the fiber axis direction. An "end-on" view showed that the sheets are wavy with a few sharp angles. The stereopair of the core region of a P-75s fiber showed sheets having sharper angles than those in the P-55s. Layer-like packing of the carbon sheets could also be seen. The fracture surface of a P-120 fiber showed sheets with very sharp angles (especially compared to the P-55s and P-75s fiber images) and which are not wavy along the fiber axis direction like those in the P-55s fiber. "Steps" of fractured sheets could also be seen.

Selected fibers were also fractured longitudinally by placing the fibers between two pieces of double-stick tape and then peeling the tape apart. Fractured fibers that were still partially embedded in the tape were imaged uncoated. The stereopair of a P-100 showed continuous sheets over 1 micron in length.

The conclusion of the report was that stereopairs will prove to be very useful for analyzing the three-dimensional nature of carbon fibers. Height measurements can be made from stereopairs and will be done with the P-series micrographs in future work at the Massachusetts Institute of Technology (MIT).

TASK: 142

TASK TITLE: Fragment Based Ab Initio Calculation Method: "Geometry Optimization Based on Approximate Ab Initio Theory"

TASK OBJECTIVE: Development and validation of computer code.

SCIENTIST: Guru P. Das, Ph.D.

DESCRIPTION OF WORK:

Currently the standard approach to the geometry optimization of large molecular systems consists of two molecular software packages: the Molecular Mechanics programs (MM2, MM3, etc.) and the Molecular Orbital Package (MOPAC). The former uses empirical methods, while the latter uses semiempirical ab initio methods and is believed to be more reliable.

In the present study an algorithm, based on the approximate fragment-based ab initio method (recently proposed by the author and applied for the evaluation of the NLO properties of some selected systems), was developed for performing geometry optimizations on large molecular systems. In this method the molecular system is considered to consist of fragments which are defined simply as "heavy" atoms (e.g., C, N, O, S, etc.) or their hydrogenated radicals. The important feature of the present fragment concept is the recognition that these fragments arrange themselves in the total system in geometries that undergo only minor changes from molecule to molecule. The fragments within the subsystems (usually the environment of the nearest neighbors of the system under study) are treated in the ab initio framework. The algorithm is described for the planar case for simplicity and a brief outline of the modifications necessary for extending the method to non-planar situations is presented.

This is a highly flexible theoretical model by which geometry optimization can be carried out at various levels of sophistication of the wave function of the system. The model will give an alternative scheme for obtaining the geometry parameters before proceeding to calculate NLO or other properties. Because of the theoretical soundness of the method, absence of adjustable parameters and the possibility of incorporating the electron correlation, the present method may prove to be superior to either the MM or MOPAC techniques for molecular calculations.

TASK: 143

TASK TITLE: Electronic Structure Calculations in Intermetallics: "Electronic Properties of TiAl and Planar Defects in TiAl"

TASK OBJECTIVE: To establish electronic structure layer code computational techniques at the Materials Laboratory.

SCIENTIST: James M. MacLaren, Ph.D.

DESCRIPTION OF WORK:

The mechanical behavior of materials is controlled by properties of the defects rather than those of the perfect crystal itself. An obvious example of this is the observation that the strength of a crystal is controlled by properties of dislocations. The defects of importance all involve a reduction in symmetry over that of the perfect crystal. Planar defects, such as a stacking fault, result from the separation of a dislocation into partials. Thus a study of these planar defects provides important information on the properties of dislocations. In addition there is some experimental data available to which direct comparisons can be made. A further benefit of the study of planar defects is that translational symmetry is available in two directions.

The aim of the present work was to use electronic structure calculations to estimate the properties of stacking faults, and anti-phase boundaries in TiAl. This forms part of a larger study at WL/ML (Wright Laboratories Materials Directorate) on the properties of TiAl and how they may determine possible applications of TiAl. The calculations are based within the theoretical framework of density functional theory, and use the so-called local density approximation. This technique replaces the many-body interacting electron problem by an equivalent mean-field

approach. In a perfect crystal, three dimensional translational symmetry and the use of Bloch's theorem require a solution to the one-electron Schroedinger equation within one unit cell only. The reduction of symmetry, however, poses significant problems for perfect crystal approaches since there are formally an infinite number of nonunique atoms in the unit cell of the structure. This can be circumvented by the use of artificial periodic boundary conditions. The development of the layer-Korringa-Kohn-Rostoker (LKKR) method by the scientist allowed the boundary conditions appropriate to the interface to be applied. The report covers both theoretical developments to the LKKR method and the results obtained for TiAl.

Central to most angular momentum expansions of the electronic wave function are the concepts of the muffin-tin and atomic sphere approximations (ASA). The former approximates space by a potential and charge density which is spherically symmetric within so-called touching muffin-tin spheres and a constant in the interstitial, whereas the latter expands the intrasphere region to that of overlapping Wigner-Seitz spheres, leaving no interstitial region. To test the approximations, calculations were performed solely with the muffin-tin energy (muffin-tin potential and charge density), the muffin-tin ASA energy (muffin-tin potential and ASA charge density) and an ASA calculation (ASA potential and charge density).

The calculations were performed on bulk TiAl and TiAl with the simple stacking fault (SISF), complex stacking fault (CSF), (111) anti-phase boundary (APB) and (100) APB. The calculated energies, density of states, and valence charge density for the bulk crystal agreed well with those suggested by other theoretical studies. The valence charge density exhibits strong polarization between Ti atoms, indicative of some component of directional bonding. The charge around the Al atom has a large pz component, suggestive of high planar defect energies (compared to the fcc transition and simple metals). The charge density plot for the (111) APB showed the charge surrounding the Ti site is isotropic in nature. In addition, the charge density is polarized towards the displaced Ti site at the APB.

The calculated results overestimate the experimental values, probably to some extent due to the neglect of the full potential and structural relaxation, though the effects of sample purity and temperature on the experimental results are unknown. The improvement obtained on going from the MT to the ASA energy and the fact that a full ASA calculation for the SISF showed no significant improvement to the energy suggest that a full potential solution will eventually be required, especially if energies of sufficient accuracy to be useful as input to say embedded atom calculations are needed. The more directional nature of the bonding at the interface in TiAl, as compared to elemental metals, is thought to be responsible for the larger defect energies observed.

TASK: 144

TASK TITLE: Polymers: "The Synthesis of Bithiophene and Terthiophene Dicarboxylic Acid Monomers and the Synthesis of Polybenzothiazoles Prepared From These Monomers"

TASK OBJECTIVE: To synthesize novel aromatic-heterocyclic polymers for molecular composites and/or nonlinear optical applications.

SCIENTIST: Ronald C. Tomlinson, M.S.

DESCRIPTION OF WORK:

Materials which may exhibit nonlinear (NLO) optical properties, such as polybenzobisthiazole

(PBT) and polybenzobisimidazole (PBI), are currently being investigated at WL/MLBP (Polymer Branch). The majority of the research effort at MLBP is focused on the synthesis and NLO evaluation of model compounds (those containing the PBX heterocyclic ring system) in order to accumulate a data base of structure versus NLO property relationships. Preliminary data indicated that the extension of the conjugated π electrons will enhance the NLO response. This was demonstrated with benzodiimidazole and benzodithiazole model compounds containing phenyl, vinylbenzene, thiophene and vinylthiophene pendants.

Recently, it was shown that poly-2,5-thiophene exhibits large NLO activity. To support the NLO data base and reveal if there is a direct comparison of the NLO properties of a model compound versus that of a polymer containing the same moieties, an attempt was made to synthesize the aromatic-heterocyclic thiophene containing polymers poly[(benzo[1,2-d:4,5-d']bisthiazole-2,6-diyl)-5,5"-(2,2':5',2"-terthiophene)] and the model compound 2,6-di[5-(2,2':5',2"-terthiophene)]benzo-[1,2-d:4,5-d']-bisthioazole.

An attempt was made to produce the model compound by condensation between 2,2':5',2"-terthiophene-5-carboxylic acid and 2,5-diamino-1,4-benzenedithiol dihydrochloride in 1,2-dichlorobenzene containing PPSE and tributylamine. Unfortunately, the reaction was unsuccessful. The reaction should be studied further since this method has been shown to give a similar model compound, 2,6-di[5-(2,2'-bithiophene)]benzo[1,2-d:4,5-d']-bisthioazole.

Poly[(benzo[1,2-di:4,5-d']bisthiazole-2,6-diyl)-5,5"-(2,2':5',2"-terthiophene)] was prepared from the condensation of 2,2':5',2"-terthiophene-5,5"-dicarbonyl chloride with 2,5-diamino-1,4-benzenedithiol dihydrochloride in 83% PPA by the P_2O_5 adjustment method at 165 °C. Two trials resulted in polymers with intrinsic viscosities of 0.40 and 0.44 dL/g. The low viscosity values were attributed to possibly impure starting monomer, the purity of which is presently being investigated.

TASK: 145

TASK TITLE: Processing Science of Organic Structural Materials

TASK OBJECTIVE: *To develop innovative processing approaches to fabricate molecular composite specimens with good reinforcement efficiency.*

SCIENTIST: Yih-Fang Chen, Ph.D., Adtech Systems Research

DESCRIPTION OF WORK:

The focus of the project was on understanding the rheological behavior and reaction kinetics for poly(amic amide) with different leaving groups that can serve as matrices in molecular composites to achieve molecular dispersion and maximum reinforcement efficiency. The samples were processed under different processing conditions and mechanically characterized. The polymers with leaving groups containing the nadic unit which yield three-dimensional thermoset networks upon reaction are referred to as in situ molecular composite candidates. The other polymers without the nadic unit in the leaving group are designed to investigate the effect of the leaving group structure on the rheological behavior and reaction kinetics.

Two series of polymers were mainly used in the study. The first series, known as poly(amic amide/di-nadic imide-3A (PAA/DNI-3A or PAA/DNI), was synthesized via adjusting the pyromellitic dienhydride (PMDA) and tetramethyl benzidine (TMB) monomer ratio, resulting in polymers, with

the same reactive leaving group, having intrinsic viscosities between 0.34 and 3.90 dL/g and molecular weights ranging from 12,000 to 254,000. The second series of polymers have different nonreactive leaving groups (R = ethyl, butyl, etc. and PI-3A) and are referred to as PAA/di-R. Since the viscosity varied from 1.41 to 3.60 dL/g it was felt that the polymer backbone length varied. Therefore, a third series similar to the second but with the same polymer backbones was used for the more detailed studies.

The rheological behavior of the polymers was studied using torsion impregnated cloth analysis (TICA) experiments. FTIR spectra were used to monitor the chemical conversion reaction of poly(amic amide) to polyimide and to obtain kinetic information to perform a kinetic data analysis for the reactions. The results and conclusions from the TICA experiments were:

1. For the PAA/di-R polymers, the softening effect of the aliphilic pendant becomes more and more significant as the pendant size increases. This suggests that aliphilic amine pendants can act as a plasticizer only when the alkyl length exceeds 6 carbon units. For example, PAA/di-decyl or PAA/di-dodecyl have very wide processing windows, showed pronounced drops in viscosity during transition to polyimide, and showed vitrification transition peaks in the tan delta curves. The moduli of the polyimides stayed at the same high values as the temperature increased up to 360 °C and the final moduli are larger than the ones before transitions. This is good evidence of the formation of rigid-rod polymers.

   The results were different for poly(amic amide)/di-phthalimide-3A (PAA/DPI) suggesting that DPI is not a good plasticizer. Also, the final modulus was lower after transition and decreased with the temperature suggesting that the DPI pendant contributes significantly to the modulus.

2. The data suggested that the PAA/DNI-3A systems have a very narrow processing window. The cross-linking part (DNI-3A) became degraded when the imide formed. The system is not very stable at high temperature with ambient pressure. The results suggested that PAA/DNI-3A is not a very good candidate for molecular composite processing.

3. The blend of PAA/DNI-3A and PAA/di-dodecyl polymers may maintain a good processing window and form a cross-linking matrix. But this system may violate the requirement of in situ molecular composite since some nonreacted leaving groups (didodecyl amine) are involved.

The FTIR spectra results showed that after reaction at high temperature, the absorbance intensity decreased substantially in PAA/di-butyl and PAA/di-dodecyl rather than in PAA/DNI or PAA/DPI system, which meant that the leaving group in the former system degraded and vaporized during the imidization at elevated temperature. In the solid phase, after complete imidization the asymmetric and symmetric N-H stretching vibration bands should disappear (no N-H units exist in the final imide system). This behavior was shown for PAA/di-butyl PAA/di-dodecyl after reaction for 2 to 3 hours, but in PAA/DNI or PAA/DPI the results indicated the ring closure imidization was not quite complete.

The results of the kinetic data analysis at 260 °C showed two reaction rate constants corresponding to the two-stage first-order reaction processes. For all polymers the second stage imidization is much slower than the first stage (by an order of magnitude in most cases). The imidization rate for the reactive polymers PAA/DNI with small molecular weight approached that of the nonreactive polymers. For PAA/DNI polymers the higher the molecular weight the slower the imidization rates, especially for the second stage.

The results also demonstrated that the PAA/DNI polymers with high molecular weight (iv > 1.0) did not achieve complete imidization at 260 °C but for PAA/DNI with iv = 1.01 at 280 °C complete imidization did occur. For the PAA/di-R nonreactive polymers and PAA/DNI with iv < 1.0 imidization at 260 °C was complete.

In summary, the imidization rate of poly(amic amide) is dependent on the reaction temperature and the chemical structure. The more rigid the whole structure, including the backbone and leaving group, the slower the reaction rate. Below some temperature the imidization reaction is incomplete.

TASK: 146

TASK TITLE: Research in Chemical Vapor Deposition in Ceramic Composites

TASK OBJECTIVE: Determine techniques for the variation of morphologies and microstructures of CVD SiC coatings and extend the techniques to coating of continuous fibers.

SCIENTIST: Jason Guth, Ph.D.

DESCRIPTION OF WORK:

The research involved the construction and operation of a chemical vapor deposition (CVD) system for coating fibers for use in ceramic matrix composites. During the task both carbon and silicon carbide (SiC) deposition were studied. Both coatings were produced in batch tests and not on continuous filaments as ultimately desired. Carbon was deposited from methane onto sapphire filaments for use in a sapphire fiber reinforced yttrium aluminum garnet (YAG) matrix composite. A process was found which should produce thick, adherent coatings. When a fiber winding apparatus is installed and tested, this process may be used on continuous lengths of fiber. Silicon carbide was deposited from methyltrichlorosilane onto fibers, carbon rods and graphite yarns. This system is being studied in conjunction with the EMTEC CT22 project to model CVD processes.

The CVD system has proved capable of producing batch coatings on a variety of substrates at a number of different temperatures and pressures.

In addition to the system hardware, a manual was constructed to detail the operation of the system. Included in the manual are schematics, operating manuals for purchased equipment, and vendor bulletins for replacement and repair parts.

TASK: 147

TASK TITLE: Molecular Beam Epitaxy of Strained Layer Superlattices

TASK OBJECTIVE: To develop and apply techniques and methods for the growth of InGaSb on (100) and (111) GaSb substrates. To investigate high energy electron diffraction as a tool to quantify optimum growth conditions.

SCIENTIST: Michael A. Capano, Ph.D.

DESCRIPTION OF WORK:

The primary objective during the study was to maintain the Rigaku X-ray diffraction system (generator and thin-film diffractometer) and to prepare for the installation of the BEDE Model 150 double-crystal diffractometer. First the radiation enclosure was enlarged to accommodate the Model 150 by allowing full range of motion for the reference and specimen crystal axes. Early problems with the radiation enclosure fail-safe system and the X-ray collimator were resolved. The computer system, interface board and software were also installed. Testing of the Model 150 was completed and all circuit boards on the MINICAM interface (provided by BEDE) were found to function properly. Preliminary scans were taken with the Model 150 as a first step towards aligning the diffractometer.

Other activities undertaken included reviewing the theory for specular reflection of X-rays. By comparing experimental reflectivity profiles with theory, information regarding the depth dependence of the electron density becomes available which can be used to obtain specimen parameters, such as layer thickness, in epitaxially-grown structures. Modification of the Model 150 diffractometer will be required to perform these experiments.

Once the BEDE diffractometer is installed, experimental investigations of III-V, metal/semiconductor and, possibly, ceramic superconducting structures will be undertaken using the complementary techniques of X-ray diffraction and transmission electron microscopy.

TASK: 148

TASK TITLE: Quantitative Analysis of Plate Modes for NDE

TASK OBJECTIVE: Identify and/or develop methods to extract in-plane material properties from theoretical plate mode models for organic and metal matrix composites.

SCIENTIST: Adnan H. Nayfeh, Ph.D.

DESCRIPTION OF WORK:

In the study the scientist determined the extent to which it is possible to identify specific plate modes in unidirectional and biaxial composites whose propagation is primarily associated with those in-plane elastic constants which are currently immeasurable. In an effort to assess the interfacial bonding conditions at fiber-matrix interfaces of metal matrix composites, the scientist utilized analytical and numerical models capable of predicting differences between situations in which the bonding is perfect (rigid-bonding condition) and situations in which the fibers are pulled out completely from all or part of the structure. The mechanical properties of the metal matrix composite were derived in terms of its fiber and matrix properties and volume fractions. Since it was assumed that both fiber and matrix constituent materials are isotropic, the unidirectional fiber arrangement used results in a transversely isotropic composite. The numerical values for the isotropic properties belonging to the TiAl matrix and to the SiC fiber are given in the report.

In order to obtain composite properties, an approximate analysis was formulated in which the composite medium is replaced by a homogeneous medium and the fiber-matrix interfacial continuity conditions are utilized. First, a layered structure composed of fiber and matrix layers is analyzed, deriving from the parallel-stress model the properties of "compound" layer 1. In the second step, the final fibrous model is established by treating the composite as consisting of the compound layer stacked in series with the (matrix) layer 2. The absence of fibers is simulated by complete holes. For such a situation, the properties of the resulting medium can be obtained by

setting the density and all of the properties pertaining to the fibers to zero. This results in degraded mechanical properties of the total composites.

The above analysis was implemented in a software package. The modeling procedure and results were based on ultrasonic wave interaction with a plate consisting of four layers, in order to obtain an estimation (leaky plate mode) of in-plane properties. The sensitivity of the model to changes in the fiber volume fraction was illustrated by calculating the variations of bulk wave speeds (longitudinal, transverse and two shear) as functions of the volume fraction for rigidly bonded fibers to the matrix and for circular holes (absence of fibers). Bulk composite properties were calculated, based on an estimated 30% fiber volume fraction, for the presence and absence of fibers. Ultrasonic fundamental symmetric mode dispersions for the first leaky plate mode were calculated for the cases of rigidly bonded fiber-matrix (perfect bonds) and for the absence of fibers (circular holes). Predictions of properties for in between cases where only some of the fibers are missing were calculated as estimates of wave speeds. The resulting wave speeds were obtained for low frequency (to estimate longitudinal wave speed) and for high frequency (to estimate shear properties).

Future work will concentrate on situations where the interface is weak due to breakage along all or parts of the fiber matrix interface.

TASK: 149

TASK TITLE: NDE Signal Processing Research: "Application of Neural Networks for Classification of Ultrasonic Signals"

TASK OBJECTIVE: Identify and/or develop improved signal processing methods for the quantitative extraction of flaw information from ultrasonic and X-ray CT images.

SCIENTIST: T. Raju Damarla, Ph.D.

DESCRIPTION OF WORK:

The task of classifying ultrasonic signals obtained from various materials under test for flaw detection has traditionally fallen on the shoulders of a trained operator. The whole process is tedious and subject to the discretion of the operator working under strenuous conditions. Moreover the process takes large amounts of time as the data involved is very large.

Artificial neural networks are well suited for tasks, such as the classification of ultrasonic signals, involving large amounts of data where decisions have to be made regarding the flaw characteristics, flaw sizes, etc. The study centered on the development of a neural network "Backpropagation" learning algorithm, used in self-learning mode, to accomplish this task. The network is presented a large set of time-domain signals and is allowed to select, on its own, a subset of appropriate training signals which are used to train the neural network to recognize and classify them. The trained network then is used for classification of a set of ultrasonic signals with flaws and without flaws (obtained from material with and without impact damage). The network performs nearest-neighbor classification.

Also studied was an approach in which time-domain signals are compressed using fast Fourier transforms (FFT) into frequency domain signals. There are many sections of the time domain signal that do not provide useful information about the flaws. Compressing the data reduces the

number of input neurons needed in the neural network, thus reducing the size of the problem. The compressed data were used for the classification of signals, as described above. The resultant classification was compared with the time-domain signal classification and it was found that the frequency technique using the compressed signals yielded comparable, if not better, classification signals. This implies that original time-domain data can be compressed and used for flaw detection, thereby reducing storage and time requirements for the classification of data.

TASK: 150

TASK TITLE: Crystallography Discovery System

TASK OBJECTIVE: To develop a system which when coupled to an electron microscope is capable of reasoning about the diffraction patterns required from known and unknown materials.

SCIENTIST: Jack Park, ThinkAlong Software, Inc.

DESCRIPTION OF WORK:

The report represents an early draft of a paper which discusses both the ultimate goal of the project, the development of a crystallography discovery system, and some steps along the way to that goal. The design of a small expert system written in Tiny-5 for diffraction studies on simple cubic structures is reviewed. Tiny-5 is a small, PC-based expert system shell on which application knowledge bases may be compiled and executed. One such knowledge base (KB) is the Crystallography KB which is capable of "looking at" representations of a transmission electron microscopy (TEM) diffraction pattern of some simple cubic structure, and determining the nature of that structure. The review presents the algorithm (based on domain knowledge using an existing database of diffraction patterns) applied in that expert system, then places that algorithm in a larger context, that of discovering the nature of crystalline structures not known to the expert system a priori.

The results of the review have led the scientist to bypass completion of the expert system in favor of development of a heuristic knowledge base to be used with The Scholar's Companion (TSC). TSC is a discovery system being applied to other domains such as process control. The elements of such a knowledge base were outlined and an exploration of the issues of knowledge representation for the three-dimensional domain of diffraction patterns was begun.

TASK: 151

TASK TITLE: High Temperature Superconductive Film Growth: "Deposition of High Quality High Temperature Superconducting YBaCuO Thin Film by Laser Ablation Method"

TASK OBJECTIVE: Growth of high temperature superconductive films of $BiSrCaCuO_x$ materials system.

SCIENTIST: Donald D. W. Chung, Ph.D.

DESCRIPTION OF WORK:

The objectives of the investigation were three fold:

1. Preparation of high quality thin films by means of laser ablation of bulk superconducting ceramic targets under low pressure in a vacuum chamber.
2. To establish a system with processing parameters for the deposition of high quality high temperature superconducting films.
3. To analyze magnetic and electrical data from the superconducting film measurements and to correlate it with the structural property data.

To determine the desired film growth processes several film properties were investigated as a function of the following deposition parameters: substrate temperature, oxygen pressure, target-substrate distance, and the physical condition of the target. The superconducting films were evaluated by (1) A.C. magnetic susceptibility, (2) critical current density, (3) X-ray diffraction, and (4) scanning electron microscopy (SEM).

The film growth behavior was dependent on the sensitivity of the substrate temperature as well as the oxygen pressure. Films deposited at a substrate temperature lower than 650 °C were semi-crystalline and nonsuperconducting, while those deposited at temperatures above 650 °C were crystalline with superconducting properties. Optimal epitaxial growth with the c-axis perpendicular to the substrate plane was obtained for an oxygen pressure between 100 - 200 mTorr and a substrate temperature between 730 °C - 780 °C. The X-ray diffraction pattern showed a highly [001] orientation on $SrTiO_3$ substrates.

Post-heat treatment, mainly the cooling rate, was found to significantly influence the quality of the superconducting properties of the films. Films quenched from the deposition temperature to ambient temperature at a cooling rate of 50 °C/min showed poor superconducting properties, while those cooled at a rate less than 10 °C/min required no additional post-heat treatment to obtain high quality superconducting properties.

The high quality high temperature film process conditions were also affected by the types of target properties used for laser ablation. A large-grained dense-ceramic target permitted much better superconducting properties than that of a smaller grained material. This result seems to be quite contrary to the predictions made by a number of other researchers.

In conclusion, the overall film process data evaluation showed good results but there is room for improvement. Several ideas for system modifications and future projects are given in the report.

TASK: 152

TASK TITLE: Partial Interface Debonding in Brittle Matrix Composites (BMC)

TASK OBJECTIVE: To derive a model to predict the initiation and growth of fiber-matrix interfacial debonding in a unidirectional BMC. The model shall be based on an extension of the capabilities of the NDSANDS computer code.

SCIENTIST: Gyaneshwar P. Tandon, Ph.D.

DESCRIPTION OF WORK:

In the present study an approximate model to study the influence of partial debonding angle θ^* on effective composite moduli was developed. It was based on the micromechanical model NDSANDS previously developed to examine the effect of an imperfect interface on the elastic response of a unidirectional composite. The previous model considered only interface boundary conditions that are independent of axial coordinate z and circumferential coordinate θ. In the present model the case where debonding may occur over a portion of the interface given by $\theta \pm \theta^*$, $\pi + \theta^*$ for all values of z. Thus the model consists of the combination of analyses for bonded and unbonded interface conditions. The equations were developed by considering a concentric cylinder representative volume element of a unidirectional composite under the application of displacement boundary conditions.

There are various aspects to the problem of interfacial debonding, such as the prediction of initiation, growth, and extent of debonding, and the effect of debonding on composite response, say, effective composite moduli. In the present study, attention was restricted to the latter problem; i.e., the effect of θ^*, as well as constituent material properties and volume fraction, on composite moduli was considered. Both volume-averaged strains and surface strains as measures of composite strain were considered in the definition of composite moduli.

Two numerical examples were performed on two composites: Nicalon fiber/1723 Corning glass matrix, and SiC fiber composites made with various glass matrices. For the Nicalon/1723 Glass, composite values for the effective stiffness matrix (coefficients) using both surface strains and volume-averaged strains are reported for various debonding angles. There is considerable difference between the values using surface strains and volume-averaged strains in the analysis. Also, the stiffness tensor is unsymmetric, as was observed in a previous study. Effective Young's modulus and Poisson ratios determined using both surface strains and volume average strains are also reported for various debonding angles.

The second example was used to test the validity of the model by correlating the results with the experimental data generated by Chatterjee. The constituent properties of SiC fiber composites made with two different glass matrices (B and C) are reported. The experimental results led to the conclusion that the major damage mode was debonding of the fiber-matrix interface. The composite transverse Young's modulus for various debonding angles was calculated and compared to the experimental results. The surface strain definition was employed since the experimental measurements were based on the use of strain gages. The results imply an initial debonding angle, θ^*, of approximately 37° and 26° and final values of 90° and 42° for matrices B and C, respectively. The calculated and experimental values for the composite transverse Young's modulus at these debonding angles show fairly good agreement. While the results are not a direct validation of the model, they are physically plausible, thus providing some confidence in the quality of the type of model presented. Finally, while the surface strain definition is appropriate for use in comparing theory versus experiment, the general representation for composite moduli in mulitlayer components has yet to be worked out.

TASK: 153

TASK TITLE: Analysis of Composite Components: "Residual Stresses in Thermoplastic Matrix Composites During Processing"

TASK OBJECTIVE: To perform finite element, heat transfer and strain analysis in order to predict component response to external environments.

SCIENTIST: Shing-Chung Yen, Ph.D.

DESCRIPTION OF WORK:

Perhaps the most difficult task that one may face in the analysis of the residual stress development is the continuing change of viscoelastic material properties due to the change of molecular and chemical state (e.g., crystal-morphology, degree of cure, etc.) during cooling. In particular, for a thermoplastic composite material (carbon/PEEK), the coefficient of thermal expansion (CTE), the degree of crystallinity, and crystal-morphology of the matrix changes continuously with temperature and cooling rate. This implies that at least several sets of master curves and shift factors related to the viscoelastic properties for different states of crystallinity and crystal-morphology must be established in order to determine the state of stress of composite after being cured. The time integration using the Boltzmann-type formulation to determine the residual stress must be carefully conducted.

In the study, engineering analyses were performed to quantify the residual stresses in fiber reinforced composites resulting from the manufacturing/fabrication processes (time, temperature and pressure) required to produce structural grade composite material. Parameters considered included resin type (thermoset/thermoplastic) fiber type (carbon/glass) fiber orientation and ply stack-up orientation.

An analytical procedure to determine the curing residual stress development of the thermoplastic composite structures was developed. The analytical background of the computational procedures was based on linear viscoelasticity theory, lamination theory (micromechanics and macromechanics), and the crystal-morphology reaction of thermoplastic material. The details of the analytical derivation are given in the theoretical background.

Macromechanics was used to establish the stress development in both the fiber and matrix undergoing a continuous deformation process. Micromechanics was used to establish the viscoelastic orthotropic material properties of a composite laminate. Lamination theory was also used to determine the time-delay responses related to the thermal history of a cooling process. The viscoelasticity was introduced in the analyses involving the properties of the matrix material.

Two computer programs based on the analytical equations were also developed (written in FORTRAN) for IBM PC compatible systems. They are presented with sample input data for an interactive computer analysis of the residual stresses development during the processing of thermoplastic composite laminates. One of the computer programs was designed to provide an interactive data input to establish the data file for the RSTRESS (Residual Stress) program. The RSTRESS program requires both fiber and matrix properties as input. Only the temperature-dependent properties are required for the fiber material. For the matrix material, knowledge of time, temperature, and chemically (crystallinity) dependent properties must be given. Accumulated composite layer stresses are calculated and updated at every incremental time step.

Finally, a list of recommendations concerning the future development of the procedure for the estimate of curing residual stresses in the thermoplastic composite structures are given. This includes a recommended algorithm for the development of a computational procedure as a part of an expert system for a process control module for residual stress.

TASK: 154

TASK TITLE: Polymers: "Preparation of Electrically Conducting Poly(benzazole)s"

TASK OBJECTIVE: Synthesis of ordered polymers.

SCIENTIST: Kevin L. Cooper, Ph.D.

DESCRIPTION OF WORK:

The activation energy of conjugated π-electron containing polymers is greater than 1.5 eV. Hence, these materials act as insulators ($< 10^{-10}$ S/cm). However, these macromolecules have a high electron affinity and low ionization potential and, therefore, can be readily oxidized or reduced by ionizing agents. This leads to an electrically conductive or semiconductive polymer.

From a polymer chemist's point of view, polymers which have been successfully fabricated into conducting fibers or films generally have three basic characteristics: a conjugated π-orbital system, an ordered linear structure, and a low ionization potential. Poly(benzazole)s, aromatic rigid-rod heterocyclic polymers, have a conjugated π-orbital system and can be fabricated into highly ordered fibers by dry jet-wet spinning of anisotropic solutions of polyphosphoric acid. Consequently, in order to create a conductive material, poly(benzazole)s must be modified to induce ionization. Therefore, the effort in the study included the synthesis of the poly(benzazole)s and the requisite monomers, as well as a study of polycondensation conditions.

One system which was investigated was the compound dihydroxy poly(benzothiazole) (I), which contains a six-membered cyclic phosphate ester ring. This polymer can undergo ionization by removal of a proton from the cyclic phosphate ester. These materials are highly thermoxidatively stable, are potentially ionizable and resist hydrolysis from a variety of strong acids and bases. The conductive and mechanical properties are currently under investigation.

A new procedure for synthesizing dihydroxy dicarboxylic acid arylene compounds was found and is presented in the report. Specifically, the monomers 2,3-dihydroxybenzene-1,4-dicarboxylic acid (II) and 1,5-dihydroxy-2,6-dicarboxylic acid naphthalene were produced and are under investigation.

A model compound was prepared by reacting compound II with ortho-aminophenol. The compound was identified with FTIR, mass spectroscopy and elemental analysis.

Finally, preliminary investigations of the bis-carboxylation of catechol appeared to be unsuccessful. However, it is hoped that the naphthalene derivative will lead to pseudo-ladder polymers that will have interesting conductive properties.

TASK: 155

TASK TITLE: Synthesis and Characterization of Crown Ethers and Other Macromolecular Complexes of the Lanthanide and Transition Metal Ions

TASK OBJECTIVE: To investigate several entirely new classes of potentially optically active compounds. To synthesize new compounds and modify existing compounds, and to correlate their chemical structure and optical characteristics.

SCIENTIST: Shyama P. Sinha, Ph.D., University of Dayton Research Institute

DESCRIPTION OF WORK:

In this study, crown ethers and other macromolecular complexes of the lanthanide and transition metal ions were synthesized for optical nonlinearity measurements. Their structures

and composition were altered to achieve the highest nonlinear coefficients.

The major activity of this research was focused to synthesize and characterize lanthanide complexes of 18-crown-6-ether ($C_{12}H_{24}O_6$). Complexes were characterized by elementary analysis and spectroscopic studies.

The following lanthanide-crown ether complexes were synthesized in a non-aqueous (CH_3CN) medium:

(a) M(18-crown-6-ether) $(NO_3)_3$ where M = Pr, Nd
(b) M_4(18-crown-6-ether)$_3(NO_3)_{12}$ where M = Sm, Eu, Gd, Tb, Er, Dy, Tm, Yb, and Y.

Spectral studies of these complexes involved the scanning of the UV, VIS, and near infrared (NIR) region from 190 to 900nm of the spectrum.

Two lanthanide complexes, e.g., Eu(III)-18-crown-6-nitrate and Nd(III)-18-crown-nitrate, were selected for extensive spectral studies.

Two complexes of composition Eu(III) (18-crown-6) $(NO_3)_3$ but having very different crystal morphology were synthesized. These two complexes exhibited very interesting fluoroescence properties. Both complexes exhibited the characteristic red fluoroescence originating from the $^5D_0$ excited levels of Eu(III) and terminating at the $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, and $^7F_4$ levels of the ground state multiplets. The most interesting part of this investigation was the discovery of two different excited state lifetimes in the two isomeric forms of the EU(III) complexes. One form exhibited an excited state lifetime value $\tau^5D_0 = 1860\mu S$ while the other isomer gave a τ value of $1355\mu S$. Arising from this research, was a research paper that was presented at the Nonlinear Optics and Material Symposium of the Electrochemical Society Meeting in Seattle during October 14-19, 1990.

Acetonitrile solutions of Nd(III) (18-crown-6) $(NO_3)_3$ complex were tested for their third order hyperpolarizability. The following $\chi(3)$ values were measured:

$\chi(3)$ CS_2 : 2.85×10^{-12}esu
Nd-18-crown-6-$(NO_3)_3$: 0.13×10^{-12}esu
Acetonitrile (solvent) : 0.09×10^{-12}esu

The $\chi(3)$ values were found to depend both on the concentration of the Nd-complex and on the probe energy.

During this research attention was also focused on the very powerful theoretical tool of predicting the dipole moments, electronic charges and hyperpolarizabilities of inorganic and organic compounds. A study of the molecular orbital calculations of the organic ligands, solvents, and selected inorganic compounds was initiated.

By examining the substitution effects of the electron donating and electron withdrawing groups, some interesting correlation has been observed, using the Molecular Orbital Calculation package (MOPAC) developed at the Air Force Academy in Colorado Springs. Over fifty selected compounds and substitution effect studies on several systems have already been studied. This study still remains incomplete. The aim is to compile extensive tables of properties for the electron densities, dipole moments, polarizabilities and hyperpolarizabilities that would be useful in predicting the nonlinear optical characteristics of organic and inorganic systems.

TASK: 156

TASK TITLE: Molecular Composite Processing

TASK OBJECTIVE: To develop techniques for processing in situ rod molecular composite precursors into high-modulus bulk materials.

SCIENTIST: Yih-Fang Chen, Ph.D., Adtech Systems Research

DESCRIPTION OF WORK:

The focus of the project was on understanding the chemistry and reaction kinetics of in situ rod precursors (specifically polyimide) and correlating them with rheological properties as a function of processing histories. The effectiveness of the processing conditions was characterized by mechanical testing.

Most polyimide products have so far been synthesized from poly(amic acid) or poly(amic ester) precursors, which have the inherent difficulty of the removal of the by-product (water or alcohol) during the condensation step. To circumvent this problem, a new approach known as "in situ molecular composite" can be used. This concept combines the ideas from rigid-rod molecular composite and PMR (polymerization of monomeric reactants) techniques. This approach conceptually can form rigid-rod molecules embedded in thermoset matrix simultaneously. It circumvents the rod aggregation and the solvent removal problems. In addition, the precursor, poly(amic acid), for in-situ molecular composites, is a coil type polymer which can be easily dissolved in aprotic solvents like DMAc (dimethyl acetamide), DMF (dimethyl formamide), and NMP (n-methyl pyrollidone).

The main objective of the present work was the study of the kinetics of polyimide formation from poly(amic amide) systems for the in situ molecular composite applications. The approach developed in the study has two unique features; one is the use of the IR substraction technique instead of the original spectra, and the other is to provide a new method for analyzing the first-order reaction kinetics. The subtraction technique avoids the base-line or material background uncertainties and the data analysis is valid for any first-order reactions without regarding its final degree of reaction completion.

The material used in the study was poly(amic amide)/dinadic imide-3A (PAA/DNI-3A or PAA/DNI) synthesized by reacting PMDA and TMB monomers to yield a poly(amic amide), which was sequentially converted to polyisoimide, and finally to poly(amic dialkyl amid). The leaving group of this compound is an alkyl group terminated with norbornene.

The chemistry and rheology of the polymers were studied by several methods: TICA, TGA/MS (at elevated temperatures over 200 °C), DSC (for DNI-3A and PAA/DNI-3A at both ambient and high pressure of 750 psi), and FTIR. FTIR spectra were also used to monitor the chemical conversion reaction of poly(amic amide) to polyimide and to obtain kinetic information to perform a kinetic data analysis for the reactions.

The TICA (Torsion Impregnated Cloth Analysis) experiments were conducted using the Rheological Dynamic Spectrometer (RDS) instrument in both cure mode and isothermal scans at 240 and 280 °C. The results indicated that the overall processing window is very narrow compared to epoxy systems. The isothermal scan results matched those from FTIR and both indicate that the whole reaction process consists of two different stages. The early stage occurs rapidly while the rate of the later stage is slow. This finding indicates that the early fast stage is due to the

material softening effect and the late slow stage is due to the material. Also, the TICA and FTIR results show that the two-stage first-order amide-imide conversion of PAA/DNI-3A systems is viscosity controlled.

The results of the TGA/MS and DSC experiments showed that cyclopentadiene cracks down (evolves) at about 230 °C by retro-Diels Alder reaction under ambient pressure, high pressure, or vacuum environments and the phenomena are temperature driven. However, high pressures prevented the loss of cyclopentadiene from the system allowing it to get involved in the cross-linking reactions.

Finally, the results of the kinetic studies led to several conclusions. First, the absorbance subtraction technique (ΔA technique) proved to be an accurate way to evaluate the kinetic parameters from raw FTIR data. Second, the increasing rate of imide formation is equal to the decreasing rate of the amide disappearance, implying that no intermediate compound occurs during amide-imide conversion. Last, the amide-imide conversion is a two-stage first-order reaction process. The reaction rates have the same order of magnitude but are much smaller than the PMR-15 systems at a given temperature. In other words, it takes higher temperatures for PAA/DNI-3A to react at the same rate as PMR-15. Below 240 °C, PAA/DNI-3A shows almost no imidization.

TASK: 157

TASK TITLE: NLO Polymer Processing: "Characterization and Analysis of Defects in Nonlinear Optical Molecular Composite Films"

TASK OBJECTIVE: To develop techniques for processing ordered polymers into optical quality films.

SCIENTIST: Rajeev Mehta, M.S., Adtech Systems Research, Inc.

DESCRIPTION OF WORK:

During the study, work was done on several related projects: development of the processing technology of optical quality specimens of rigid-rod polymer fibers and films prepared from PBT, 6F-PBO, ZYTEL 330, and Lubrizol; upgrading the processing equipment; attempt to develop a technique for laying an extruded film over a microscopic slide with the help of a spectrally transparent epoxy; and development of an analytical method to get film and fiber extrusion conditions from capillary rheometer experiments. The main objective was to identify the optical defects of the films so that the technique and the equipment can be improved to generate waveguide quality films with other nonlinear optical (NLO) polymers.

Several types of thin films were prepared by extruding acidic solutions of the above NLO polymers through a coathanger die. All the films, except those having 6F-PBO polymer and pure nylon films, were of high enough optical quality to permit measurements of their third-order nonlinear susceptibility (χ^3). The values of χ^3 were substantially higher than those previously reported. The enhanced optical quality is suspected to be the reason. However, the films were not of sufficient quality for wave guiding experiments. For wave guiding experiments, optical loss must be minimized. There are two factors contributing to optical loss: optical absorption, and scattering due to defects. Identifying the defects will improve NLO properties and will help in characterizing the specimens that were used for NLO measurements.

A detailed film defects analysis of samples prepared from PBZT, 6F-PBO, and ZYTEL 330 was performed using optical microscopy and SEM. Five types of films were studied: PBZT extruded from a 1% solution, 50/50 PBZT/ZYTEL 330 extruded from a 2% solution, 50/50 PBZT/ZYTEL 330 extruded from a 3% solution, 50/50 PBZT/6F-PBO extruded from a 2% solution, and 6F-PBO extruded from a 5% solution. Four kinds of defects were observed in the extruded films: voids (presence of bubbles), solid particles, lines in the transverse direction, and lines in the machine direction. The characterization of the defects and the steps taken to eliminate them are discussed in detail in the report.

TASK: 158

TASK TITLE: Compressive Strength of PAN Fiber

TASK OBJECTIVE: To correlate the structural changes of PAN fibers with the compressive properties.

SCIENTIST: Unnikrishnan Santhosh, M.S., Adtech Systems Research, Inc.

DESCRIPTION OF WORK:

The structures of PAN (polyacrylonitrile) fibers at various stages of carbonization and graphitization were characterized and correlated with the compressive behavior of the fibers. Specifically, measurements of the tensile modulus and strength and the compressive strength of the Courtaulds carbon fibers (PAN precursor and eight derivative carbon fibers) were carried out on an INSTRON-1130 tensile testing machine. The tensile property measurements were based on the ASTM Standard D3379-75. The fiber recoil test was used to estimate the compressive strength of the fiber. A brief description of the test procedure including the determination of the corrected fiber modulus is given in the report.

The results of the tensile tests demonstrated that the PAN precursor and the stabilized fibers were viscoelastic; i.e., they exhibited stress-relaxation behavior under a constant strain. Also, the elastic tensile moduli of these fibers depends on the applied strain rate. The stress-strain curves of the carbonized fibers and the graphitized fibers all exhibited almost perfect linear, elastic behavior up to the tensile failure point. The tensile modulus, tensile strength, and tensile failure strain for the different Courtaulds fibers are reported. These properties are compared with those determined at Courtaulds Research by the resinated strand test with Shell 828® epoxy and there is good agreement between the two.

The modulus increased continuously while the strain to failure decreased monotonically with increasing degree of heat treatment. The tensile strength peaked near the early part of the graphitization zone and decreased with higher graphitization temperature, in spite of the fact that the modulus increased steadily. This behavior is in agreement with similar observations available in the literature about heat treatment effects on PAN-based carbon fibers.

The recoil compressive test was performed using a tensile test setup and an electric arc. Only the non-PAN and nonstabilized fibers were tested. The values of the compressive strength (the average values of the upper and the lower strength limits above and below which all the samples fail or do not fail, respectively) are reported. The compressive strength values are not in as good agreement as in the case of the tensile properties, with those obtained at Courtaulds Research by the compressive tow test in Shell 828® difunctional resin.

The experimental data show that the compressive strength starts increasing after the stabilization stage and appears to peak during the early part of graphitization. The heat-treatment temperature where the compressive strength attains the maximum value seems to be near the point where the tensile strength also reaches its greatest value. This may indicate that some common factors, morphological or otherwise, affect both the tensile strength and the compressive strength of the PAN-based carbon fibers.

Scanning Electron Microscopy (SEM) micrographs of the tensile and recoil fracture surfaces were also taken. The tensile failure ends of the PAN precursor fiber taken from a fractured tensile test specimen show a lot of damage and evidence of plastic deformation. The cross-section appears to show a distinct skin or sheath which show extensive elongation and axial splitting.

The side view of the end of a stabilized fiber which failed in the tension tests shows axial splits along the fiber, plastic deformation of the end, and partial pullout of the skin of the fiber are all visible. The tensile failure ends of a fiber at the early part of carbonization and that of a graphitized fiber are typical of all the other fibers and show a relatively 'clean' fracture surface, with minimum plastic deformation and change in diameter at the broken ends. The end views show a granular morphology, with evidence of some kind of axial orientation of the microstructure. The micrographs of the fractured end of the high modulus Courtaulds carbon fiber broken in the tension tests confirm the particulate morphology of the carbon fiber. However, the anisotropic characteristic of the fiber can still be inferred from the axial splitting seen at the broken end of the fiber and the broken surface showing the particulate structure protruding from the fracture surface.

The results of SEM on the recoil fracture surfaces revealed a typical (tension-compression) bending mode failure of the fiber. The recoil fracture surface for at least two of the fibers show that approximately two-thirds of the cross-sectional area has undergone tensile failure while the remaining third of the fiber has failed in compression.

It has been reported previousiy that kink bands develop in PAN-based carbon fibers under the application of a compressive load. Kink bands were observed in a specimen of the Courtaulds derivative carbon fibers which did not fail the recoil test. This shows that these PAN-based carbon fibers can kink in a manner similar to oriented polymer fibers without actually breaking. If the appearance of kink bands was used as the criterion to detect compressive failure instead of what was used, then the compressive strengths reported could possibly overestimate the true compressive strength. The strain to failure of the carbon fibers, especially those having higher modulus, is very small compared to that of polymeric fibers and the tensile strengths of these fibers are also much smaller. The observed failure of the carbon fibers during the recoil test was viewed as occurring by a two-step process: first the fiber, subjected to the recoil compressive stress, kinks at a weak section or at the section nearest the tab; and next the bending stresses at the kinked section induces a tensile failure on the tensile side of the bend and breaks the fiber. It is therefore possible for the true crushing strength of the PAN carbon fiber, identified with the compressively failed part of the fiber cross-section, to be many times higher than the kinking stress and may in fact be higher that the tensile strength, as is true for many common materials.

TASK: 159

TASK TITLE: Polymer Computational Chemistry: "Electronic Structures of Conjugated Polymers"

TASK OBJECTIVE: NLO property computations.

SCIENTIST: Tahir Cagin, Ph.D.

DESCRIPTION OF WORK:

In polymers, just as in the three-dimensional crystalline solids, the interaction of polymer unit cell with all the other neighboring unit cells leads to the formation of electronic bands. The highest occupied electronic levels constitute the valence band (VB) and the lowest unoccupied electronic level the conduction band (CB). The difference between the conduction band and the valence band, the band gap (E_g), determines the intrinsic electronic properties of the polymer (such as its electrical conductivity). Saturated polymers are typically insulators, while conjugated polymers are generally expected to be semiconductors.

In the present study semiempirical quantum molecular/crystal orbital methods were applied, using a modified version of the program MOSOL at the AM1 and MNDO levels, to obtain the optimized geometries, total energies, and energy band gaps of conjugated polymers. The objective was to study the relations between the size and structure of monomers and the calculated band gaps, and the effect of heteroatom replacement on the band gaps. Polymers were systematically studied, starting from polymers with smaller and simpler monomers to polymers with larger size monomers and polymers with heterocyclic monomers. The specific polymers studied were:

1. The polyacetylene (PA) isomers (trans-PA, cis-transoid PA, trans-cisoid PA, trans-regular PA, and cis-regular PA), model polymers with 4-, 5-, or 6- membered rings obtained by introducing α-, β-, and γ-, bridging vinylene groups into PA (polycyclobutadienylene (PCB), polyfulvalene (PF), and polyparaphenylene (PPP)), and other model polymers constructed by incorporating an increasing number of sp^2 carbons between the 5- or 6- membered rings of these polymers.

2. The heterocyclic polymers obtained from some of the above polymers by substituting N, NH, S,or O for CH in the 5-membered ring on the PA backbone, and PPP derivatives with extended planar monomers obtained by introducing NH, S, or O bridging groups between phenyl rings.

3. Other heterocyclic polymers in which thiophene, pyrrole and furan are the basic chemical structures. The monomers of these polymers are made up of the fused rings of thiophene, pyrrole and furan extending along the polymer axis. The objective in this case was to determine the effect of the monomer size on the electronic structure of such polymers.

4. The rigid-rod polymers, poly-p-phenylene benzobisthiazole (PBZT), poly-p-phenylene benzobisoxazole (PBO) and poly benzobisimidazole (PBI).

5. Ladders or multi-ladders of carbon π-electron networks such as polyacene and graphitic ribbons constructed from polyacene.

The results of the study led to several conclusions. The calculated band gaps for pure conjugated polymers were all in the semiconducting to insulating range. Still, some interesting variations in band gap values were observed. The hydrocarbon chains containing five- or six-membered rings were observed to have calculated band gaps on the same order. The band gap values differed as much as 1 eV from one compound to another. The band gaps for heterocyclic polymers with sulphur substitutions, such as polybis-thiophene and polyisothionaphtene (PITN), are lower compared to similar hydrocarbon chains or heterocyclic polymers with different substituent atoms of groups. PITN has the lowest E_g (~4.1 eV, 1.5 eV below that of its precursor) of all heterocyclic model polymers. For PCB, PF, and PPP the E_g values were between 6 to 8 eV

and in the order PCB > PPP > PF. The extended monomers obtained from PPP via bridging atoms or groups also showed variations in band gaps, but in this case the most effective bridging entity was the NH group, causing a substantial decrease in band gaps when compared to that of PPP (~1.34 eV). In the case when there are two local minima for the polymer corresponding to aromatic and quinoid forms, the lower band gap corresponds to the energetically more stable one. Polythiophene (PT) and polythieno(3,2)thiophene (PTh32Th) have the aromatic form as the energetically more stable structure whereas PITN is more stable in its quinoid form. The higher minima quinoid forms for PT and PTh32Th and aromatic form for PITN have much lower band gaps. The ordered rigid-rod polymers, PBT, PBO, and PBI, have comparably large E_g's (~7 eV). The extended polymers based on fused rings of pyrrole, furan and thiophene have lower band gaps compared to related smaller monomer size polymers, but the decrease in band gaps as a function of monomer size is not very large, at least in comparison to the decrease observed for quinoid vs. aromatic local minimum structures of the same compound. Some interesting variations in band gap values were observed for polyacene and the extended structures based on polyacene. Polyacene ribbons show considerably lower E_g's than the other polymers studied. The larger the polyacene ribbon (as the monomers extend in the perpendicular direction to the polymer axis), the lower the band gap (0.56 eV for the largest structure).

The calculations performed using the MNDO Hamiltonian resulted in large band gaps compared to the AM1 results. Both methods yielded the same total energy for the model systems studied and the calculated geometries are only slightly affected by the use of the different Hamiltonians.

Finally, the scientist employed the extended Huckel method at the AM1 optimized geometries to calculate the band structures of PT, PITN and PTh32Th, both in their aromatic and quinoid forms. In addition to the polymer presented in the report, the optimum geometries for PPy32Py and PFu32Fu, both in their aromatic and quinoid forms, were also obtained. The Huckel results showed that this class of polymers have substantially lower band gaps, especially, the quinoid form of PPy32Py which has a band gap of 0.06 eV. The corresponding semiempirical crystal orbital method yielded a band gap of 4.05 eV for the same polymer.

TASK: 160

TASK TITLE: Crystallography Discovery System

TASK OBJECTIVE: To generate a knowledge base (set of rates) for characterizing metal crystal lattice formations.

SCIENTIST: Alan G. Jackson, Ph.D.

DESCRIPTION OF WORK:

The objective of the study was to participate in the generation of a knowledge base related to crystallography which could be used in the Discovery System concept. The methods and procedures used for transmission electron microscopy (TEM) electron diffraction pattern analysis were emphasized, and test cases were generated to test the limits of the knowledge base.

The project is the initial effort not directly related to programing in the construction of a crystallography discovery system. Previous success with the application of the Discovery concept to autoclaving of polymers prompted interest in extending the concept to a more general application not immediately tied to instrumentation but which would be usable for such control in

the future. An additional feature would be to provide the scientist or engineer using such a system with assistance in analyzing and collecting data used for characterizing metal crystal structures.

The immediate approach was to study the analysis of electron diffraction patterns, since TEM as a research tool is a fundamental method in characterization work and uses crystallography concepts and methods. This was accomplished by examining the process of electron diffraction analysis in terms of analytical equations required and their application and limitations, and then to consider the qualitative techniques employed by researcher when difficulties in accomplishing the analyses are encountered.

Several test cases, depending on the knowns and the purpose of the experiment, were developed. The simplest case is when all data is known, in which case application of the standard crystallography equations is the only effort necessary. When only the crystal system is known as well as the elements present (but not their stoichiometry), the task is more difficult, but is still approachable using quantitative equations. The worst case is when nothing about the phase is known other than the elements present. This case requires the same approach as the previous case with the addition of searches of crystal databases for archtypes which have the same or similar atom ratios as the specimen. Experimentally these ratios can be obtained using energy dispersive spectroscopy in situ.

Since the analysis approach is multifaceted, the simplest cases were attempted first in order to provide a basis for attacking the more difficult situations. Test diffraction patterns were generated from simple cubic crystal structures. The coordinates, in polar form, of the diffraction spots were provided to ThinkAlong Software as a simple test case for the discovery system to identify the indices of the g-vectors in the patterns and the zones present. This was successfully demonstrated to WL/MLBP (Polymer Branch). A more subtle pattern from an Nb_3Si crystal, based on real diffraction pattern data as opposed to simulated data, was submitted next. The system was developed to the point where the analysis is partially complete. The probable g-vector magnitudes and angles between the vectors have been generated, but the indexing task and zone axis identification task remain incomplete to date.

A detailed review of symmetry aspects of diffraction was also performed in an attempt to delineate more clearly what features of symmetry were used and why. Also, the matrices characterizing the three-dimensional crystal were examined in detail and reduced to appropriate two-dimensional matrices. Such knowledge of the matrices has allowed the generation of the symmetry recognition algorithm used in the system. Extension of this algorithm must be done to provide for an alternative symmetry recognition route in the pattern analysis method.

In addition, the use of polygon recognition algorithms was considered. A first analysis of this approach suggests that this may be an interesting and perhaps unique method for analyzing patterns. Nets of polygons, whether regular, semi-regular or other types, can be handled simply by using available software. All diffraction patterns can be arranged into a net of polygons. Analysis can be applied for two objectives: generation of the direct lattice positions by applying Fourier transform methods to the net, or utilizing net recognition algorithms to separate two or more patterns which may be present in a single image.

TASK: 161

TASK TITLE: Statistical Process Control and Self-Directed Process Control

TASK OBJECTIVE: To research the merits and adaptations of statistical process control and self-directed process control.

SCIENTIST: Thomas E. Sharp, M.S.

DESCRIPTION OF WORK:

The report covers two topics related to Self-Directed Optimization (SDO) and Self-Directed Control (SDC). First, the test protocol that was used to test the self-directed optimizer on the composite curing simulator is described. Then an overview and a comparison are given of the off-line quality control techniques described by Taguchi and Bhote.

The purpose of the test was to show that the SDO system is applicable to a process controlled by an SDC system. SDO was tested on a simulation of a composite curing process. The goal of the SDO system is to determine the value of the constants used in the composite curing knowledge base that minimizes the cost of the parts produced.

The report shows how SDO might improve a cure cycle generated by an SDC system. The SDC system was unable to generate the optimum cure cycle because it is limited by internal constants. SDO will determine the settings of all of the internal constants that will allow the SDC system to generate the optimum cure cycle.

The cost of the parts produced for the test was chosen to be a function of the total processing time and the final fiber volume of the parts produced. Ideally other part characteristics would be included in the part-cost function but fiber volume is the only part characteristic that is generated by the composite curing simulator being used.

The test hardware setup consists of an IBM PC/AT connected to an Apple Mac II via a serial cable. The composite curing simulator is run on the IBM PC/AT and the SDC system is implemented in QPAL on the Mac II.

The test software setup consists of several programs. The simulator used was one written in FORTRAN by Dr. William Lee (University of Dayton), modified to predict resin flow in the composite part and the final fiber volume of the part. The knowledge base used was the knowledge base supplied by Universal Technology on the QPAL distribution disk and modified to be used with the new composite curing simulator.

The SDO software used is written in HyperTalk and runs on the Mac II. The control parameters to adjust and the cost function for the parts produced must be defined before the optimization can start. The knowledge base was examined and all of the constants used (control parameters) were identified. All of the knowledge base constants are given in the report.

The cost function used is a polynomial with two terms. The first term is the total processing time, which is minimized. The second term is the fiber volume, which has a target value. A Taguchi's loss function is used to predict the cost of this term.

The test protocol is defined by the SDO system. The simulator used is totally deterministic. The SDO system is allowed to run until there is no significant change in the cost of the parts being produced, or until a physical constraint is reached. No tests had been run at the time the report was written.

The report also gives a comparison of the off-line quality control techniques of Genichi Taguchi

and Keki Bhote. Off-line quality control methods are technical aids for quality and cost control in process (or product) design. The goal of off-line quality control methods is to improve the process design in order to improve quality and reduce cost. Experimental methods are used to obtain this improvement.

The author first separates Taguchi's tools from his quality philosophy. This was done because Bhote uses some of Taguchi's philosophy as the foundation for his work, but ignores some of the most important ideas of Taguchi. Then a comparison is made of the tools that Taguchi and Bhote advocate using during off-line quality control and how they relate to Taguchi's quality philosophy. The report shows that Bhote's tools are useful and simpler than Taguchi's tools at some tasks, but that Bhote does not address all of the details of Taguchi's quality philosophy. Finally, the report gives a description of Taguchi's quality philosophy and a description of the tools used by both Taguchi and Bhote.

TASK: 162

TASK TITLE: Crystallography Discovery System

TASK OBJECTIVE: To develop a system which when coupled to an electron microscope is capable of reasoning about the diffraction patterns required from known and unknown materials.

SCIENTIST: Jack Park, ThinkAlong Software, Inc.

DESCRIPTION OF WORK:

Progress was made on two fronts of research regarding the coupling of a discovery system, The Scholar's Companion (TSC), to a Transmission Electron Microscope (TEM) for the purpose of studying diffraction patterns of crystal structures. The basic syntactic approach has been to develop a knowledge base for TSC. A second approach has been to implement a small "discovery" program in the TSC environment suitable for experimentation with a tiling analysis approach.

Both approaches appear to have merit, but each offers unique features. It is conjectured as a result of the research that the combination of a tiling and an algorithmic analysis approach will benefit the discovery system.

The research indicated that it is clearly possible and desirable to implement a system capable of automated diffraction pattern analysis. However, a few algorithmic systems on personal computers are available to perform this task on a variety of diffraction patterns. A shell of a candidate architecture for discovery in the domain of crystallography was built and demonstrated. The work led directly to a system capable of analyzing a range of diffraction patterns, and further capable of learning to analyze patterns not within its programmed capabilities. At present, the system includes a database of atoms based on the periodic table, and a knowledge base about crystal structures which is capable of growing at runtime. The system has successfully indexed cubic structures and will soon index hex and tetragonal structures.

The system is also capable of being coupled to a TEM such that it performs the analysis itself, conducting experiments under its own control. Through dialog with materials scientists, the TSC-based system then learns or assists in the discovery of patterns based on novel materials, or novel material defects.

TASK: 163

TASK TITLE: Synthesis of Spiropyrans and other Polyene Molecular Complexes for Nonlinear Optical Properties

TASK OBJECTIVE: To investigate several entirely new classes of potentially optically active compounds. In this investigation an attempt will be made to synthesize new compounds and to modify existing compounds and to correlate their chemical structure and their optical characteristics.

SCIENTIST: L.V. Natarajan, Ph.D.

DESCRIPTION OF WORK:

During the study, a number of organic materials were tested for nonlinear optical behavior. The study on optical limiting by a series of trans-α, ω-diphenyl polyenes was completed. The influence of planarity, substitution of donor and acceptor groups and the extent of π electron delocalization on the nonlinear thresholds in an optical limiting geometry were examined. A saturation effect of optical-limiting nonlinear thresholds consistent with the theoretical work was observed at 10-11 π electron bonds. The temporal profiles of the transmitted laser pulses and the power dependence of the nonlinear thresholds as a function of spot sizes and wave length were examined. These examinations led to the conclusion that the nonlinear mechanism was quasi steady-state self-focusing. Nonlinear thresholds an order of magnitude lower, and thus n_2 and $\chi^{(3)}$ values an order of magnitude higher than the well known self-focusing media CS_2 were observed. Our studies demonstrate that this series of polyenes are efficient broad-band nonresonant optical-limiting materials. The results and conclusions of the work are presented in the paper, "Optical Limiting in Solutions of Diphenyl Polyenes," which was submitted for publication in the professional journal APPLIED OPTICS and is attached to the report.

In addition, the optical limiting measurements were extended to other types of biologically important polyenes, namely, the retinol family. Trans-retinol, trans-retinal, and trans-retinoic acid were examined and found to have threshold values of 10 μJ at 532 nm. Detailed studies were made to determine the mechanism involved in the nonlinear process. The other polyenes studied during the task period were diphenyl acetylene, 1,4-diphenyl butadiene.

Polypeptide molecules were also examined for nonlinear optical response. Poly-benzyl-glutamate was doped with 6-nitrospiropyran and aligned by shearing on a glass plate. The samples were tested for second harmonic generation and found to have only very weak response. The results suggest the samples may need to be aligned by applying a DC field to get high values.

Also during the study, the following synthetic work was developed to make new nonlinear optical materials. Synthesis of polyglutamic acid modified with 1-(β-hydroxyethyl)-3,3-dimethyl-6^1-nitrospiro(indoline-2,2^1[2H-1]benzopyran) was performed and characterization of this polyglutamic acid bonded to spiropyran was done by gel permeation chromatography. This modified polypeptide will be tested for optical limiting and also second harmonic generation. Another synthesis successfully accomplished was attaching 6-nitrospyropyran to 4-allyloxy-benzoic acid. This molecule is photochromic and the polymer made by bulk polymerization will be expected to show high nonlinear response, as spiropyrans are good materials of second harmonic generation.

TASK: 164

TASK TITLE: Compression Behavior of Composite Materials

TASK OBJECTIVE: To develop models for predicting compression behavior of composite materials.

SCIENTIST: Seng Tan, Ph.D., Adtech Systems Research

DESCRIPTION OF WORK:

From the study of the currently existing compression test methods for composite laminates, one finds that the compressive strengths of unidirectional composites measured by different test methods vary significantly. This diversity suggests the need of analyzing these test methods carefully.

The scientist developed analytical models for predicting the compressive strength of composite materials. Micromechanics of the fiber and fiber/matrix interaction were considered. A stress analysis of compression test methods such as the Celanese, IITRI, and mini-sandwich beam was also performed. Particular concern was paid to the development of interlaminar stresses in these specimens. The report is organized into essentially three different papers briefly described below.

Two of the most commonly used compression test methods are the Celanese and Illinois Institute of Technology Research Institute (IITRI) test methods which are part of the standard ASTM test procedures, Test Method for Compressive Properties of Unidirectional or Crossply Fiber-Resin Composites (ASTM D 3410-87). The main difference between the two methods is the grip design of the fixtures, which allows the IITRI specimens to be thicker. The objective of the study was to analyze and evaluate the two compression test methods (specimens). The results of this study are given in the two papers, "Analysis of ASTM D 3410 Compression Test Specimens" and "Stress Analysis and the Testing of Celanese and IITRI Specimens," attached to the task final report submitted to WL/MLBM (Wright Laboratories Materials Directorate Mechanics and Surface Interactions Branch).

A quadrilateral isoparametric finite element method (and resulting computer program), based on two-dimensional constitutive relations for stresses of an orthotropic laminate, was utilized to analyze the stress-strain distributions of the Celanese and IITRI compression specimens. Strain-displacement relations of elastic-materials and a strength of materials approach were both utilized in the analysis. Uniform displacement and stress boundary conditions were both applied at the end-tab surfaces to formulate the problem. The stress distributions of these specimens are illustrated in the report.

The results show that both of the boundary conditions can be applied to analyze the Celanese specimen with nearly the same result within the gage length section and around the peak value of the stress concentrations, which occurs near the tab tip. Under the end tab region, different boundary conditions (stress versus displacement) result in significantly different results. For a thicker IITRI specimen, the stress concentrations and the stress profiles obtained by the two boundary conditions are considerably different. The stress concentrations obtained by the uniform displacement boundary conditions are worse than those under uniform stress boundary conditions for both specimens. It is believed that the physical test matches the uniform displacement boundary conditions better for the theoretical analysis for two reasons: the stiffness of the grips is much higher than that of the end tab, and the matching surfaces are flat between the machine grips and the end tabs of the specimen.

Parametric studies were performed to show the effect of stress distributions in the

unidirectional Celanese and IITRI specimens due to the thickness of the adhesive layer, the laminate thickness and the end tab material. The results of these studies showed that: the thickness of the adhesive layer has no noticeable effect on the stress distributions of the laminate, the laminate thickness has significant effect on the stress distributions, and a more compliant tab material can help to reduce the stress concentrations around the tab-tip area of the specimen. For thick IITRI specimens, the stresses are nonuniform through the thickness of the entire laminate.

An experimental study of the stiffness and strength of a $[0]_{12}$ Celanese specimen, fabricated from Hercules graphite/epoxy AS4/3502 prepreg, was also performed to examine the theoretical analysis and to aid in understanding why the Celanese-measured compressive strength is lower than that measured by other test methods. The experimental moduli were measured and given in the report.

The results of this part of the study led to the following conclusions:

1. The longitudinal compressive modulus of a unidirectional laminate can be evaluated accurately (before buckling occurs) using these specimens. For thicker IITRI specimens, the stress concentrations need to be carefully considered to accurately interpret the moduli.

2. The apparent strength of a unidirectional graphite/epoxy laminate measured by the $[0]_{12}$ Celanese specimen is much lower than the "true" compressive strength because it fails due to global buckling. The IITRI test method would seem to be better since it can accommodate a laminate with various thicknesses. However, there is no evidence that thick IITRI specimens will give the "true" compressive strength. Therefore, the Celanese and the IITRI test methods need to be modified for measuring the compressive strength of unidirectional graphite/epoxy composites.

The last part of the study concerned the development of a better test method for the measurement of the compressive strength of unidirectional composites. The mini-sandwich test specimen (method) was studied as a replacement to the above two tests. This specimen is an adaptation and modification of the conventional honey-comb core sandwich specimen. However, the mini-sandwich specimen is much smaller and utilizes 3501-6 or APC2 epoxy for the core material for thermoset and thermoplastic composites, respectively. Better results were obtained when the composite skins were two to four plies. The IITRI test fixture was used for the testing of the specimen. Experimental results have shown that the compressive strength measured by this method is significantly higher than that evaluated using Celanese or IITRI methods.

The main objective was to analyze the mini-sandwich specimen to reveal why it gives much higher strength values than the other test methods. The mini-sandwich specimen was modeled and analyzed using a quadrilateral isoparametric finite element method. To facilitate and expedite the analysis, a finite element mesh generator was developed.

TASK: 165

TASK TITLE: Mechanics of Natural Composite Laminates: "A Sensitivity Study of the Mechanical Behavior of Fiber-Reinforced Composite Materials"

TASK OBJECTIVE: To look at natural composites such as the bess bug, and analyze their structure as to the potential application to novel design concepts in synthetic composites.

SCIENTIST: Joseph E. Saliba, Ph.D., University of Dayton Research Institute

DESCRIPTION OF WORK:

The study was initiated to investigate the structural response of the bessbeetle to determine potential advantageous ramifications and effects on the optimization of synthetic composite materials. The cuticle, or exoskeleton, of the bessbeetle (Odontotaenius disjunctus) is a natural polymeric composite that is structurally similar to man-made fiber reinforced composites. However, the insect cuticle uses fibers which vary in cross-sectional size and shape through the thickness. The reason for the variation is uncertain. The main objective of the present study was threefold:

1. A sensitivity study to examine the effect of fiber shape variation, volume fraction, and modulus ratio of the constituents (E_f/E_m) on the principal stresses and deflection of circular, and two opposite elliptical fibers laminate.

2. A sensitivity study to examine the effect of changing the ratio of the major axis to the minor one on the transverse modulus and the principal stresses.

3. A sensitivity study to examine the effect of volume fraction and modulus ratio on the transverse modulus.

Information was limited on the micromechanics of elliptical fiber-reinforced composites. The lack of information caused problems when it came time to use classical laminate theory for computing or approximating the modulus of elasticity in the lateral direction. Therefore, two methods were developed for the approximation of the transverse modulus for a single lamina.

The first method is based on the rule of mixtures of elementary mechanics of materials and deals with unidirectional continuous fibers. In this method the transverse modulus does not take into consideration the shape of the fiber and geometrically speaking is only a function of the volume fraction. The second approach is based on the Halpin-Tsai equations. This method can model a wide array of possible reinforcement geometries and in that sense is very global.

To show that plane strain could be used on a typical laminate, a three-dimensional finite-element model with circular fiber was first generated. The stress distribution due to a transverse unit load was shown to be uniform along the length of the fiber. Therefore, it was concluded that plane strain could be safely used, thus reducing the size of the finite element models.

The results of the micromechanics sensitivity study of various parameters are presented in the report. Variables such as fiber size and shape, fiber volume fraction, and ratio of modulus of elasticity of fiber over matrix (E_f/E_m) were changed one variable at a time, and the response quantities such as stress and transverse modulus are presented.

TASK: 166

TASK TITLE: Deformation Processing Studies of TiAl

TASK OBJECTIVE: To determine the optimum processing conditions for rolling and extruding various gamma titanium aluminide alloys.

SCIENTIST: S. L. Semiatin, Ph.D. and Soo-Ik Oh, Ph.D., Battelle Memorial Institute

DESCRIPTION OF WORK:

The overall objective of the study was to assist the Air Force in short- and long-term efforts to establish optimum processing conditions for rolling, extrusion, etc. of gamma titanium aluminides and other advanced intermetallic alloys. This objective was to be met by participating in the design and conduct of a research and development plan incorporating an appropriate combination of material property characterization studies, determination of interface effects, process models, and process model validations. To this end the following specific tasks were conducted:

1. The persistence of segregation for a typical near-gamma titanium aluminide, Ti-47Al-2.7Nb-0.3Ta (at%), was established through an extensive heat treatment and microprobe investigation. The work indicated that microsegregation in ingot metallurgy near-gamma titanium aluminides is manifested by a nonuniform phase distribution and not major solute distribution nonuniformities within a given phase.

2. Deformation and heat treatment parameters were established for breakdown of the coarse grain lamellar structure that is developed during homogenization heat treatment of ingot metallurgy near-gamma titanium aluminides. Using these parameters, a fine-grain equiaxed gamma structure (with alpha-two at the grain boundaries) was produced.

3. Deformation processing studies were initiated for a cast + HIP'ed near-gamma titanium aluminide. This comprised the tensile testing of Ti-49Al-2.5Nb-1.75Mn to determine a fracture criterion and complementary isothermal forging trials at various temperatures and strain rates. The process conditions for the forging trials gave rise to material which was either sound or contained surface cracks, thereby providing a data base for process model validation.

4. Simulations of the hot tensile test and canned extrusion process were conducted to provide input to the design of deformation processes for breakdown of cast near-gamma titanium aluminides.

5. A microhardness investigation was conducted on Ti-48Al-2.5Nb-0.3Ta, produced by both ingot metallurgy and powder techniques, to assess the contribution of various factors to the strength of near-gamma titanium aluminides.

TASK: 167

TASK TITLE: Molecular Dynamics of Rigid-Rod Polymers

TASK OBJECTIVE: To apply molecular dynamics techniques to understanding time dependent properties of rigid-rod polymers.

SCIENTIST: Barry L. Farmer, Ph.D.

DESCRIPTION OF WORK:

The results of molecular dynamics (MD) simulations of poly-p-phenylene benzobisoxazole (PBO) and poly-p-phenylene benzobisthiazole (PBZT) which were reported previously showed those molecules to be surprisingly flexible in spite of their rod-like topologies. The soft deformation mode responsible for this flexibility was identified as an out-of-plane bending motion.

Clearly, the force constants governing such deformation are critically important, and the validity of the results especially depend on their accuracy. A comparison of the results for out-of-plane bending deformation calculated by the molecular mechanics (MM) method (using the same force field as used in molecular dynamics) and the semiempirical molecular orbital method (AM1) was made in the present study. Several other calculations were carried out as well.

Molecular dynamics simulations were extended to consider poly(para-phenylene) (PPP). First, the MM force field (Tripos) was modified to give agreement with results of AM1 calculations on biphenyl for the energy of rotation about the inter-ring single bond versus the torsion angle. A MM minimization using the modified force field produced results similar to those from AM1 calculations.

Molecular dynamics simulations using the native and modified Tripos force fields were carried out on a molecule containing 14 phenyl rings. Both force fields produced similar effects. The end-to-end distance variation represents a reduction of about 5-6% from the fully extended chain, a surprising degree of flexibility for a molecule characterized as a rigid-rod.

The second set of calculations involved MD simulations (using the native Tripos force field) of ribbon- to sheet-like graphitic molecules to investigate the effect of lateral dimension of a rigid-rod-like molecule on its flexibility. Polyacene and more sheet-like molecules consisting of 2, 4, 8, and 16 fused polyacene ribbons were investigated. In each case, the ribbons were 22 rings (~54 Angstroms) in length.

The results showed that the sheets retain considerable flexibility. Both polyacene and the wider ribbons exhibit twisting. The extent of nonplanarity that occurs is remarkable, bringing immediately to mind the extensively twisted and folded models that have been advanced to describe the arrangements of the graphitic sheets in the morphology of graphite fibers. The end-to-end distances change from 2-6%, with the smaller changes corresponding to the larger sheets.

In terms of the impact on flexibility, there does not seem to be a dramatic stiffening of the molecules upon extending the structure into two dimensions. Not surprisingly, the out-of-plane bending motions that admit to flexibility in the rigid-rod polymers persist into the ribbons and sheets. The twisting observed in narrow ribbons is dampened somewhat upon increasing the width of the ribbons, but even almost equi-axed sheets remain flexible.

In addition to the above calculations, AM1 semiempirical molecular orbital calculations of bending deformation energies were performed to test the validity of the force constants used in PPP, PBO, and PMZT. Biphenyl, naphthalene, phenyl benzobisthiazole, and phenyl benzobisoxazole were constrained into bent geometries and energies were calculated and minimized with respect to all other geometrical parameters. Both initial and final AM1 geometries were used to calculate the MM energies for the constrained molecules using both Tripos force fields.

For biphenyl, the results showed the torsion angle from MM increases as the bend angle increases, while AM1 shows the torsion angle to decrease slightly. Also, the MM results indicate greater resistance to the bending deformation than the AM1 results. Similar results were seen for naphthalene. Better agreement between the methods may be possible by further modification of the MM force field. Both AM1 and MM energies for PBO bent at the phenyl carbon and at the heterocycle carbon are also shown. The energy from both methods increases more rapidly for bending at the heterocycle than at the phenyl carbon, and again more rapidly than do the AM1 values. The results for PBZT are somewhat contrary to the results for PBO in that bending at

the heterocycle is somewhat more energetically favorable than bending at the phenyl ring.

Finally, AM1 calculations were performed to investigate effects of single and multiple protonation on the nitrogen, oxygen, and sulfur atoms of the heterocycle. The heats of formation and bond order of the inter-ring bond are given in the report. For singly protonated PBO and PBZT, the energy is lowest for protonation at the nitrogen atom nearest to the phenyl ring, where some delocalization of charge is possible. Protonation of the oxygen or sulfur atoms results in higher energies, especially for sulfur, than protonation at nitrogen atoms. Multiple protonations led to similar results, in that multiple protonations at nitrogen atoms were favored over cases in which an oxygen or sulfur were involved. Also, single protonation at the oxygen in PBO results in opening of the five-member ring.

To investigate the ring opening problem ab initio calculations using Gaussian 86 were performed to obtain the energies and minimized geometries for model compounds having structures that should respond to protonation in the same way as the heterocycles of interest. Energies were calculated at the RHF/3-21G*, RHF/6-31G**, and MP2//6-31G** levels for the fragments most relevant to PBO ring opening. The RHF/3-21G* level was used to explore other possible structures, as well as for fragments relevant to PBZT.

In order of increasing energies, the AM1 and ab initio methods rank the various structural fragments similarly. However, the ab initio results do not support the likelihood of ring opening.

TASK: 168

TASK TITLE: Nonlinear Optical Materials - Molecular Orbitals

TASK OBJECTIVE: Development of molecular orbital plotting routines/programs.

SCIENTIST: Douglas A. Smith, Ph.D.

DESCRIPTION OF WORK:

The broad objective of the study was the development of molecular orbital plotting routines and programs for use in the theoretical and computational study of the nonlinear optical properties of molecules; specifically, programs capable of plotting two- and three-dimensional orbitals and their projections in both the absence and the presence of electric fields. The molecular orbitals can be generated by semiempirical methods, such as MOPAC 5.0, and ab initio methods, such as Gaussian 8x. In addition, applications of these visualization methods for the understanding of nonlinear optical behavior at the molecular level were made.

Molecular optical properties, specifically α, β, and γ, can be evaluated theoretically by using the derivative method based on energy or dipole moment calculations. The α, β, and γ tensors are the coefficients of the second, third, and fourth order terms, respectively, in an expansion of the energy as a function of the field. The first step in the calculation of the theoretical optical nonlinearity requires a geometry optimization of the molecular structure. This ability is present in MOPAC 5.0.

In order to more effectively carry out the research, there was a need to develop or adapt existing software to provide both two- and three-dimensional graphical output. Specifically, the programs DENSITY and DRAW were modified to run on Apollo DN4500 workstations (or any other Apollo 68030 or 68040 machine) and on any X-windowing terminal by including terminal

drivers and eliminating any hardware dependencies in the main code. The PSI88 program was also ported to UNIX-based operating systems. Any computer that uses GKS (Graphics Kernel System) graphics libraries can be used to run and generate graphical output for a wide variety of terminals and hardcopy devices. PSI88 also has its own PostScript driver, so it can also generate output for any PostScript device.

The use of the keyword POLAR in MOPAC 5.0 was also expanded to allow not only use of the standard or modified POLAR and FFHPOL routines, but also to invoke a new routine, PLRGRF, so that the graphics output is generated both before and after application of an electric field. The FORTRAN code for the modified POLAR and PLRGRF routines is attached to the report. The keyword is now trifunctional. If POLAR is specified it functions as originally written (applies an orientationally averaged electric field of 0.001 au). If POLAR = #.### is supplied then the orientationally averaged electric field has a magnitude of #.###. If POLAR = (X.X,Y.Y,Z.Z) is supplied then the magnitude and direction of the applied electric field are defined by X.X, Y.Y, and Z.Z and no orientational averaging is done.

Once the software was functional, the hypothesis that microscopic optical nonlinearities and molecular orbital distortions can be correlated and can therefore provide an understanding of the origin of nonlinear optical behavior was tested. All transoid, 1,3-trans,5-hexatriene, C_6H_8, was used as a test case. All calculations involved using the ab initio MP2/6-31G* optimized geometry provided by Dr. Douglas S. Dudis of WL/MLBP and performing a MOPAC 5.0 AM1 single point calculation with the keywords POLAR = (X.X,Y.Y,Z.Z) and GRAPH. The results of the calculations (3-D orbital plots) for the HOMO, LUMO, HOMO-1 (second HOMO), and completely bonding molecular orbital in the absence and presence of the electric field are presented in the report.

The observed changes in orbitals can be understood as being dependant upon the combined effects of the applied electric field coupled with the effect of the neighboring orbitals. Thus, it seems there is indeed a simple rationale for the effect of an applied electric field on molecular orbitals. Correlation of this phenomenon with nonlinear optical properties will now require a significant effort on a significant number of experimentally well-characterized molecules.

TASK: 169

TASK TITLE: Polymer Morphology

TASK OBJECTIVE: The structure analysis of ordered polymer fibers.

SCIENTIST: Albert V. Fratini, Ph.D.

DESCRIPTION OF WORK:

During the research the X-ray crystal structures of three thiophene-containing compounds were investigated in order to gain a better understanding of the relationship between molecular structure, crystal packing and the enhanced third-order nonlinear optical λ^3 behavior of thiophene-based monomer and polymer systems. The research complements and supports ongoing computational efforts to predict the effects of structural modifications on the observed nonlinear optical properties of these materials.

The three thiophene compounds which were extensively studied were, 1-nitro-2-(2-thienyl)-ethene or 2-(2-nitroethenyl)thiophene (I), 2-(2-benzothiazolyl)-1-(2-thienyl)ethene (II) and a disubstituted thiophene derivative, $C_{21}H_{16}N_2S$, (III). X-ray data collection was conducted with Mo

K_α radiation (λ = 0.71073 Angstroms) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal, incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained from the least-squares refinement of the setting angles of 14, 18, and 25 reflections for I, II, and III, respectively. The structures were solved using the SHELX direct methods program and refined by full matrix least-squares. Experimental results reported include: cell constants, crystal form, space group, bond distances and angles, torsion angles, atom coordinates, thermal parameters, anisotropic thermal parameters, and least-squares planes. The crystal form/(space group) for I, II, and III was found to be triclinic/(P1 bar), monoclinic/($P2_1/c$), and monoclinic/(acentric Cc), respectively. Also, measurements of omega scans of several intense reflections for compounds I and II indicated poor crystal quality. In addition, for compound II, selected bond distances obtained from the X-ray structure and from molecular orbital calculations (using MOPAC AM1) were compared.

In addition to the extensive X-ray study of the three thiophene compounds discussed above, a comparison of selected bond distances and angles for six related thiophene derivatives was made. The extent of π-electron delocalizaiton observed in the side chains and its effect on the geometries was discussed.

TASK: 171

TASK TITLE: Polymers: "Synthesis of Ordered Polymers"

TASK OBJECTIVE: Synthesis of Ordered Polymers.

SCIENTIST: Dale Hill, Ph.D.

DESCRIPTION OF WORK:

Rigid-rod molecular composites (RRMC) have recently become an important area of research. An RRMC is a composite material consisting of a rigid-rod-like polymer which is dispersed on the molecular level in a flexible-coil-like polymeric matrix. The primary approach taken thus far, for fabricating molecular composites, has been the physical blending of rigid-rod polymers with coil polymers. The problem with this approach is that the rod-like molecules often aggregate in solution. As a result of the incomplete dispersion of the rod polymer on a molecular level, the aspect ratio is greatly reduced. Consequently, the modulus and strength of the materials are greatly reduced.

Recently the first example of a new class of rigid-rod molecular composite polymers which have a specific ionic interaction between the coil matrix and the rigid-rod has been prepared. This ionic rigid-rod molecular composite (IRRMC) was prepared by the physical blending of poly(2-acrylamido-2-methylpropanesulfonic acid) (HAMPS-homopolymer) and poly-p-phenylene benzobisthiazole (PBZT). The ionic interaction is a result of the protonation of PBZT by the sulfonic acid pendant group on the HAMPS- homopolymer. The blend exhibited significantly less aggregation than that of previously prepared blends which had no ionic interaction between the rod and coil matrix.

An important question to address is, can a significant reduction in rod aggregation be achieved by blending a coil component which does have an ionic interaction with the rod polymer but which does not have a high entanglement molecular weight. One of the primary objectives of the present study was to answer this question. A secondary goal was the preparation of an IRRMC in which the coil matrix has a T_g.

The IRRMC system which was studied consisted of alkyl sulfonated polyamide (ASPA) and PBZT, in which the pendant sulfonic acid groups of ASPA can protonate the PBZT. The first step was the preparation of ASPA. This was accomplished by first producing a polyamide polymer intermediate made by the condensation polymerization of isophthaloyl dichloride and 1,3-bis(3-aminophenoxy)benzene. The polyamide polymer has a T_g at 173.9°C and $[\eta]$ = 0.73.

ASPA was synthesized by using two different methods to deprotonate the polyimide polymer followed by reaction of the resulting anion with 1,3-propanesultone. The course of the reactions was monitored using FTIR. The first deprotonation method used the anion of dimethyl sulfoxide (DMSO) as the base (formed by the reaction of DMSO and NaH). This was followed by the addition of the 1,3-propanesultone. After some initial problems extracting all the DMSO were solved, a hygroscopic powder containing no DMSO was obtained.

The second method used to deprotonate the polyamide used the base lithium bis(trimethylsilylamide). This was followed by the addition of the 1,3-propanesultone. The reaction was performed in a mixed solvent system of THF/DMAc/DMSO. LiASPA was obtained in 79.7% yield. It was hygroscopic and soluble in water, methanol, DMSO, and DMF. No T_g was detected by differential scanning calorimetry (DSC) analysis. GPC analysis indicated that the hydrodynamic volume ranged from 3.9×10^6 to 3.8×10^3 and at the peak of the elution curve was 3.9×10^5, compared to polystyrene standard.

An important question that was addressed is the degree of substitution of the polyamide backbone with pendant alkyl sulfonate groups. The polymer could have three types of repeat units depending on the number of amide nitrogen atoms which reacted with alkyl sulfonate in each polymer unit. The extent of substitution reaction at the amide nitrogen was determined by $^{13}C\{^1H\}$ NMR spectroscopy. The results indicated the degree of substitution is $\geq 95\%$.

The ASPA/PBZT blends were made by dissolving LiASPA in methane sulfuric acid (MSA) followed by the addition of PBZT at three different composition ratios. The composition of the resulting blend was determined by FTIR analysis. Three different coagulant solvents were used: water, methanol, and isopropanol. The composition of the polymer resulting from the different initial ratios and various coagulation solvents is shown in the report. The highest percent yield of polymer and percent PBZT composition of the blend occurred for an initial ASPA/PBZT ratio of 30:70 and isopropanol as the coagulant solvent.

TASK: 172

TASK TITLE: Polymers : "Preparation of Electrically Conducting Polybenzazoles"

TASK OBJECTIVE: Synthesis of ordered polymers.

SCIENTIST: Jom Pin J. Chen, Ph.D.

DESCRIPTION OF WORK:

The objective of the research was the synthesis and study of novel rigid-rod conducting polymers, such as polybenzazole (PBZ) and its derivatives, especially polybenzothiazole (PBT) and polybenzoxazole (PBO), and the requisite monomers used in the synthesis. As polymers, polybenzazoles have received an extensive interest for their excellent tensile strength and modulus, chemical and thermal stability, and environmental resistance. A conducting polybenzazole is expected to have similar properties as PBZ, and be able to be used as advanced

conducting materials in aircraft, instrumentation, and civilian industries.

Most polymers which have successfully produced conducting fibers have three basic characteristics: a conjugated π-orbital system (as found in PBZ); an ordered linear structure (PBZ forms an anisotropic solution in polyphosphoric acid, PPA, and can be fabricated into highly ordered fibers by dry-jet wet spinning method); and potential for ionization. In order to gain conductive properties, polybenzazoles must be modified to be capable of ionization. Two approaches for the modification of PBZ were taken in the study: to synthesize self-protonated PBZ, and to synthesize hydroxy-PBZ.

The synthesis and study of self-protonated PBZ, which is PBZ with a pendent containing a strong acidic proton capable of protonating the nitrogen in the polymer backbone, were attempted by sulfonating several compounds similar to PBT. The results of the sulfonation reactions indicated that a regular PBT will not undergo sulfonation since the protons on PBT are deactivated by the electron withdrawing benzothiazole group.

The synthesis and study of hydroxy-PBZ. PBZ with a pendent hydroxy group which can undergo ionization in base by removal of the proton on the hydroxy group, were also investigated. Dihydroxy-PBZ polymers have been studied by other members in the lab and it was found that the strong intramolecular hydrogen bonding of the polymer leads to formation of a pseudo-ladder structure, and chemical rupture of the hydrogen bonding is infeasible. An alternative method to prepare the hydroxy-PBZ-type polymer is the use of biphenyl dicarboxylic acid with a hydroxy group at the meta position as the monomer.

An initial attempt to prepare a dihydroxybiphenyl-PBT (DHBP-PBT) by the polycondensation of a biphenyl diacid monomer and diaminodithiobenzene in PPA instead gave the hydroxy PBT, poly-(4,4'-(1,1'-biphenyl-2,2'-diyl-hydrogen phosphate)benzobisthiazole) (BPP-PBT). While not the desired DHBP-PBT, it may be just as interesting. The phosphoric acid diester is capable of forming strong intermolecular hydrogen bonds, thus perhaps improving the compressive strength of the fiber. Also, BPP-PBT has the potential for ionization (through the acid proton of the phosphoric group), and is likely to be able to convert into a conducting fiber. The acidic hydrogen could also be removed by base to give metal salts or ionic complexes.

In addition, the polycondensation of diaminodithiobenzene with 4,4'-dicarboxy-2,2'-dihydroxybiphenyl and terephthalic acid in the mole ratio, 1:3, 1:1, and 3:1, gave three corresponding copolymers (BPP-TA-PBT) with intrinsic viscosities of 11.0, 11.2, and 10.0 dL/g, respectively. The appearance of the yellow-green copolymer dopes is similar to that of regular PBT.

Finally,poly-(4,4'-(1,1'-biphenyl-2,2'-diyl-hydrogenphosphate)benzobisoxazole)(BPP-PBO)was prepared from dicarboxydihydroxybiphenyl and diaminodihydroxybenzene. The polymer in PPA is brown and transparent. The intrinsic viscosity is 3.97 dL/g (MSA, 30 °C).

TASK: 173

TASK TITLE: Theory of Electromagnetic Waves Propagating in Nonlinear Anisotropic Optical Materials

TASK OBJECTIVE: To gain a greater understanding of the interaction of light and externally applied electric fields with nonlinear optical materials.

SCIENTIST: David S. Moroi, Ph.D.

DESCRIPTION OF WORK:

To gain a greater understanding of the interaction of light and externally applied electric fields with nonlinear anisotropic optical materials, such as barium titanate ($BaTiO_3$) and strontium barium niobate, analytical solutions to Maxwell equations for the electromagnetic fields in various approximations were obtained. The analytical solutions will help interpret the experimental measurements which include electro-optic effects, guided wave optics, and optical phase conjugation.

The equation for the electric field of an electromagnetic wave propagating in a source-free nonlinear anisotropic medium with a dielectric function and a constant permeability was used as the starting point for the derivations. In the present investigation, only the χ^2 terms were considered because they completely dominate the χ^3 terms. Also, the second harmonic of the original electromagnetic wave is generated by the χ^2 terms. In the calculations either the transverse electric mode (TEM 1) or transverse magnetic mode (TMM 1) was used for the original electromagnetic wave of the first harmonic. Likewise, TEM 2 or TMM 2 was used for the second harmonic fields. This approach was taken for two reasons: an experiment which utilizes one of these modes can be more easily designed to test the theory, and the nonlinear electromagnetic wave equations are greatly simplified. Using the slowly varying amplitude approximation (SVAA) and the exact calculations whenever possible, attempts were made to obtain analytical solutions to the Maxwell equations for a nonlinear medium with a 4 mm crystalline symmetry, such as $BaTiO_3$, in which an additional external low frequency AC electric field is applied. The following results were obtained from the calculations:

1. Using TEM 1 and TEM 2:
   The solutions are plane waves, but in general, the dispersion relation for each harmonic field is not consistent.

2. Using TEM 1 and TMM2:
   The exact solutions for the nonlinear wave equations are Jacobi's elliptic functions, provided that the direction of the electric field for the second harmonic is fixed. In general, the solutions in SVAA are also Jacobi's elliptic functions. However, for the case of perfect phase matching they are reduced to the expressions for surface waves. The dispersion relations were not yet obtained.

3. Using TMM 1 and TEM 2:
   No satisfactory solutions existed so far.

4. Using TMM 1 and TMM 2:
   Both the exact solutions and the solutions in SVAA appear to be Jacobi's elliptic functions. The dispersion relations were not yet obtained.

The report concludes by making several recommendations for future work.

TASK: 174

TASK TITLE: Molecular Beam Epitaxy of Strained Layer Superlattices

TASK OBJECTIVE: To develop and apply techniques and methods for the growth of nGaSb on

(001) and (111) GaSb substrates. To investigate the utility of high-energy electron diffraction as a tool to quantify optimum growth conditions.

SCIENTIST: Michael A. Capano, Ph.D.

DESCRIPTION OF WORK:

In the study double-crystal X-ray diffractometry (DXRD) was utilized to determine strain and crystallinity of GaAs epitaxial layers. The initial period of the study involved the setup and testing of the double-crystal X-ray diffractometer. A series of diagnostic tests were run and experimental rocking curves were taken from specimens consisting of a single InGaAs layer on InP (001) and a AlGaAs/GaAs superlattice on GaAs (001).

The major objective of the research was to characterize GaAs layers, grown at 200 °C by Molecular Beam Epitaxy (MBE) on (001) GaAs substrates, using DXRD. The general motivation for the investigation was the development of buffer layers which exhibit superior characteristics in electronic devices. The specific goal was to assess the crystalline quality of these low-temperature GaAs buffer layers as a function of layer thickness and to determine a maximum useful thickness.

Samples of GaAs layers with thickness of 1, 2, 3, 4, 5, and 20 microns were then examined by DXRD. The surface symmetric (004) reflection was initially used to measure the excess As content (through peak splitting) and the crystal quality (through Full-Width at Half-Maximum, FWHM, measurement). Results showed that the excess As content varied slightly with thickness and that the FWHM increased nearly linearly with thickness, indicating that the degradation of crystalline quality scales directly with thickness.

Surface asymmetric (224) reflection rocking curves, using the glancing-incidence configuration for the (224) reflection, were also taken from the specimens. These experiments showed that the 2 micron GaAs layer was not exactly lattice matched as reported in the literature. Experiments using thin-film diffractometry conclusively showed that the top surface layers in the 2- and 20-micron layers were polycrystalline. Thus, the maximum useful thickness appears to be below 2 microns for low-temperature GaAs buffer layers. This finding contradicted previously reported data.

Following the low-temperature GaAs characterization, 12 MBE specimens, including the systems InGaAs/InP, GaAsSb/InP, InAlAs/InP, and AlAsSb/InP, were examined with DXRD to determine the composition of these ternary layers. In all cases, the (004) symmetric reflection was used to measure the perpendicular lattice expansion (compression) which can be directly related to the composition parameter.

Other experimental activities included DXRD characterization of SiGe films on Si as a means of evaluating the performance of the BEDE 150 double-crystal X-ray diffractometer. Three thickness of SiGe layers were examined in both symmetric and asymmetric diffraction geometries in an attempt to characterize lattice parameter changes and defect structure development with increasing strain energy. Satisfactory data were obtained.

In addition, three other experimental studies were undertaken. The first GaSb specimens were grown on the Varian Gen II MBE by Dr. M. Y. Yen (WL/MLBM). Evaluation of the crystalline quality of this specimen involved DXRD measurements of peak shapes. In all cases, the GaSb peak was well defined and indicated good overall crystallinity. Also, an experimental program was begun to study the strain relaxation in InGaAs films on GaAs. As a first test

specimen a single 45 nm thick $In_{0.07}Ga_{0.93}As$ layer on GaAs was analyzed. Finally, TEM studies were begun on the strain relaxation in III-V semiconductor heterostructures.

TASK: 175

TASK TITLE: Experimental Verification of CAST3: "Computer Modeling of 3-D Canned Extrusion Through a Streamlined Die and Upsetting Between Inclined Platens"

TASK OBJECTIVE: To design and conduct experiments for verifying the analytical capabilities of the Air Force finite element code for predicting the three-dimensional solidification behavior of castings.

SCIENTIST: Lohitha Dewasurendra, Ph.D.

DESCRIPTION OF WORK:

The ALPID3D finite element simulation program was used to study the following two models:

1. Round-to-rectangular canned extrusion of G24M alloy with type 304 stainless steel can through a cubic streamlined die. The hole in the lid of the can was neglected and the core (G24M) was assumed to be of the same size as the inner cavity of the can.

   The die was designed to have a rectangular product section of 2:1 aspect ratio with an extrusion ratio of 6:1. The cubic streamlined die was designed by using the integrated extrusion process design package XTRUDER.

   The flow stress data against strain, strain rate and temperature were determined for both the can material (type 304) and the core material G24M. The flow stress distribution of the G24M alloy at various strains is shown in the report.

   Due to symmetry, only the one- quarter model of the die was used in the simulation. The finite element mesh for the die was generated by PATRAN from the die profile created with XTRUDER and by adding the actual die thickness, die land, and the billet container. The simulation was further simplified by prescribing billet pushing velocity at the bottom of the billet instead of pushing it with a ram which may slow down the convergence.

   Hence, this neglects the thermal effects at the bottom of the billet. The deformed mesh, strain contours, temperature contours and strain rate distribution at a stroke of 1.93 inches are shown in the report.

2. The simulation of upsetting of a cylindrical billet with inclined platens was carried out with G24M as the billet material. Due to symmetry introduced by the inclination of the platens, one-quarter of the billet had to be used in the simulation instead of one-eighth model in the case of horizontal platens.

   The initial billet mesh and the final grid distortion are shown in the report. An inner circle of 1.3" in diameter drawn on the top face of the initial billet was deformed to be an ellipse with a major axis of 1.61531" and a minor axis of 1.61530" and the outer circle (2.6" dia.) was deformed to be an ellipse with a major axis of 3.45298" and a minor axis of 3.45288."

The results led to the following conclusions:

1. The can was observed to be thinning out at the top edge of the core. The core could be designed to have a tapered nose in order to avoid a possible fracture of the can at this critical section. The newly developed FEM code ALPID3D was found to be very effective in handling the very complex die contact encountered in this simulation.

2. In the case of upsetting of a cylindrical billet with inclined platens, the circles on the top face of the billet remained almost circles after 50% height reduction and did not deform to be ellipses as seen in the experiment.

3. Another simulation was carried out to see whether any anisotropic friction conditions played any role in this phenomenon. The ALPID3D program was modified to incorporate different friction factors in x and y directions and the simulation did not show any significant difference due to the anisotropic friction condition.

TASK: 176

TASK TITLE: Behavior of Mesophase Pitch in the Fabrication of Graphite Foams

TASK OBJECTIVE: To study and characterize the rheological properties of mesophase pitch when mixed with both bubble nucleative agents and blowing agents and to determine the oxygen stabilization conditions for the foams produced therefrom.

SCIENTIST: Phillip G. Wapner, Ph.D.

DESCRIPTION OF WORK:

The overall goal of the research was twofold: first determine whether it is possible to make carbon foams from mesophase pitch which are uniform and reproducible, and second ascertain whether these foams have any useful physical properties, in particular, whether they have good load-bearing capabilities at high temperatures with low density. The preliminary phase of the project was successfully completed. It involved the design and selection of processing equipment needed for mesophase production and the development of a research technique for screening candidate mesophase preparations prior to actual foam-blowing experiments. In addition a comprehensive review of the literature was performed covering several areas: mesophase manufacture, characterization, and solubility; foam manufacture; general and polymer surface tension measurements; and relevant patents. In order to achieve the overall goals, several subtasks were undertaken:

1. The development of mesophase production capabilities at WL/MLBC. This is necessary because precise control of foam properties requires strict control of feedstock viscosity and surface tension. A reliable, in-house source of mesophase is needed if meaningful conclusions are to be drawn about whether carbon foam production is feasible. A 1.5 gallon Parr high-pressure stirred mesophase batch reactor was selected and delivery was expected by November 1990.

2. The development of mesophase separation capabilities at WL/MLBC. This is necessary because mesophase production is a two-phase process. The polymerized product (mesophase) is not soluble in its monomer (usually isotropic pitch), but instead forms "spheres" which grow larger as reaction proceeds towards completion. Mesophase formed early in the process does not behave the same as that formed later, when both are

separated from unreacted isotropic pitch and compared as 100% mesophase specimens. They appear to have different molecular weights and different molecular weight distributions. Two successful separation processes are solvent extraction and centrifugation. The centrifugation method was chosen and a large capacity (2 liter) Beckman, Inc. centrifuge was procured.

3. The development of mesophase surface tension measurement capabilities at WL/MLBC. This is necessary because of the two physical properties important to foam production, surface tension and viscosity; surface tension is by far more critical.

Concerning item 3, the literature review on foams revealed that the success of the project depended upon a systematic screening of possible mesophase/additive combinations using surface-tension measurements. The criteria are simple, a successful foam-forming candidate must have a lower surface tension than pure mesophase. Thus, candidates should be screened via their surface tension characteristics. The literature search found no information concerning mesophase surface tension measurements. Thus, two techniques were selected for actual experimental work. They are the pendant drop technique and the maximum differential bubble pressure (MDBP) technique. The latter method is preferred because problems with diffusion and evaporation of additives are minimized and it mimics the way foams are actually formed. However, it is more difficult to perform and requires a calibration (i.e., it is a relative technique, not an absolute one). The pendant drop method is absolute, so it will be performed first using pure mesophase (no diffusion or evaporation problems because there are no additives). The results will be used to calibrate the MDBP method and the method will be used in all actual mesophase/additive screening tests. A mesophase surface-tension apparatus was designed and construction was expected to be completed in a follow-on research effort.

TASK: 177

TASK TITLE: Shubnikov-de Haas Effect in Semiconductor Heterostructures

TASK OBJECTIVE: To develop techniques for measurement of carrier concentration, effective mass and scattering time in two-dimensional electron gases.

SCIENTIST: Ikai Lo, Ph.D.

DESCRIPTION OF WORK:

The electron transport properties of two-dimensional electron gas (2DEG) systems have been extensively studied during the last decade. It is well known that the two-dimensional electron mobility at low temperatures in the modulation-doped GaAs/AlGaAs heterostructures is dominated by the ionized-impurity scattering, and depends strongly on the carrier concentration. For GaAs/AlGaAs heterostructures with thin spacer layers, the mobility increases with the carrier concentration of the two-dimensional electron gas. The scattering time increases with carrier concentration primarily because of the increased Fermi wave vector of the electrons. When the electrons populate the second subband, the Hall mobility drops because of the onset of intersubband scattering. The Shubnikov-de Haas (SdH) measurements provide the information to determine the intersubband scattering in these materials.

In the present study, the Shubnikov-de Haas effect on GaAs/AlGaAs heterostructures grown by MOCVD was measured for magnetic fields up to 4.5 T and temperatures from 1.5 to 4.2 K. The effective mass of the two-dimensional electron gas was determined from the temperature

dependence of the SdH amplitude. The carrier concentration of the sample was varied via the persistent photo conductivity (PPC) effect. The results showed that the carrier concentration of the two-dimensional electron gas decreased with the thickness of spacer layer between 50 and 100 Angstroms and the mobility of the electron increased with the thickness for the low carrier concentration samples. It was also found that there is only a single set of SdH oscillations at the lowest carrier concentration. As the carrier concentration increases the SdH oscillations show two periodicities, which indicates the population of the second subband of the two-dimensional electron gas. The electronic properties of these two subbands are under investigation. In addition, for the higher carrier concentration samples the mobility drops slightly with carrier concentration. The SdH measurements on a similar structure grown by MBE were also done for comparison.

TASK: 178

TASK TITLE: Research in Chemical Vapor Deposition in Ceramic Composites

TASK OBJECTIVE: To determine further deposition parameters and techniques for the variation of morphologies and microstructures of CVD SiC and C coatings and extend the techniques to coating of continuous fibers.

SCIENTIST: Jason Guth, Ph.D.

DESCRIPTION OF WORK:

The research conducted was a continuation of Tasks 110 and 146. The emphasis was on the determination of the effect relevant processing parameters have on the final morphologies and microstructures of silicon carbide and carbon coatings grown to various thicknesses by chemical vapor deposition (CVD). Also, the CVD apparatus was modified to obtain enhanced coatings of continuous fibers.

Silicon carbide was deposited from methyltrichlorosilane (MTS) onto 0.125" graphite rods at 1200 °C and 1300 °C (6.6kPa) to simulate deposition on fibers and to enable cross-sectioning for thickness determination. The important results were: the deposition rate increases with increasing MTS input concentration, with the order being close to one, and the deposition rate increases with increasing total flow rate and increasing temperature. Other similar studies have found that the deposition of SiC from MTS is zeroth order at 3.3 kPa and first order at high pressures and that the deposition rate increases with temperature up to about 1400-1450 °C.

One deposition parameter studied that has not been previously investigated is the change in reaction along the length of a substrate. In the current study, the effect of reactant depletion and product generation of subsequent deposition was studied. It was found that the deposit thickness decreases along the length of the rod-shaped substrate. The growth rate at three points along the length of the rod for three different MTS input concentrations is graphically depicted in the report. While the general trend is increasing growth rate with increasing MTS concentrations, the growth rate dependance slows as the distance from the inlet increases.

For carbon coatings, the goal is to reproducibly deposit carbon of any desired thickness onto fibers while simultaneously controlling the surface morphology. Carbon coatings were deposited onto sapphire and Textron SCS-0 silicon carbide fibers using methane at ambient pressure (740-750 torr) and in the temperature range from 1000 to 1300 °C. The thickness and microstructures were examined as a function of process parameters.

Although in principle the thickness can be varied by the rate of pull through the furnace, the actual deposit depends on the microstructure of the substrate. For example, in some experiments with the SCS-0 fiber, it could be pulled fast to obtain a thin coating but the coating was not continuous. There is some limit to the thickness below which the coating is not fully dense and therefore not continuous. This has to do with the nucleation and growth habit of carbon on SiC. In general a smooth surface such as glass or sapphire results in a fairly smooth coating while a rough surface such as polycrystalline SiC results in a rough-surfaced deposit. It appears that on smooth surfaces the coating is basically heteroepitaxial (laminar). In this type of deposit, smooth, continuous layers are put down on top of each other. On rough surfaces such as SCS-0, individual sites nucleate and grow normal to the surface and eventually coalesce by lateral growth, leading to a deposit structure which is inherently less dense. To test this hypothesis, the surface of some SCS-0 fibers were oxidized and then coated. The coating was still fairly rough but did begin to look more like the laminar deposits.

Another phenomenon leading to rough surfaced deposits is the gas phase nucleation of "powder" particles which can stick to the growing surface. When these stick to a laminar type growing deposit, they are simply covered over by sheets of the growing deposit, which leads to a bumpy but smooth surface. In the case of rough deposits on SCS-0 fibers, the two types of deposits (surface and gas phase nucleated) could not be differentiated. In all cases, the surface of the carbon deposit is much rougher than the initial surface of the fiber.

In addition, the temperature of deposition influences the deposit microstructure. Rougher deposits occurred on sapphire fibers at lower temperatures while on SCS-0 fibers they occurred at higher temperatures. One would expect lower temperatures to lead to finer grained deposits. There may also be a transition between polycrystalline and laminar growth. On sapphire surfaces the temperature for this transition seems to be about 1200 °C. No laminar type deposits were found on SCS-0 but no coatings were attempted at 1300 °C. However, at 1200 °C deposition on SCS-0 is even rougher than at 1100 °C and much less continuous.

Finally, approximately 20 feet of continuously carbon-coated sapphire filament was processed and delivered for fabrication of composites. All of the coated filament was very smooth and the coating was fairly adherent unlike most of the previous attempts at coating sapphire.

TASK: 179

TASK TITLE: Fragment Based Ab Initio Calculation Method: "Approach to Geometry Optimization in Molecular Calculations: Application to Solitons in Polyacetylene"

TASK OBJECTIVE: Enhancement and application of computer code.

SCIENTIST: Guru P. Das, Ph.D.

DESCRIPTION OF WORK:

Currently the standard approach to the geometry optimization of large molecular systems consists of two molecular software packages: the Molecular Mechanics programs (MM2, MM3, etc.), and the Molecular Orbital Package (MOPAC). The former uses empirical methods, while the latter uses semiempirical ab initio methods and is believed to be more reliable.

In the present study an algorithm, based on the approximate fragment-based ab initio method (recently proposed by the author and applied for the evaluation of the nonlinear optical (NLO)

properties of some selected systems), was developed for performing geometry optimizations on large molecular systems. In this method the molecular system is considered to consist of fragments which are defined simply as "heavy" atoms (e.g., C, N, O, S, etc.) or their hydrogenated radicals. The important feature of the present fragment concept is the recognition that these fragments arrange themselves in the total system in geometries that undergo only minor changes from molecule to molecule. The fragments within the subsystems (usually the environment of the nearest neighbors of the system under study) are treated in the ab initio framework. For simplicity, the algorithm is described for planar systems only.

The main goal of the study was to supply an approximate ab initio route to geometry optimizations in polyatomic systems without the exorbitant cost that usually accompanies rigorous ab initio calculations. As an illustration of the method, it was applied to several systems: benzene, fluorobenzene, and solitons in polyacetylene. All of the cases selected are planar. The CH radical fragment and the C3H3 subsystem were treated at the ab initio level. A double-zeta Dunning-Huzinaga basis set was used in the calculations.

For benzene two sets of calculations were performed: a full-symmetry calculation in which the geometry optimization was done only with respect to the variation of the bond length (i.e., the whole system undergoes simultaneous identical change in all the bond lengths), and a calculation without symmetry in which ten geometries around $r_1 = r_2 = 2.65$ bohr are used for the C_3H_3 subsystem. The equilibrium bond distance calculated for the full-symmetry and no-symmetry cases are 2.665 and 2.668 bohr, respectively (compared to the experimental value of 2.64 bohr).

For fluorobenzene, only the variation of the CF bond length was considered. Along with C_3H_3, ab initio calculations of the C_3H_2F subsystem were undertaken for three CF bond distances, 2.36, 2.46 and 2.56 bohr. The calculated equilibrium bond distance for CF was found to be 2.44 bohr, in good agreement with the observed value.

Finally, preliminary calculations for polyacetylene solitons consisting of 5, 9, 13, 17, and 21 CH fragments were performed. The parameters for each CH fragment were based on the C_3H_3 subsystem (with the H atoms in the trans-polyacetylene orientation and positions from their respective carbon atoms). Ten geometries were considered about a symmetric geometry of the subsytems. The geometry for all the solitons are presented in the report and all agree semi-quantitatively with those from semiempirical calculations.

In conclusion, the results show this is a highly flexible theoretical model by which geometry optimization can be carried out at various levels of sophistication of the wave function of the system. The model gives an alternative scheme for obtaining the geometry parameters before proceeding to calculate NLO or other properties. Because of the theoretical soundness of the method, absence of adjustable parameters and the possibility of incorporating the electron correlation, the present method may prove to be superior to either the MM or MOPAC techniques for molecular calculations.

TASK: 180

TASK TITLE: NDE Signal Processing Research: "Application of Neural Networks for Classification of Ultrasonic Signals"

TASK OBJECTIVE: Identify and/or develop improved signal processing methods for the quantitative extraction of flaw information from ultrasonic and X-ray CT images. If existing network architectures are not suitable, alternative

algorithms may be explored.

SCIENTIST: T. Raju Damarla, Ph.D.

DESCRIPTION OF WORK:

The task of classifying ultrasonic signals obtained from various materials under test for flaw detection has traditionally fallen on the shoulders of a trained operator. The whole process is tedious and subject to the discretion of the operator working under strenuous conditions. Moreover, the process takes large amounts of time as the data involved are very large.

Artificial neural networks are well suited for tasks, such as the classification of ultrasonic and X-ray CT signals, involving large amounts of data where decisions have to be made regarding the flaw characteristics, flaw sizes, etc. The present study centered on the application of neural networks for the classification of ultrasonic data. Several learning algorithms for neural networks were considered. In particular, Backpropagation and Kohonen's feature extraction algorithm were found to be better suited for ultrasonic data classification.

The impact damaged signals are different from location to location depending on how far the sampled signal is from the actual impact. Since the signals vary in both amplitude and phase, depending on the location of the sample from the center of impact, a single net trained on the data obtained from a single location does not give correct classification of the entire set of data. In order to classify the whole data two networks are needed, one trained on the signals from the center of impact and another trained on signals obtained from the far end of impact.

The Backpropagation learning algorithm is incorporated in a self-learning mode in order that the net would select the necessary training patterns. The network is presented a large set of signals and is allowed to select, on its own, a subset of appropriate training signals which are used to train the neural network to recognize and classify them. The trained network then is used for classification of a set of ultrasonic signals with flaws and without flaws (obtained from material with and without impact damage). It was found that the architecture for the neural network plays an important role. It was also established that when the input set of nodes in a network using backpropagation is large, better results are obtained when the network is partially connected as opposed to the fully connected net.

Classification of 40000 ultrasonic signals in both the time and frequency domains provided excellent results (92% of accurate classification) considering the fact that only 12 signals were used for training both nets. On the whole, classification in the frequency domain provided the best results. Classification by Kohonen's feature extraction algorithm was found to be far inferior compared to classification by the Backpropagation algorithm in self-learning mode, both in the time and frequency domains.

From the results obtained so far it was concluded that neural networks can be successfully employed for classification of ultrasonic signals.

TASK: 181

TASK TITLE: Passivation of GaAs Surfaces

TASK OBJECTIVE: To investigate dry chemical methods to passivate GaAs. It is important to fabricate GaAs surfaces and interfaces with a low number of defect

electronic states. Wet chemical treatments with sulfur compounds have been reported to produce passivated GaAs surfaces.

SCIENTIST: Richard Gilbert, Ph.D., Ambrose-Gormley, Inc.

DESCRIPTION OF WORK:

The necessity to produce limited addition GaAs devices emphasizes the importance of selecting the optimal surface preparation procedure. Various methods have been suggested to modify the electronic properties of GaAs and other semiconductor surfaces. The performance of devices, fabricated from these pretreated materials, that are to be used in sensitive environments where reliability and longevity are of paramount interest will be influenced by the selected pretreatment process. The project goal was to examine the pretreatment options available and characterize the effects of these processes with respect to the GaAs surface before and after treatment.

The interaction of GaAs with various sulfides (NH_2S, Na_2S, and H_2S) in acidic and basic media was examined using SIMS, AES, and current-voltage measurements. A report on previous on-site experimentation (Material Laboratory R&D Status Report Number 19, February 1990) provides specific details of studies done with ammonium hydroxide etched GaAs surfaces. Auger spectra for an acid etched GaAs surface exposed to a sulfide source for a period of time under specific illumination conditions and for a similarly acid etched GaAs surface exposed to an alternate sulfide source under different time and illumination conditions suggest the influence of the chemical treatments on the GaAs surface. In general, the experimental results from the project suggest that the surface sulfide can be dictated by the specific treatments and that the treatments will provide predictable passivation characteristics to the GaAs surface.

TASK: 182

TASK TITLE: QPA In Situ Process Control Research

TASK OBJECTIVE: To implement autonomous state space parameter acquisition of process nonlinearities, including required support elements, for Qualitative Process Automation research.

SCIENTIST: Jeffrey J. Heyob, M.S.

DESCRIPTION OF WORK:

The objective of the research was to implement autonomous state space parameter acquisition of process nonlinearities, including required support elements for Qualitative Process Automation (QPA) research. To this effort the scientist developed a McIntosh-based computer system for interactive qualitative control of the Molecular Beam Epitaxy (MBE) process. An extensible process database structure was designed to support QPA of MBE. The scientist also conducted necessary computer system tests with the MBE process to demonstrate functionality of autonomous Proportional-Integral-Derivative (PID) controller tuning of qualitative MBE process automation.

In addition to the above, the scientist documented current autonomous PID controller tuning research. This is described in the report, "Optimum PID Control Path Mapping," which details research effort for automating the selection of control constants for PID process controls. The

report introduces the PID controller with a brief history of manual PID tuning efforts, where process responses are logged from known disturbances and a set of optimum PID constants are determined from extracted characteristics. Following the introduction, an overview of current industry efforts to automate the PID extraction process are described. The similarities of automated PID tuning methods with manual tuning methods are described along with the limitations accepted by these methods.

Present limitations in automated PID control constant tuning is the basis for the research performed in this task. The manual tuning methods are typically time-consuming and are either fine-tuned to yield optimum process response for specific process events or they are loosely-tuned to yield a compromised response over a wide range of process events. Automatically tuning PID controllers typically tune for a compromised response for a wide range of process events. Optimizing an automatic PID tuner typically yields unacceptable process response for events other than the specific type of process event for which the controller was tuned. Specifying very rigorous constraints on an automatic PID tuner generally increases the tuning failure rate of the controller and necessitates retuning when process conditions need to be changed.

"Optimum PID Control Path Mapping" removes automatic PID tuning limitations by employing a novel technique for extracting physical characteristics about the controlled process. This technique is an extension of "reaction curve" tuning and is used to map a profile of the process characteristics over the operating range of the process. Specific process parameters are extracted at five tuning points distributed across the process operating range. These five parameter points are then filtered by "Least-Squares-Estimation" and fitted to a second-order polynomial to remove any process aberrations. The resulting equations are used to calculate optimum PID constants and then transmit these constants digitally to the controller. The definition of 'optimum' is then determined dynamically by the immediate demand required of the process. Optimum may need to be for a variable magnitude positive or negative step change for the process or may need to be steady-state with optimum disturbance rejection. This ability to redefine the term optimum elevates the PID controller above 'set-it-and-forget-it' and enables it to maintain optimum process control over a wide range of process demands.

TASK: 183

TASK TITLE: Intelligent Systems Improvements to Design/Engineering Systems and Control of Manufacturing

TASK OBJECTIVE: To conduct a literature search in the use of Computer Aided Design/Engineering and develop a bibliography on Intelligent Systems Control of Complex Manufacturing Processes.

SCIENTIST: Alley Butler, M.S.

DESCRIPTION OF WORK:

Over the last 6 years dramatic progress has been made with the application of artificial intelligence (AI) and expert systems techniques to engineering and design problems. The present study consisted of performing a literature search and the report reviews the current trends and techniques. In this regard, an extensive set of tables summarizing published prototypes is provided. Additionally, an informal analysis notes that frame- and rule-based systems are the predominant architecture, and Lisp is the most often used language. Other languages frequently employed include: Prolog, the OPS series (OPS3, OPS5, etc.), and especially constructed languages. The

report further discusses currently used methods for the representation of heuristic knowledge, and it reviews articles on several newer methods of representing heuristic information; notably fuzzy sets, neural networks, and qualitative process theory. More conventional systems which use frames, rules, blackboards, and predicates are also surveyed. Inference methods are examined, and the importance of the various design models is highlighted. Additionally, published information on the elicitation of knowledge for expert systems is discussed, and the superiority of verbal protocol analysis is recognized. Problems which involve interface to CAD systems are also covered, and the need for feature-based systems is emphasized. Finally, the following conclusions regarding future research possibilities were drawn:

1. The majority of existing research work has concentrated on specific domain systems, and the more challenging problem of developing general or generic design systems has not been as actively pursued. Work on general/generic systems for design and engineering begs for increased emphasis within the research community.

2. Most of the systems reported in the literature use a rule-based chaining mechanism, yet this method has not been proved as the best technique by any measure other than sheer number of working systems. Perhaps some type of research which justifies this trend is warranted.

3. The design model for an intelligent system is a critical issue upon which the architecture of an entire system depends. Greater efforts need to be made to improve design models and their ability to provide an efficient structure for system inference.

4. It is apparent that protocol analysis, followed by interview techniques and observation of behavior are the most efficient methods for knowledge elicitation when a knowledge engineer is working directly with an expert designer or engineer. However, when one or both humans are removed from the knowledge acquisition process, the techniques and choices become less clear. Additional efforts to automate the knowledge acquisition process could save many man-hours of work per system; therefore, this area of investigation could prove most promising.

5. It is apparent that the solid modeling systems in existing CAD software do not provide an adequate interface capability for applications with intelligent systems. Therefore, there is a desperate need for the implementation of feature-based design architectures.

6. Finally, there are many different techniques and methods which have been employed by different researchers. A consensus regarding which theories work best under a given set of conditions has yet to emerge. Any work which helps to clarify and classify techniques so that a global set of theories could be defined would be most helpful.

TASK: 184

TASK TITLE: Systems Integration of Concurrent Engineering Systems: The Episodal Associative Memory (EAM)

TASK OBJECTIVE: To accomplish design and implementation of system level integration of communication and control structures for computer-integrated-manufacturing systems, and especially for the Rapid Design System (RDS).

SCIENTIST: Kam Komeyli, M.S.

DESCRIPTION OF WORK:

The Episodal Associative Memory (EAM) is a memory which stores and retrieves designs on the basis of similarity. In storing information, designs are self-organized into separate clusters on the basis of similarity. Clustering is carried out automatically at many levels and an entire design comprising geometry, fabrication plan, inspection plan, and so on is represented by a hierarchical structure of clusters. However, search and retrieval are fast and efficient and informative associations are preserved.

To date, the EAM has been developed mostly in the context of design geometry. The components designed and implemented include the User Interface and Display, the Design Information Translator, the Design Conformation Standardization Function, the Network Switch, and the neural-net functions organize, assign, associate, map-learn and map-activate.

User Interface and Display

A user interface for the EAM was developed and implemented to allow a user to interact directly with the EAM and have access to all that is stored in the EAM. When a user, while working in the FBDE, wishes to access the EAM, the system-level controller (yet to be implemented) switches to the user interface. Unlike the FBDE display, the EAM display allows the user to view two designs at the same time, one being the 'cue' and the other any one of a number of retrieved designs, considered to be similar to the cue. The user interface and display consist of four panes:

1. The Static Display pane is used for displaying a 3-D view of the search cue, the design of current interest. The information (generated in the FBDE environment) used in retrieval might include all or part of the design episode consisting of part geometry and/or other header information (e.g., function, environment, etc.) for the design episode of interest.

2. The Dynamic Display pane is used for displaying a 3-D view of a retrieved design episode.

3. The Episode Data Structure pane is used for displaying the design episode in tree hierarchy format. This provides a view of how clusters are formed and regrouped at different levels in EAM space.

4. The Design Selection List pane is used, once the search request has been given to the EAM, for displaying the names of design episodes that are in the cluster closest to the search cue. The designer can interactively select any design episode from the selection list and view its geometry in the dynamic display.

Design Geometry Data Translator

In the Concept Modeler and the FBDE, designs are described in terms of "mutable parts," in which the format is suitable for maintaining parametric relationships but not suitable for permanent storage. A translator was implemented for transforming FBDE designs into files of features, suitable for permanent storage, and for translating EAM files back into a mutable parts representation.

Design Conformation Standardization Function

A program was developed for reorienting every FBDE design so that when stored, each and

every design episode is in a standard display orientation. For example, the part geometry will be reoriented so that the magnitude of the height dimension (y-axis), is less than that of the width (x-axis) which in turn is less than that of the depth (z-axis). Also, the number of features attached to the front surface will be equal to or greater than those attached to the back face, and the number of features attached to the top face will be equal to or greater than those attached to the bottom face. These rules of orientation will help facilitate storage and retrieval on the basis of similarity.

TASK: 185

TASK TITLE: Constitutive Modeling of Metal Matrix Composites

TASK OBJECTIVE: To develop and implement constitutive models for metal matrix composites for use in finite element computer codes for thermal and mechanical stress analysis.

SCIENTIST: James A. Sherwood, Ph.D. and Marcia J. Boyle, B.S.

DESCRIPTION OF WORK:

During the study an analysis of the stress distribution in a titanium aluminide/SiC fiber composite resulting from thermomechanical loads was initiated. The thermomechanical response was studied using the temperature-dependent bilinear elastoplastic material model employed in the ADINA finite element code and a temperature-dependent viscoplastic constitutive model, which utilizes unified state variable theory including back and drag stress-state variables, and is incorporated into ADINA via a user supplied subroutine (capable of handling both 3-D and 2-D elements).

Several examples were done to demonstrate the usefulness of the models and the finite element codes. The first two examples were used to test the models. The modified ADINA code was used to calculate the tensile response of a TiAl uniaxial bar as a function of temperature and strain. The results show that the saturation stresses and elastic moduli increase with decreasing temperature. Also, the model captures the stress-drop phenomenon that has been experimentally observed to occur at 204 and 316 °C, which is something the bilinear elastoplastic model cannot do.

The second test example modeled the thermomechanical response of a TiAl bar subjected to a thermal fluctuation and restrained from axial displacements (constrained at both ends). The results from both the ADINA and modified ADINA codes demonstrate essentially the same material response during the process. However, during the cooling process the bilinear model exhibits discontinuous stress behavior as a function of temperature.

After completion of the tests a study was conducted using a fully three-dimensional finite element model of a unit cell of the composite to yield a basis for the magnitude of the residual stresses that build up in the matrix during the manufacturing process. The model (F.E. mesh) was generated by the ADINAIN preprocessor and evaluated using both the original and modified ADINA codes. Several simulations were run to validate the model:

1. Investigation of the significance of end effects on the stress response of the composite.

2. Stress-strain response of the composite structure during one thermal cycle using the bilinear material model without contact elements.

3. Stress-strain response of the composite structure during one thermal cycle using the unified constitutive model with contact elements.

4. Simulation of a thermal cyclic load followed by a cyclic mechanical load at constant temperature using both models.

5. Simulation of a thermal cyclic load followed by a constant mechanical load combined with a temperature cycle using the unified constitutive model.

The results of the study led to several conclusions:

1. The results of the thermal cycling of the constrained bar indicates reasonable material behavior for the cooling half of the cycle.

2. The significance of end effects on the stress response of the composite are important. However, the fiber diameter appears to have little influence on how far into the model end effects are important and unit cell width is the probable controlling factor.

3. The results from the three-dimensional study indicated that an axisymmetric model of the composite system is sufficient.

4. Finally, the finite element mesh should be optimized so that improved accuracy can be obtained in any future calculations.

TASK: 186

TASK TITLE: Knowledge Base Development for Qualitative Process Automation

TASK OBJECTIVE: To improve the strategy for controlling voids in autoclave cured advanced composites.

SCIENTIST: Moshe Ungarish, Ph.D.

DESCRIPTION OF WORK:

Dielectric cure monitoring has been widely recognized as a useful method for investigation changes occurring in thermosetting systems during the polymerization process. It provides a means for studying molecular properties in both liquid and solid states, and has been used for analyzing complex resin systems and monitoring cure response under the actual production environment.

Earlier work by the scientist showed that the dielectric dissipation factor exhibits the same characteristic behavior for different families of resin systems subjected to a cure cycle. Typically, following an initial increase, a minimum or plateau occurs, indicative of low viscosity values. Later, another peak in the curve followed by an asymptotic behavior is caused by the cross-linking reaction. From this, valuable information regarding the timing of pressure application, and the kinetics and duration of the cross-linking reaction can be extracted. Thus an optimization procedure, consisting of two stages, combining laboratory experiments with autoclave processing was established for use in devising cure cycles.

Qualitative Process Automation (QPA) developed at the Materials Laboratory (WL/MLBC)

eliminates the need of the two-stage approach and the manual adjustment of the cure cycle, while still using the information accumulated on the behavior of the dielectric curves. Presently, the control strategy used in the autoclave application of QPA has been to compact and cure the laminate as rapidly as possible, without allowing undesirable damage to occur.

In the present study a knowledge base employing the characteristic behavior of the dielectric dissipation factor during a cure cycle, as discussed above, was developed for use with QPA. Pressure is applied in the softening of flow region, when the dissipation factor approaches a minimum. The cross-linking temperature of the final hold can also be inferred from the dissipation factor behavior, in situ, while the cure progresses. Also, heating rates are restricted to a certain range in which the dielectric dissipation factor curves clearly display the peaks necessary for determining the various process states. The process is divided into two plans: Cure and Cooldown. The Cure plan is different from the one in the current knowledge base and contains seven episodes whose goal is to achieve certain states:

1. Achieve-InHeat-Up
2. Achieve-Softening
3. Achieve-Compaction
4. TempHold
5. Achieve-SecHeat-Up
6. Achieve-Rxn
7. Achieve-Crosslinking

In addition to these, three other episodes intended to prevent overtemperature, large gradients, and a runaway reaction are included, as they are in the current knowledge base. Eight process states, used in conjunction with the above seven episodes, are also defined. They are discussed individually along with the relevant episode in detail in the report.

In addition to the above work on QPA, time was devoted to analyzing data obtained in the Materials Laboratory with microdielectric sensors, since the dissipation factor curves used in the QPA were obtained with parallel plate geometry capacitor-type sensors. This was done to determine whether the type of sensor has any influence on the qualitative characteristic behavior of the dielectric measurements. It was found that polarization effects encountered with the low conductivity Micromet microdielectric sensors induced discontinuities in the curves, since default values were recorded for the various dielectric quantities when those effects were felt. Therefore, it was decided to experiment with high conductivity-type microdielectric sensors recently acquired. From the dielectric loss factor and permittivity values the dissipation curve was calculated and compared to the other curves obtained with the capacitor-type sensors and an LCR meter. The results point to similar characteristic behavior of the dissipation curves, independent of the type of sensors used, namely high conductivity microdielectric or capacitor-type sensors.

TASK: 187

TASK TITLE: Molecule Stabilities of Lubricants

TASK OBJECTIVE: To evaluate the relative stabilities of various molecules of possible interest as synthetic polymers.

SCIENTIST: Ella Grace Wilcox, B.S.

DESCRIPTION OF WORK:

The purpose of the research was to evaluate the relative stabilities of various molecules of possible interest as synthetic polymers. The approach involved drawing molecules on a graphics terminal and making calculations on the molecules. The data was correlated with the structures using bond lengths and angles, as well as electron densities and electrostatic potentials associated with particular atoms.

CHEM-X molecular modeling programs were used to analyze the perfluorodioxolane ($C_3F_6O_2$) molecule as a possible synthetic lubricant for aircraft engines. The MOPAC (Molecular Orbital Package) program using MNDO (Modified Neglect of Differential Overlap) and PM_3 (Parametrized $Model_3$) routines was run for all molecular models. Perfluorodioxolane has 44 molecular orbitals, 33 of which are occupied by electrons. Both MNDO and PM_3 calculations were used to obtain graphical pictures of the molecular orbitals and electrostatic potential.

The results of the two semiempirical approaches were analyzed and compared. It was found that the two methods give vastly different graphical pictures of the orbitals, especially the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital). Electrostatic potential maps also showed tremendous differences. Since these are primarily the orbitals at which molecular reactions occur and the electrostatic potential influences reactions, it was concluded that further study is necessary on perfluorodioxolane, perhaps at the ab initio level, before any definite statements about the molecule can be made, or before attempting laboratory synthesis.

TASK: 188

TASK TITLE: Fatigue Crack Propagation in Titanium Alloys: "Fatigue Characterization of Silicon Carbide Fiber-Reinforced Aluminosilicate Glass"

TASK OBJECTIVE: To evaluate the influence of hold time on the fatigue crack propagation rates in titanium alloys at elevated temperatures.

SCIENTIST: P. Andrew Blatt, B.S.

DESCRIPTION OF WORK:

Advanced composite materials capable of operating at high temperatures while experiencing both static and dynamic loading conditions are needed for many high technology applications. Fiber-reinforced ceramic matrix composites (CMC's) are attractive candidates for these systems due to their low density and use of high specific strength fiber reinforcements. This combination permits very high temperature operation while providing higher damage tolerances and less brittle failure modes than monolithic ceramics. Successful design and implementation of these materials will require a thorough understanding of both monotonic fracture and fatigue behavior.

The goal of the preliminary study was to gain a fundamental understanding of the critical fatigue characteristics which control not only overall life, but which also regulate design considerations in ceramic matrix composites. In order to assist in understanding fundamental damage mechanisms and damage accumulation in CMC's under tension-tension fatigue, an experimental program was conducted using the Nicalon™/Aluminosilicate (SiC/1723) glass composite system. Laminae of this material were stacked into a graphite die to obtain unidirectional and cross-ply panels with a fiber volume fraction of approximately 45%. Fatigue testing was performed at various maximum fatigue stress levels in air at room-temperature and at elevated temperatures

using a horizontal servo-hydraulic test station in order to examine the relationships between the matrix microcracking stress level (σM_C), the proportional limit(s) (σ_{PL} or σ_{PL1} and σ_{PL2}) and the fatigue behavior of the material. Strain measurements were made using a quartz-rod high-temperature extensometer. The σ_{MC} and σ_{PL} were determined previously by Zawada and Butkus from monotonic tension tests on unidirectional specimens. In the present study the effects of fatigue stress level, loss in stiffness during cyclic loading, and residual strengths were investigated. Of interest was the amount and severity of damage which would occur at these stress levels. Damage was equated with a loss in modulus of a tested specimen.

Fatigue testing demonstrated that losses in modulus during cyclic loading indicate damage accumulation. The damage can and does occur at stress levels well below the proportional limit of this material. This confirms the trend for the matrix microcracking stress level to be below the proportional limit. Loss of stiffness during cyclic loading below the proportional limit will have serious implications on component design requirements.

The phenomenon of modulus recovery noticed during the latter portions of fatigue tests run at intermediate stresses (between σ_{MC} and σ_{PL}) has several possible explanations, but all are based on damage accumulation and interaction of fatigue-produced debris with the still intact fiber-matrix system.

The results of the experiments at elevated temperatures showed that the initial modulus decreased as the temperature increased. However, the modulus remained nearly constant for the remainder of the specimens life. The only exception being at 800 °C, where the modulus showed significant loss of stiffness up to failure. Also, the fatigue life decreased noticeably as the temperature was increased.

It is still uncertain whether the behavior exhibited by this SiC/1723 ceramic matrix composite system is indicative of behavior of other CMC systems. Future experiments by researchers at the Material Laboratory will address this concern.

TASK: 189

TASK TITLE: Growth on Nonlinear Optical Crystals by Aqueous Solution Growth

TASK OBJECTIVE: To grow and characterize nonlinear optical crystals for frequency conversion.

SCIENTIST: Uma B. Ramabadran, Ph.D.

DESCRIPTION OF WORK:

The aim of the project was to grow and characterize nonlinear optical materials. Specifically, potassium dihydrogen phosphate (KDP) was to be used as a calibration standard to compare with the novel material L-arginine phosphate (LAP).

An experimental setup to grow these nonlinear materials by the temperature reduction method was constructed. A seed crystal of KDP was grown by evaporation at room temperature and then subjected to further growth by temperature reduction. This provided starting crystals for growing large KDP. Solubility curves were measured as a function of temperature and the data obtained compared to that obtained previously. The crystals were also tested for second harmonic generation using a pulsed Nd-YAG laser and exhibited frequency doubling.

A systematic literature search to obtain complete available information on LAP was also undertaken. LAP was then manufactured by reacting L-arginine with phosphoric acid. Seed crystals were grown and then subjected to further growth by temperature reduction. The LAP crystals demonstrated frequency doubling with both the Nd-YAG and cw Ti-Sapphire lasers.

Several other tasks were also undertaken. A seed crystal of copper-doped KDP was grown by evaporation for future characterization, and seeds of Fe^{+2} and Fe^{+3} doped-KDP were grown to investigate the possibility of generating an artificially fabricated photorefractive material.

An effort was made to fabricate a new nonlinear material, triallyl thiourea copper chloride. This material has been generated only in powder form as yet. It was also demonstrated that it is possible to generate a cw SHG in a crystal of lithium triborate using the Ti-Sapphire laser.

In addition, a Mach-Zehnder interferometer was assembled and the electro-optic coefficient of strontium barium titanate was measured. This setup will also be used to measure the electro-optic coefficients of the newly fabricated crystals.

In summary, all the necessary materials to grow LAP are ready and large-size crystal growth was begun. In the future, doped LAP crystals will also be grown and their properties investigated.

TASK: 190

TASK TITLE: Polymers

TASK OBJECTIVE: To synthesize novel aromatic-heterocyclic polymers for nonlinear optical applications.

SCIENTIST: B. Robert McKellar, Ph.D.

DESCRIPTION OF WORK:

The study focused on the problem of improving optical quality and processibility of polymers with nonlinear activity by working toward synthesizing block and graft copolymers containing thiophene and benzobisthiazole aromatic heterocycles. The block-copolymer approach included a TPBT block and a 6F-PBO block. The initial task was the preparation of the monomers necessary for the synthesis of TPBT and 6F-PBO. TPBT and 6F-PBO homopolymers of differing molecular weights were then synthesized by varying the proportions of certain monomer.

In the block-copolymer method two different approaches were employed to synthesize block copolymers. The first approach involved reacting the two homopolymers. The second approach involved reacting thioplene poly-p-phenylene benzobisthiazole (TPBT) homopolymer with 6F-PBO monomers. It has not yet been conclusively determined whether the products of the reactions are copolymers or physical blends.

The graft copolymer approach involves the synthesis of a thiophene PBT (TPBT) with aryl ether pendant groups on the thiophene ring. The phenyl ring of the pendant would provide a graft site for the formation of a graft copolymer with a thermoplastic matrix such as with a poly ether ketone (PEK). In addition, the aryl ether pendants would serve as electron donating substituents, which have been shown to enhance the χ^3 nonlinear optical (NLO) response in model compounds. Preliminary work on this approach was accomplished by synthesizing the following thiophene containing monomers containing appropriate aryl ether pendant groups:

3-(2,6-dimethylphenoxy)thiophene, 3-(2,6-dimethylphenylthio)thiophene, 3-(2,6-dimethylphenylthio)thiophene-2,5-dicarboxylic acid, 3-(2,6-dimethylphenylthio)thiophene-2,5-dicarbonyl chloride. Either the carboxylic acid or carbonyl chloride are suitable monomers for the synthesis of a TPBT with aryl thioether pendant groups on the thiophene ring.

The structures and properties of the monomers and polymers synthesized in the study were analyzed using several chemical and spectroscopic methods: TGA/MS, differential scanning calorimetry (DSC/TMA), GC, TLC, NMR, FTIR, and MS. Molecular weights, viscosities and T_g values are reported.

TASK: 191

TASK TITLE: Research in Chemical Vapor Deposition in Ceramic Composites

TASK OBJECTIVE: To determine the variation in interfacial shear properties with coating thickness.

SCIENTIST: Jason Guth, Ph.D.

DESCRIPTION OF WORK:

The research conducted was a continuation of Tasks 110 and 146. The emphasis of the research was the study of silicon carbide and carbon coatings grown to various thicknesses by chemical vapor deposition (CVD). The coatings were characterized using appropriate microscopic techniques (such as SEM).

Silicon carbide deposition was studied to aid in a model development effort. Several deposition experiments using different periods of time were performed at 1300 °Cand 150 torr (20 kPa) using a 3 mm OD graphite rod as the substrate. The resulting deposits were characterized for the thickness as a function of position along the reactor and time.

Carbon deposition on Textron SCS-0 silicon carbide fibers was studied using methane, acetylene, and propane as the carbon source reagents. The results obtained were compared to similar experiments using sapphire fibers as the substrate (Task 146). In general the carbon deposits formed on SiC fibers are much rougher than those formed on either sapphire or fused quartz. Nucleation appears to be more difficult on the SiC substrates leading to rougher, more porous deposits, while the deposits on sapphire and fused quartz are much more laminar or heteroepitaxial. In attempting to deposit thin coatings on the SiC fibers, only small islands and not continuous films were formed.

Use of acetylene as the source reagent leads to homogeneous nucleation in the gas phase and no or tree-like deposits on the fiber. Propane also leads to tree-like deposits at high concentrations. Deposits produced using lower propane concentrations appear to be more uniform like those deposited from methane. However, these samples were not yet examined using SEM so no results could be given as to the exact nature of the deposits. One possible benefit of using propane in place of methane is that deposition temperatures can be reduced. This may be important for producing carbon coatings on sapphire filaments where the difference in thermal expansion results in spalling of the coating. Acetylene may also produce uniform coatings at temperatures lower than the 1000 °C experiments studied during the research.

TASK: 192

TASK TITLE: Acoustic Emission Techniques in Materials Characterization

TASK OBJECTIVE: To use acoustic emission (AE) techniques to characterize complex materials systems such as titanium aluminides, metal matrix composites, and ceramic matrix composites in support of research activities in the WL Materials Directorate Metals and Ceramics Division. Hardware and software systems for novel AE testing techniques will be set up.

SCIENTIST: Itzhak Roman, Ph.D.

DESCRIPTION OF WORK:

The research activity conducted by the scientist centered on two main areas. First, preliminary experimentation aimed at developing capabilities of characterizing interfacial properties of advanced Metal Matrix Composites (MMC's) was carried out. Monofilament composite samples made of SCS-6 fibers in an σ_2 (Ti-24Al-11Nb) matrix were subjected to fiber push-out tests and the resulting samples were examined using optical and SEM metallography and fractography. The results of measured interfacial shear strength correlated well with reported values in the literature. The fractographic and metallographic studies indicated fiber-matrix separation occurred either between the two carbon-rich outer layers of the fiber and the matrix or within the carbon-rich outer layers themselves. SEM micrographs also showed some cracking of the C layers and it is relatively smooth, but its topography has some shallow circumferential markings and localized dimples typical of the CVD process.

In addition to the above studies, preparatory actions were taken to facilitate the employment of a new technique, Acoustic Emission (AE) testing, in the Metals and Ceramics Division. These included designing and preparation of test specimens (monofilament tensile, monolithic tensile and compact tension samples), a tension test fixture (which enables the attachment of an AE piezoelectric transducer to the flat edge of round tensile samples), and auxiliary equipment.

TASK: 194

TASK TITLE: Intelligent Systems Improvements to Design/Engineering Systems

TASK OBJECTIVE: To examine applications of Intelligent System techniques to the engineering problem which involves the Layout of Process Manufacturing Facilities.

SCIENTIST: Alley Butler, M.S.

DESCRIPTION OF WORK:

System reliability is an important parameter in the design of aircraft, spacecraft, manufacturing facilities, and modern utility systems. Over the last several decades researchers have used many different methods to determine complex system reliability. The goal of the project was to show that a symbolic logic intelligent system can be effectively used to assist with the analysis of complex, multicomponent systems. The present research used new and novel techniques which are based on artificial intelligence and expert systems to determine system reliability. The method is based on a symbolic logic prototype system which provides symbolic representation for overall system reliability when there is a single input and single output. It uses Moskawitz's

factoring theorem on a recursive basis to repeatedly reduce complex systems/subsystems to simpler systems. Eventually, these simpler systems are further reduced into easily resolved series-parallel arrangements.

This symbolic logic prototype system uses a heuristic "hill climbing" search algorithm which seeks to identify the pivotal or complex component. Once this pivotal component is selected, additional procedures which are also heuristically based are used to symbolically recognize other components within the resulting subgraphs which are made superfluous by the selection of the pivot component. These superfluous components are removed, and the simplification process is allowed to continue on a recursive basis. Once further recursive analysis is not needed, additional rules are employed to reduce the result to a system recognizable form in terms of series-parallel components. Finally, a "symbolic processor" is used to convert this recognized form into a symbolic sum of products equation representing the overall system.

This symbolic logic system was developed in Prolog for convenience as a research tool, but it is believed that Lisp, OPS5, Forth, or any other commonly used intelligent system language could be employed. As a prototype, no attempt to optimize memory or processing speed was made; however, these issues should be a major consideration for any continuing research effort now that the viability of this technique has been demonstrated.

The development of this symbolic logic system has provided insight into both the development of intelligent systems, and into the design and analysis of complex systems for reliability. The following specific conclusions and recommendations on many separate issues were provided:

1. The symbolic logic system was demonstrated on only a limited number of cases. Additional test cases have been collected from the literature and should be used to test the robustness of the system.

2. The "hill climbing" search mechanism does operate effectively to reach a solution; however, it also can provide arbitrary selections of the pivot when two different search paths have the same indices. Therefore, an initial knowledge elicitation session was conducted with a reliability engineer and the effort to improve and expand the heuristics will continue when the opportunity becomes available.

3. It is recommended that if the work is extended, that the lessons learned in this work be used in a new system which is developed "from scratch." This would allow the maximum optimization of the system.

4. Finally, the research did prove that a symbolic logic intelligent system can be effectively used to assist with the analysis of complex, multicomponent systems.

TASK: 195

TASK TITLE: Episodal Associative Memory (EAM)

TASK OBJECTIVE: To conduct research and evaluation of the EAM for use in the Rapid Design System.

SCIENTIST: Kam Komeyli, M.S.

DESCRIPTION OF WORK:

The Episodal Associative Memory (EAM) is a memory which stores and retrieves designs on the basis of similarity. In storing information, designs are self-organized into separate clusters on the basis of similarity. Clustering is carried out automatically at many levels and an entire design comprising geometry, fabrication plan, inspection plan, and so on is represented by a hierarchical structure of clusters. However, search and retrieval are fast and efficient and informative associations are preserved.

The present report is a supplement to a report submitted for task 184 and describes the progress made on the Episodal Associative Memory (EAM) during the study:

1. A user interface was modified to incorporate the standardization of a part so that it can show the original design and its standard orientation. The interface also incorporates the generation of a pattern that can be fed into the NNET software for processing.

2. The NNET software was loaded and linked to the Wisdom Systems Concept Modeler™. The necessary routines and links for direct calling of the NNET subroutines which are in C from Lucid Common Lisp are in the construction process.

3. Research on the standardization of the features within the design is nearly completed. The standardized features are now through hole, through slot, and blind hole.

TASK: 197

TASK TITLE: Synthesis of Spiropyrans and other Polyene Molecular Complexes for Nonlinear Optical Properties

TASK OBJECTIVE: To investigate several entirely new classes of potentially optically active compounds. In this investigation an attempt will be made to synthesize new compounds and to modify existing compounds and to correlate their chemical structure and their optical characteristics.

SCIENTIST: L.V. Natarajan, Ph.D.

DESCRIPTION OF WORK:

A number of organometallic (Lanthanide crown ether and related compounds), organic (anthraquinones and diphenyl polyenes), and bioorganic (retinols and polypeptides) molecules were synthesized and characterized (using absorption and luminescence techniques) as part of the task of developing efficient nonlinear optical materials for laser hardening purposes. The nonlinear optical response of the molecules was determined by power in and power out experiments, using a Nd:Yag laser at 532 nm.

The biologically significant class of polyenes, namely β-carotene, retinols (trans-retinol, trans-retinal, and trans-retinoic acid), and diphenyl polyenes were found to be efficient nonresonant optical limiters at 532 and 1064 nm. The diphenyl polyenes were very impressive when compared to CS_2. The onset of nonlinearity was at much lower fluences and the optical density changes were large. The mechanism of nonlinear behavior leading to optical limiting in the diphenyl polyenes was characterized as "self focusing." A comparison of threshold values for nonlinearity for different polyenes at the same concentration showed that the best nonlinear behavior in terms of low threshold value is shown by diphenyl octatetraene. It was also shown that there is a relationship between the number of conjugated double bonds and optical limiting

(the efficiency increases up to about 10 double bonds and then levels off). Another interesting result observed was that the nonlinear behavior, as seen from optical limiting, of cis-stilbene was much less efficient when compared to its molecular isomer, trans-stilbene.

Another class of bioorganic molecules studied were polypeptides. Poly-benzyl-glutamate was doped with 6-nitrospiropyran and tested for second harmonic generation, but showed only very weak response. The results suggested that they need to be aligned by applying a DC field to get high values.

Also, an interesting class of nonlinear optical chromophore linked polypeptide was synthesized. Synthesis of polyglutamic acid modified with 1-(β-hydroxyethyl)-3,3-dimethyl-6-nitrospiro(indoline-2,-2[2H-1]benzopyran) was made and characterization was done by gel permeation chromatography. An interesting change from a helical conformation to a random coil conformation was noted on irradiating the photochromic polypeptide with light. This is an interesting example of a photochemically triggered reversible conformational change in a biopolymer.

In addition one other class of organic molecules, namely liquid crystal and liquid crystal polymers, was studied for nonlinear optical response. The liquid crystal E7 showed a very low nonlinear threshold when the direction of alignment was parallel to the laser polarization. A much higher value was observed when the alignment was perpendicular. Also, the optical density changes with E7 were very sharp and very large.

Finally, a liquid crystalline oligomer containing a photochromic unit of allyloxy-benzoyl nitrospiropyran was synthesized. The resulting product was both photochromic and cholesteric. The nonlinear optical (NLO) behavior is still under investigation.

The scientist points out the need for carrying out more measurements using different techniques, like degenerate four-wave mixing, electric field-induced second-harmonic generation, etc., to evaluate the NLO response of the materials.

TASK: 199

TASK TITLE: QPA In Situ Process Control Research

TASK OBJECTIVE: To implement autonomous state space parameter acquisition of process nonlinearities, including required support elements, for Qualitative Process Automation research.

SCIENTIST: Jeffrey J. Heyob, M.S.

DESCRIPTION OF WORK:

The objective of the research was to implement autonomous state space parameter acquisition of process nonlinearities, including required support elements for Qualitative Process Automation (QPA) research. To this effort the scientist developed a McIntosh-based computer system for interactive qualitative control of the Molecular Beam Epitaxy (MBE) process. An extensible process database structure was designed to support QPA of MBE. The scientist also conducted necessary computer system tests with the MBE process to demonstrate functionality of autonomous Proportional-Integral-Derivative (PID) controller tuning of qualitative MBE process automation.

In addition to the above, the scientist documented current autonomous PID controller tuning research. This is described in the report "Optimum PID Control Path Mapping" which details research effort for automating the selection of control constants for PID process controls. The report introduces the PID controller with a brief history of manual PID tuning efforts, where process responses are logged from known disturbances and a set of optimum PID constants are determined from extracted characteristics. Following the introduction, an overview of current industry efforts to automate the PID extraction process is described. The similarities of automated PID tuning methods with manual tuning methods are described along with the limitations accepted by these methods.

Present limitations in automated PID control constant tuning is the basis for the research performed in this task. The manual tuning methods are typically time-consuming and are either fine-tuned to yield optimum process response for specific process events or they are loosely tuned to yield a compromised response over a wide range of process events. Automatically tuning PID controllers typically tune for a compromised response for a wide range of process events. Optimizing an automatic PID tuner typically yields unacceptable process response for events other than the specific type of process event for which the controller was tuned. Specifying very rigorous constraints on an automatic PID tuner generally increases the tuning failure rate of the controller and necessitates retuning when process conditions need to be changed.

"Optimum PID Control Path Mapping" removes automatic PID tuning limitations by employing a novel technique for extracting physical characteristics about the controlled process. This technique is an extension of "reaction curve" tuning and is used to map a profile of the process characteristics over the operating range of the process. Specific process parameters are extracted at five tuning points distributed across the process operating range. These five parameter points are then filtered by "Least-Squares-Estimation" and fitted to a second-order polynomial to remove any process aberrations. The resulting equations are used to calculate optimum PID constants and then transmit these constants digitally to the controller. The definition of 'optimum' is then determined dynamically by the immediate demand required of the process. Optimum may need to be for a variable magnitude positive or negative step change for the process or may need to be steady-state with optimum disturbance rejection. This ability to redefine the term optimum elevates the PID controller above 'set-it-and-forget-it' and enables it to maintain optimum process control over a wide range of process demands.

TASK: 200

TASK TITLE: Behavior of Mesophase Pitch in the Fabrication of Graphite Foams

TASK OBJECTIVE: To study and characterize the rheological properties of mesophase pitch when mixed with both bubble nucleative agents and blowing agents and to determine the oxygen stabilization conditions for the foams produced therefrom.

SCIENTIST: Phillip G. Wapner, Ph.D.

DESCRIPTION OF WORK:

The overall goal of the research was twofold: first, determine whether it is possible to make carbon foams from mesophase pitch which are uniform and reproducible; and second, ascertain whether these foams have any useful physical properties, in particular, whether they have good load bearing capabilities at high temperatures with low density. During the study the second

phase of the project was successfully completed. It involved the setup of processing equipment needed for mesophase production and the development of a research technique for screening candidate mesophase preparations prior to actual foam-blowing experiments. In order to achieve the overall goals, several subtasks were formulated:

1. The development of mesophase production capabilities at WL/MLBC. This is necessary because precise control of foam properties requires strict control of feedstock viscosity and surface tension. However, the manufacturing conditions used by most producers of mesophase are proprietary so little information concerning its manufacture and properties is provided. Thus, a reliable, in-house source of mesophase is needed if meaningful conclusions are to be drawn about whether carbon foam production is feasible. A 1.5 gallon Parr high-pressure stirred mesophase batch reactor was obtained and used for this purpose.

2. The development of mesophase separation capabilities at WL/MLBC. This is necessary because mesophase production is a two-phase process. The polymerized product (mesophase) is not soluble in its monomer (usually isotropic pitch), but instead forms "spheres" which grow larger as reaction proceeds towards completion. Mesophase formed early in the process does not behave the same as that formed later, when both are separated from unreacted isotropic pitch and compared as 100% mesophase specimens. They appear to have different molecular weights and different molecular weight distributions. Two successful separation processes are solvent extraction and centrifugation. The centrifugation method using a large capacity (2 liter) Beckman, Inc. centrifuge was used for the separation process.

3. The development of mesophase surface tension measurement capabilities at WL/MLBC. This is necessary because of the two physical properties important to foam production, surface tension and viscosity, surface tension is by far more critical.

The main work performed dealt with the study of the surface tension of mesophase pitch. A review of the literature concerning surface tension measurements on mesophase pitch unfortunately found nothing. Thus, two techniques were selected for actual experimental work. They are the pendant drop technique and the maximum differential bubble pressure (MDBP) technique. The latter method is preferred because problems with diffusion and evaporation of additives are minimized and it mimics the way foams are actually formed. However, it is more difficult to perform and requires a calibration (i.e., it is a relative technique, not an absolute one). The pendant drop method is absolute, so an apparatus was designed and constructed using this technique to make precise surface tension measurements at temperatures up to 410 °C. The results will be used to calibrate the MDBP method and the method will be used in all actual mesophase/additive screening tests.

Measurements were made using pure mesophase (no diffusion or evaporation problems because there are no additives). The results showed that mesophase pitch has a surface tension in the range of 30 to 40 dynes/cm, depending on temperature, and is quite sensitive to oxidation, especially when the temperature is above 360 °C.

TASK: 201

TASK TITLE: Deformation Processing Studies of TiAl

TASK OBJECTIVE: To determine the optimum processing conditions for rolling and extruding

various gamma titanium aluminide alloys.

SCIENTIST: S. L. Semiatin, Ph.D., Battelle Memorial Institute

DESCRIPTION OF WORK:

The research focussed on essentially four areas: determination of grain growth kinetics during homogenization and breakdown of near gamma titanium aluminides, analysis of fracture behavior during isothermal forging, development of a novel extrusion process for intermetallics, and outlining of possible FY91 projects to be conducted in the WL Materials Directorate Metals and Ceramics Division. These are summarized below.

1. Homogenization/breakdown of near gamma titanium aluminides:

   The work under this subtask dealt with grain growth kinetics during homogenization of ingot metallurgy near-gamma titanium aluminides and subsequent breakdown of the coarse grain structure produced during homogenization. With respect to the former effort, wrought samples of Ti-46.6Al-2.7Nb-0.3Ta (at%) were heat treated at T_α + 10°C and T_α + 40°C (where T = the alpha transus temperature) for times ranging from 0.5 to 16 hours, and prepared for metallographic analysis. This work is still underway. The final grain growth results for the Ti-Al-Nb-Ta alloy will be compared to those obtained previously for the cast alloy Ti-48.4Al-1.9Nb-1.4Mn (at%).

   Preliminary work on the breakdown of the coarse grain structure developed during homogenization of near-gamma titanium aluminides was completed and summarized in the paper "Homogenization of Ingot Metallurgy Near-Gamma Titanium Aluminides" presented at the Materials Research Symposium on High Temperature Ordered Intermetallic Alloys and attached to this report. The elimination of microsegregation and subsequent breakdown of the lamellar structure in near-gamma titanium aluminides was investigated through a series of high-temperature homogenization heat treatments and isothermal hot-compression tests. The homogenization heat treatment studies revealed that microsegregation could be eliminated after approximately 5 hours or 1-1/2 hours at temperatures of 15°C or 40°C, respectively, above the transus in the single phase alpha field. Subsequent attempts to breakdown the coarse prior-alpha grain, lamellar structure were successful at low strain rates ($\sim 10^{-3}$ s^{-1}) and temperatures low in the alpha + gamma phase field, but led to wedge-cracking and gross fracture at high strain rates (~ 1 s^{-1}) high in the alpha + gamma phase field. Subsequent annealing treatments to globularize the hot-worked structure in order to obtain a uniform, fine, and stable grain structure were also identified.

2. Analysis of fracture behavior during isothermal forging of the gamma titanium aluminide G2:

   The fracture behavior of a cast gamma titanium aluminide alloy (Ti-49.5Al-2.5Nb-1.1Mn) during deformation processing was investigated using hot-tension testing and isothermal-forging experiments. In uniaxial tension, fracture ductility increased with an increase in the test temperature and a decrease in the imposed strain rate. During previously conducted open-die forging of this alloy under isothermal conditions, it was found that tensile stresses generated due to frictional effects and the associated inhomogeneous plastic deformation (i.e., barreling during pancaking) led to free-surface fracture via intergranular cracking. These failure observations were successfully predicted using data from uniaxial tension tests, finite element simulations of the isothermal forging

process, and the tensile-damage criterion originally developed by Cockcroft and Latham for predicting ductile fracture during cold working of metals. This work was summarized in the paper "Tensile Fracture Behavior of a Cast Gamma Titanium Aluminide" also presented at the symposium.

3. Development of a novel extrusion process for intermetallics:

   One of the major problems in the design of cans for extrusion of high temperature intermetallics lies in the mismatch between the flow stresses of the workpiece and can materials. Because of this, efforts were initiated to develop a process (the so-called "bican" technique) in which the can and workpiece are heated separately (to different temperatures) prior to extrusion, assembled quickly, and then extruded. The specific temperatures for the individual components are selected to provide approximately equivalent flow stresses.

TASK: 202

TASK TITLE: Molecular Beam Epitaxy of Strained Layer Superlattices

TASK OBJECTIVE: To develop, apply, and support techniques for the growth of InGaSb on (001) and (111) GaSb substrates. To investigate the utility of high-energy electron diffraction as a tool to quantify optimum growth conditions.

SCIENTIST: Michael A. Capano, Ph.D.

DESCRIPTION OF WORK:

The major objective of the research was the study of the simultaneous, Molecular Beam Epitaxy (MBE) growth of GaAs layers on GaAs (001) and GaAs (111)B substrates at low temperatures. The general motivation for the investigation was the development of buffer layers which exhibit superior characteristics in electronic devices. The specific goal was to assess the crystalline quality of these low-temperature GaAs buffer layers as a function of layer thickness and to better understand the mechanisms of low temperature growth.

The focus of the study was to characterize the crystallinity of GaAs layers, grown at 200 °C and 250 °C to a thickness of 3 microns on both (001) and (111) oriented substrates and a 3 micron layer grown on GaAs (111)B at 300 °C, using a double-crystal X-ray diffractometer (DXRD) and a wide-angle diffractometer (WAD) with a rotating specimen stage. Nondispersive, surface symmetric rocking curves were measured using the (004) reflection for the (001) specimens and the (333) reflection for the (111) specimens. The DXRD and WAD results showed the presence of a single-crystalline epitaxial layer, with a growth-temperature-dependent excess As concentration, on the (001) substrates. On the (111) substrates, only a polycrystalline layer was observed. The results are best explained by a growth-surface roughening model. A complete description of the results and a discussion are presented in the paper "X-ray Analysis of Low-Temperature MBE-Grown GaAs Layers on GaAs(001) and GaAs(111)B Surfaces."

In addition, other experimental studies were undertaken. Continued examination of GaSb specimens grown on the Varian Gen II MBE by Dr. M. Y. Yen (WL/MLBM) was performed. Evaluation of the crystalline quality of this specimen involved DXRD measurements of peak shapes. In all cases, the GaSb peak was well defined and indicated good overall crystallinity. Also, DXRD experiments of SiC films on Si were performed to assess the quality of the deposited SiC

layer. To this point, there was no success in finding a diffracted signal from these layers.

Finally, DXRD characterization of two InGaAs layers on InP (001) substrates grown by Kurt Eyink of ML showed that these layers were grown with nearly the lattice-matched composition, as required for his research.

TASK: 203

TASK TITLE: Synthesis of Ordered Polymers

TASK OBJECTIVE: Investigate the synthesis of rod-like polymers expected to exhibit strong conductive and semiconductive behavior.

SCIENTIST: Dale Hill, Ph.D.

DESCRIPTION OF WORK:

Rigid-rod molecular composites (RRMC) have recently become an important area of research. An RRMC is a composite material consisting of rigid-rod-like polymer which is dispersed on the molecular level in a flexible-coil-like polymeric matrix. A true molecular composite has higher modulus and greater strength than a conventional macroscopic composite because of the high aspect ratio (length/diameter) which is achieved from a single rigid-rod polymer molecule. The primary approach taken thus far, for fabricating molecular composites, has been the physical blending of rigid-rod polymers with coil polymers. The problem with this approach is that the rod-like molecules often aggregate in solution. As a result of the incomplete dispersion of the rod polymer on a molecular level, the aspect ratio is greatly reduced. Consequently, the modulus and strength of the materials are greatly reduced.

Blends of poly-(p-phenylene benzobisthiazole) (PBZT) and a polyamide with pendants containing sulfonic acid groups (ASPA) were prepared. The blends were made in order to determine if a significant reduction in rod aggregation could be achieved by blending a coil component which does have an ionic interaction with the rod polymer, but which does not have a high entanglement molecular weight. It was determined that a high entanglement molecular weight was necessary to prevent the loss of significant amounts of the coil polymer during coagulation. Further studies are in progress to determine the amount of phase separation in the coagulated blends.

TASK: 204

TASK TITLE: Polymers: "Preparation of Electrically Conducting Poly(benzazole)s"

TASK OBJECTIVE: Synthesis of ordered polymers

SCIENTIST: Kevin L. Cooper, Ph.D.

DESCRIPTION OF WORK:

The activation energy of conjugated π-electron containing polymers is greater than 1.5 eV. Hence, these materials act as insulators ($< 10^{-10}$ S/cm). However, these macromolecules have a high electron affinity and a low ionization potential and, therefore, can be readily oxidized or

reduced by ionizing agents. This leads to an electrically conductive or semiconductive polymer.

From a polymer chemist's point of view, polymers which have been successfully fabricated into conducting fibers or films generally have three basic characteristics: a conjugated π-orbital system, an ordered linear structure, and a low ionization potential. Poly(benzazole)s, aromatic rigid-rod heterocyclic polymers, have a conjugated π-orbital system and can be fabricated into highly ordered fibers by dry jet-wet spinning of anisotropic solutions of polyphosphoric acid. Consequently, in order to create a conductive material, poly(benzazole)s must be modified to induce ionization. Therefore, the effort in the study included the synthesis of the poly(benzazole)s and the requisite monomers, as well as a study of polycondensation conditions.

One system which has been investigated was the compound dihydroxy poly(benzothiazole) (I), which contains a six-membered cyclic phosphate ester ring. This polymer can undergo ionization by removal of a proton from the cyclic phosphate ester. These materials are highly thermoxidatively stable, are potentially ionizable, and resist hydrolysis from a variety of strong acids and bases. The conductive and mechanical properties are currently under investigation.

In the present study the synthesis or rod-like polymers which would be expected to exhibit strong conductive and semiconductive behavior was investigated. This included the synthesis of the requisite monomers as well as study of polycondensation conditions. FTIR and elemental analysis were used to identify resulting compounds.

A method for the synthesis of arylene dihydroxy, dicarboxylic acid monomers was utilized in the preparation of several monomers for use as starting blocks of in-situ forming intrinsic conductive organic polymeric fibers. The monomer, 1,5-dihydroxy naphthalene-2,6-dicarboxylic acid, was successfully synthesized via the bis-carboxylation of 1,5-dihydroxy naphthalene utilizing a magnesium catalyst under high temperature and pressure. The corresponding model compound, 2,6-(1,5-dihydroxy naphthalene) benzothiazole, was also quantitatively synthesized. However, attempts to synthesize the pseudo-ladder poly(benzothiazole) (PBT) polymer was unsuccessful. The bis-carboxylation of several other dihydroxy arylene compounds, 1,5-dihydroxy anthraquinone and 4,7-dihydroxy-1,10-phenanthroline also appeared to be unsuccessful.

The solubility of 1,5-dihydroxy naphthalene-2,6-dicarboxylic acid in polyphosphoric acid (PPA) was determined to be very low (< 1wt%), limiting its reactivity, and hence, the corresponding molecular weight of the pseudo-ladder (PBT) polymer. Synthesis of several derivatives of 1,5-dihydroxy naphthalene-2,6-dicarboxylic acid, which may have greater solubility in poly phosphoric acid (PPA), is currently under investigation.

TASK: 205

TASK TITLE: Compression Loading of Laminated Composites: "Compression Behavior of Composite Materials: Part II - Analysis of Mini-Sandwich Compression Test Specimen"

TASK OBJECTIVE: To develop stress analysis models for the compression loading of laminated composites.

SCIENTIST: Seng Tan, Ph.D., Wright Materials Research

DESCRIPTION OF WORK:

A stress analysis of a mini-sandwich compression specimen was performed using the rule-of-mixture approach (a one-dimensional analysis) and a four noded quadrilateral isoparametric finite element method which takes into account the mechanical and nonmechanical loadings. An Illinois Institute of Technology Research Institute (IITRI) fixture was chosen to test the mini-sandwich specimens since their shape is similar to that of an IITRI specimen. The load transfer mechanism from the applied load to the end tab surfaces of the specimen is similar to the IITRI fixture and IITRI specimen which was analyzed in a previous study.

A mini-sandwich specimen contains two different constituents: the skin and the core. The specimens studied were $[(AS4/3501\text{-}6)/3501\text{-}6]_s$ and $[(AS4/APC\text{-}2)/APC\text{-}2]_s$ which contain two 0-degree ply, $[0_2]$, skins. The core materials are 3501-6 epoxy and APC-2 PEEK material.

The stress-strain behaviors of both the core materials and the composites were tested using the IITRI fixture. The results showed that the stresses are uniform in the midplane ($x = 0$) of the specimen and stress concentrations exist around the tab tip. However, the magnitudes are considerably lower than those of the IITRI specimen with the same specimen thicknesses.

The compressive strengths of the two unidirectional composites were computed using the experimentally measured strengths of the mini-sandwich specimen and the stress state predicted by the present analysis. The magnitudes of the strength value are significantly higher than those evaluated using other testing methods. The present result shows that the rule-of-mixture approach can cause considerable error in the interpretation of the compressive strength of unidirectional skin composites. Large errors can also result if it is assumed that all the loads are carried by the skin materials. Also, a simplified nonlinear approach revealed that it is very critical to consider the instantaneous final material properties rather than the initial material properties to obtain an accurate stress state of the specimen prior to failure. To take these things into account a procedure to accurately determine the compressive strengths of the skin materials for mini-sandwich specimens is presented.

In addition, the advantages and disadvantages of the mini-sandwich specimen are discussed. This type of specimen prevents global buckling and the stress concentrations are less than those of an IITRI specimen. The disadvantages are twofold: a mini-sandwich specimen is, in fact, a laminated composite and, therefore, appropriate analysis is needed to predict the stresses in the skin composites due to mechanical and nonmechanical loadings; and the thicknesses of the skin composites were measured under microscopy which is somewhat inconvenient.

Finally, it is proposed that a reliable compressive fiber strength can be obtained by incorporating the present model with a micromechanic analysis.

TASK: 206

TASK TITLE: Cluster and Crystal Orbital Investigations of Electrical Conductivity Mechanisms in Conjugated Polymers

TASK OBJECTIVE: Prediction of relative effects of chemical structures on conduction processes in polymers.

SCIENTIST: Jorge Medrano, Ph.D.

DESCRIPTION OF WORK:

During the study the scientist performed semiempirical geometry and wave function optimizations on model polymers of interest as conductive materials and investigated changes as a function of chemical structure. The work concentrated on the study of the geometrical and electronic structure associated with the presence of quasi-particles in infinite polymers. The example studied was that of soliton-antisoliton pairs in infinite polyacetylene, in the singlet state. Triplets are presently being calculated. The repeat unit used to model infinite polyacetylene was C22H22 with one soliton-antisoliton pair, which was studied at different separations of the two parts. The repeat unit has to be at least this large to prevent the concentration of quasi-particles from becoming unrealistically high.

The method used to find the wave function of the infinite system was the "cluster approximation," in which cyclic boundary conditions are used. This is an approximation to a full crystal orbital (CO) calculation and is known to give excellent results when the unit cell is large enough to ensure that atoms at one end of the repeat unit have a negligible density matrix element with atoms at the other end. This condition is rigorously met in the study since the repeat units used are about 27 Angstroms long. The MOPAC 5.0 program, employing the semiempirical AM1 Hamiltonian, was used for performing the calculations. However, in at least one example the full solid-state (CO) calculation was performed as a check (using the MOSOL program), and the results from both methods were the same to four significant digits for the optimized geometrical variables, heats of formation and degrees of bonding. The geometries of all the systems studied were fully optimized using gradient techniques with due allowance for the symmetry constraints in each case. The gradient norm was usually reduced to less than 1 (kcal/Angstrom or kcal/degree), even when more than 70 geometrical variables were simultaneously optimized.

The degrees of bonding were calculated from the density matrix using definitions developed for molecular and infinite systems. These are known to provide an accurate measure of the integrated electron density associated with a bond, and have the important advantage that the same basic formulation (based on the first-order reduced density operator) is used both for molecules and infinite polymers.

Results concerning the geometrical and electronic structure are shown for separations between both parts of the soliton-antisoliton pair of 1, 5, 9 and 11 bonds. The bond length alternation and degree of bonding alternation follow each other quite closely. The bond length alternation goes to zero at the carbon atoms where each soliton is centered, as it should, and then recovers quickly. The degree of bonding does not vanish however, but decreases from about 0.74, away from a quasi-particle (also its value in unperturbed infinite polyacetylene) to about 0.65 at the carbon atoms where a soliton is centered, irrespective of the separation between soliton and anti-soliton, showing that the degree of bonding is not controlled solely by the bond length.

It is noted that the bond length alternation never changes sign in any of the cases studied (i.e., there is no real flip-over of double bonds into single or vice versa, at any point in the chain). This means that there is some sort of interaction between both parts of the soliton-antisoliton pair, even when they are as far as 11 bonds apart. The nature of the long range electronic interaction between a soliton and a neighboring antisoliton is rather subtle and is not reflected in the energy of the system as evidenced by the fact that the heat of formation per unit cell is the same for separations of 5, 9 and 11 bonds. It decreases by about 2 kcal/mol (0.087 eV) when the separation is one bond, indicating a weakly bound state and a short-range attractive interaction (at least in the singlet state).

The heats of formation per unit cell of unperturbed polyacetylene and a soliton-antisoliton pair

separated by one bond were calculated to be 141.65 and 145.27 kcal/mol, respectively. This gives an energy of formation for the pair of 3.62 kcal/mol (0.157 eV). The binding energy of 0.087 eV is one order of magnitude lower than previous results by Bredas et al, but they used a much more approximate Huckel-type method of calculation. The present result is consistent with the finding that there is no phase transition (change in bond order alternation).

TASK: 207

TASK TITLE: Synthesis of Processible Nonlinear Optical Polymers: "New Polymers for Nonlinear Optics Applications: The Synthesis of a Benzothiazole-Type Model Compound Containing Isoamyl Ether Pendant Groups"

TASK OBJECTIVE: To synthesize conjugated aromatic high molecular weight enyne polymers which are soluble in organic solvents.

SCIENTIST: Thomas Hall, Ph.D.

DESCRIPTION OF WORK:

There is extensive research activity currently underway to design new nonlinear optical (NLO) materials, due to a continuing interest in meeting materials needs in the rapidly developing fields of new electro-optic devices, optical computing and advanced sensor protection. Rigid-rod polymers such as poly(benzobisthiazole) (PBT) have generally been recognized as having excellent thermal and chemical stability; characteristics which are required for an ideal NLO material. While they cannot be considered to be new classes of polymers, and have indeed been studied for a number of years, it has only been recently that their potential as delocalized pi-electron polymeric conductors and in nonlinear optical applications has been explored. However, a serious drawback to PBT's increased use in nonlinear optical devices lies in its lack of solubility and subsequent processibility in common organic solvents. One approach to maximize solubility is to attach branched-chain substituents to the polymer framework. In addition, it would be desirable to develop new synthetic routes towards the preparation of PBT-type polymers, which usually involves the direct condensation of aromatic carboxylic acids with the appropriate aminothiophenol.

In the present study the research activity was directed towards developing an alternative method for the synthesis of modified PBT model compounds and chemically modifying the structures to improve their solubility in common organic solvents. The study demonstrated the feasibility of using an isoamyloxy substituent as a suitable solubilizing pendant-group. The report outlines the reaction scheme for the syntheses of all intermediates and target model compound, bis(2',5'-diisoamyloxybenzyl)benzobisthiazole.

TASK: 208

TASK TITLE: Crystallography Discovery System

TASK OBJECTIVE: To develop a system which when coupled to an electron microscope is capable of reasoning about the diffraction patterns required from known and unknown materials.

SCIENTIST: Jack Park, ThinkAlong Software, Inc.

DESCRIPTION OF WORK:

This research continued the development of a deductive expert system as a means to acquire expert knowledge regarding the domain of crystal diffraction pattern analysis. Progress during this task involved the implementation of the syntactic methods block of the Quality Discovery Process Automation (QDPA) system. Coding and debugging of the tetragonal indexing code continued.

Earlier QDPA code was recoded into the newer syntax of TSC (The Scholar's Companion, ThinkAlong Software's Discovery System). This involved syntactic modification from the earlier TSC-directed graphs to the newer Eurisko-like rules. These rules cover three aspects of the QPDA activity: controlling the transmission electron microscope (TEM), analyzing the pattern, and "thinking" about the results. Simple control rules have been drafted which are similar to the serial-port simulator rules of the QPD system for the autoclave. These rules are, as yet, untested. A next task will begin the development of those rules into full-fledged controls for QDPA. Further, work will also include the addition of deep-level domain knowledge on crystal growth, group theory, and tiling.

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