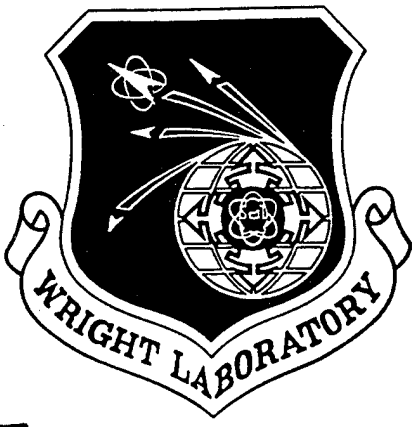
WL-TR-95-4090

CONTRIBUTIVE RESEARCH AND
DEVELOPMENT



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JULY 1994

FINAL REPORT FOR 12/26/90-07/14/95

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This technical report has been reviewed and is approved for publication.

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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 246 TASKS COMPLETED UNDER THE CONTRACT

14. SUBJECT TERMS ADVANCED FLUIDS, CERAMICS, METALLURGY MATERIAL PROC NLO, POLYMER CHARACTERIZATION, COMPOSITES, LASER HARDENING, LUBRICANTS, SEMICONDUCTORS, MATERIALS FATIGUE, MATERIALS PROCESS CONTROL, POLYMER PROCESSING

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Preface

This Final Technical Report was developed under Air Force Contract F33615-90-C-5944, 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 Manager was Ms. Angela McPherson. The SYSTRAN Project Manager was Mr. Milton Zellmer.

1.0 OVERVIEW

This final report for Contract F33615-90-C-5944 describes the objectives and accomplishments of SYSTRAN Corporation from contract inception to the end of the technical effort on 15 March 1995.

During this period, SYSTRAN 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 provided all technical and administrative management control over the project and the assigned researchers.

SYSTRAN identified and assigned a principal researcher(s) for each task requested by the Government. These researchers conducted investigations in the physical and engineering sciences and 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 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 were provided by SYSTRAN's support staff. All reports were prepared in accordance with CDRL requirements.

2.0 ACCOMPLISHMENTS

A total of 262 tasks were defined during this contributive research and development program. Of this total, 246 tasks were completed, 14 were cancelled, and 2 were not issued. Tasks 3 and 4 which were included in the initial contract request for proposal were not issued after contract award.

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 completed all documentation and graphics requirements. Monthly 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 was 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, when required.

2.3 Equipment

All equipment and materials purchases to perform specific tasks during the project were 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: Project Management/Administration

TASK OBJECTIVE: To provide support activities necessary to establish project task orders and overall contract administration.

PROGRAM MANAGER:Milton E. Zellmer

DESCRIPTION OF WORK:

The contributive research and development project required extensive management and administration activities that were not readily charged to a specific task. These activities fell into three general categories:

1. Those contract management administrative requirements to establish planning and control procedures that applied to the project as a whole. Examples are status reporting, project management meetings, and other general overall project reporting.

2. Those management activities required to establish each of the task assignments. These activities could not be charged to the task since the task was not yet approved during this phase.

3. Recording and reporting the performance and cost for the overall management and administrative activities.

This task provided project management/administration from 26 December 1990 through 25 June 1991.

TASK: 2

TASK TITLE: Discovery Systems for Materials Research

TASK OBJECTIVE: To couple a discovery system to a transmission electron microscope (TEM) and enable autonomous diffraction pattern recognition.

SCIENTIST: Jack Park, ThinkAlong Software, Inc.

DESCRIPTION OF WORK:

The discovery system, called QDPA (Qualitative Diffraction Pattern Analyzer), is being implemented to analyze crystal diffraction patterns produced during TEM (Transmission Electron Microscopy) sessions. The effort included development of a crystallography data base for QDPA, development of interface software to couple TEM to the discovery system, and evaluation of the discovery system performance on both known and unknown lattice structures.

Crystallographers collect data in the form of diffraction patterns by means of x-ray or electron microscopy. Diffraction pattern studies have traditionally been characterized by a by-hand measure and calculate exercise. Recently, the rise of personal computers has resulted in the introduction of several computer programs for diffraction pattern analysis (c.f. Park 1988). All programs introduced to date focus on methods we call *syntactic*. These methods are computerized versions of the measure and calculate tradition. They do not cover the analysis of the diffraction pattern beyond indexing and zonal analysis. Further, they do not offer scope control functions for automation of the data acquisition phase of a materials experiment.

This project developed a portion of one such set of tools: a crystallographers tool for controlling the transmission electron microscope (TEM) and for studying the diffraction patterns of interesting materials. Two important aspects of this research were symmetry detection and analogical analysis.

The primary approach to this research was that of evolutionary development of a software tool for crystallographers. The project started with an underlying expert system shell called The Scholar's Companion (TSC) (Park & Wood, 1989). Layers of new programming were then added to the shell to achieve the desired software performance. The layers, as they were developed during this research, are broken into syntactic and semantic layers.

The WDPA system applies syntactic methods to the analysis of dot patterns collected (eventually, under its control) at a TEM. Further analysis is provided by the shallow and deep theories of semantic analysis.

The detailed, development, and evaluation results are reported in Contributive Research and Development Final Report, Volume 7, Crystallography Discovery System.

TASK: 3

This task was not issued by the government.

TASK: 4

This task was not issued by the government.

TASK: 5

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:

A knowledge base for curing of advanced composites based on dielectric in situ measurements was developed. The entire process is controlled by the knowledge base using QPA(Qualitative Process Automation) procedures, with cure cycle parameters such as the temperature and duration of the final hold and pressure application being inferred from the situ sensed information.

The knowledge bases developed in this study are written in the Qualitative Process Automation Language (QPAL) following the various rules and procedures required by its specific syntax. This is a syntax used to develop a program that is executed, consisting of interrelated object definitions that contain the user's heuristics about the control of a target process. The knowledge bases are based on previous work by the author, which showed that the dielectric losses exhibit a common behavior for different families of resinous materials. Generally three regions could be identified in the dielectric dissipation factor vs. time curves. Firstly, the softening or flow region, where the curves exhibited a first peak or a plateau. In this region the viscosity attains low values. Secondly, the reaction peak, obtained when the curve reaches maximum, which is indicative of the crosslinking reaction. Finally, a region in which the dissipation factor approaches asymptotically a constant value, indicating completion of curing. An optimization procedure combining laboratory experiments with autoclave processing was used in the past. This was a two stage approach in which a cure cycle was devised after the various regions of the dielectric curve for a given material were identified in a laboratory experiment, which was followed by experimentation in an autoclave. The cure cycles could not be modified in situ during autoclave processing, requiring an iterative procedure in order to take into account the inevitable changes occurring when scaling up from the laboratory to the industrial environment of the autoclave.

QPA developed at the Materials Directorate (WL/MLBC) eliminates the need of the two-stage-approach and the iterative adjustment of the cure cycle, while still using the information accumulated on the behavior of the dielectric curves. The knowledge base has general applicability, and was specifically tested for curing carbon/phenolic prepregs with Borden SC1008 resin. The influence of heating strategy and pressure application as reflected by dielectric measurements and laminate quality were investigated. The knowledge base developed here was successfully applied to curing the above material, recommendations for optimal processing being formulated as a result of the study.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 21, Knowledge Base Development for Qualitative Process Automation (QPA).

TASK: 6

TASK TITLE: Growth of Nonlinear Optical Crystals by Aqueous Solution Growth

TASK OBJECTIVE: To grow and characterize non-linear optical crystals for frequency conversion.

SCIENTIST: Uma B. Ramabadran, Ph.D.

DESCRIPTION OF WORK:

Nonlinear optical crystals of good quality and high frequency conversion efficiency were grown by the aqueous solution temperature reduction method. The success of strategic technologies, such as laser driven inertial confinement fusion may depend on the availability of new, high performance nonlinear materials. In addition, these materials are required to generate broadband electro-optic modulators. The need to grow, characterize and develop new non linear materials is therefore immediate.

The key issues of materials selection for frequency conversion may be summarized as follows: 1) high conversion efficiency, 2) high damage threshold, 3) wide phase-match and transparency range, 4) large size with good optical homogeneity, 5) low cost and easy fabrication, and 6) chemical and mechanical stability.

To utilize a nonlinear crystal, properties such as its refractive index, second harmonic generation efficiency, electro-optic coefficient and dielectric constant must be measured.

Nonlinear optical crystals of good quality and high frequency conversion efficiency were grown by the aqueous solution temperature reduction method. The widely used potassium dihydrogen phosphate (KDP) was grown as a test material. These crystals were then doped with .0024% copper chloride (Cu:KDP) and variations in the nature of the growth process investigated. Suppression of growth along the X and Y principal axes was observed. The more recently discovered nonlinear crystal L-arginine phosphate was also grown by a similar technique. These crystals were then characterized by measuring the electro-optic coefficients using a Mach-Zehnder and the piezoelectric coefficients using a Michelson interferometer. The electro-optic coefficients of KDP(γ_{63}), Cu:KDP (γ_{63}) and Strontium Barium Niobate [SBN(γ_{13})] were measured to be 11.0 pm/V, 11.07/V, and 47.39 pm/V respectively. The γ_{13}, γ_{23}, and γ_{33} electro-optic coefficients of the new material zinc tristhiourea sulphate were measured to be 1.74, 0.4232, and 1.495 pm/V. The piezoelectric coefficient of SBN was determined to be 29.984 pm/V. The

accuracy in these measurements was estimated to be +/-10%. Second harmonic generation in these crystals was identified using continuously tunable Titanium:Sapphire laser and the range of conversion determined. The Cu:KDP crystal was cut for phase matching and exhibited second harmonic generation in the wavelength range of 850-1000mm. A separate effort involved study of the possibility of growing a new nonlinear crystal, triallyl thiourea copper chloride.

The detailed project description, method, results, and discussion are repented in Contributive Research and Development, Volume 16, Aqueous Solution Growth Optical Characterization of Nonlinear Crystals.

TASK: 7

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 Metals and Ceramic Division. To set up the hardware and software systems for novel AE testing techniques.

SCIENTIST: Itzhak Roman Ph.D.

DESCRIPTION OF WORK:

Acoustic emission is frequently produced during deformation and fracture of monolithic and composite materials. Acoustic emission monitoring has been employed extensively over the last two decades in order to gain insight into dynamic behavior of a variety of material systems undergoing deformation and fracture.

The applicability of utilizing AE as a means of gaining better understanding of the deformation and fracture mechanisms that operate in advanced titanium based materials was examined. Several different combinations of materials and loading modes were employed in this study, namely, tensile testing of monolithic titanium aluminide alloy, interfacial properties study of titanium model composites, tensile testing of Ti24A1-11Nb/SCS-6 composite and thermal fatigue testing of a Ti-24A1-11Nb/SCS-6 composite.

The work completed in the first phase of this on-going study, consisted of room temperature testing of a monolithic α_2 alloy, Ti-25A1-10Nb-3V-1Mo and interfacial properties characterization of two titanium model composites, Ti-6Al-4V/SCS-6 and Ti-24A1-11Nb/SCS-6. The findings obtained can be summarized as follows:

1) The effect of microstructure on Acoustic Emission (AE) behavior during tensile deformation

and fracture was investigated in a titanium aluminide intermetallic alloy of nominal composition Ti-25A1-10Nb-3VMo (atomic percent), tested at ambient temperature.

Both α_2 +ß and ß processing routes were utilized to produce different microstructures. Forging was done at either 1021°C or 1049°C for α_2 + ß processing and at 1104°C for ß processing. Post-forge heat treatment consisted of salt quench at 815°C for 30 minutes. Half of the material was then annealed at its forging temperature for 1 hour and given a direct age at 815°C for 2 hours.

The resulting microstructure for the α_2 +ß processing route consisted of 15-25 v/o equiaxed primary α_2, in a secondary α_2 plate/B2 matrix, and the ß processed material obviously contained only a transformed α_2 plate/B2 matrix microstructure. The material in the annealed and aged condition had much coarser secondary α_2 plates than the direct salt quenched microstructure.

Acoustic emission (AE)activity was monitored during tensile deformation. Yielding was characterized by a peak in the continuous AE level, the intensity of which depended largely on the amount of primary α_2 was absent(ß forged material) and increasing activity with v/o equiaxed primary α_2. Refining the transformed microstructure resulted in reduced intensity of the continuous AE activity.

Burst type AE preceded imminent final failure in all of the samples tested. Metallographic sectioning indicated that when the microstructure contained equiaxed primary α_2, the burst activity was due to microcracks traversing the primary α_2 grains, and arresting in the transformed microstructure. Conversely, SEM fractographic studies indicated that in the ß forged material with no primary α_2, the burst activity stemmed from intergranular fracture along the prior ß grains.

2) The interfacial region between continuous SiC fiber and titanium alloy matrix, in monofilament metal matrix composites, was characterized. The study utilized SCS-6 SiC fibers and two titanium alloys: Ti-64Al-4V and Ti-24Al-11Nb. The interfacial shear strength(ISS) was determined by two different techniques, indentation and fragmentation.

Results indicate that load is transferred from the matrix to the fiber through the bonding between fiber and matrix and by friction, which is due to residual compressive thermal stresses and surface roughness. Each fiber fracture produced a multiplicity of small pieces between adjacent larger fragments, and was accompanied by distinct, intense acoustic emission with a characteristic waveform.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 24, Acoustic Emission Characterization of Advanced Titanium Base Materials.

TASK: 8

TASK TITLE: Behavior of Mesophase Pitch in Fabrication of Graphite Foams

TASK OBJECTIVE: To study and characterize the rheological properties of mesophase pitch when mixed with both bubble nucleative agents and to determine the oxygen stabilization conditions for the foams produced therefrom.

SCIENTIST: Phillip G. Wapner, Ph.D.

DESCRIPTION OF WORK:

It was the purpose of this research project to explore the feasibility of the creation of lightweight, porous carbon foam starting with mesophase pitch. It may or may not have carbon (or other) fibers incorporated into it.

Carbon foams up to now, have always employed an isotropic pitch or resin as feedstock or were made by simply carbonizing polymeric foams such as polyurethane. Strengths were low and little reason existed to believe they could be improved. This may not be the case with highly anisotropic mesophase pitch. Briefly, what needs to be done to turn a material into a foam is to first discover a suitable foaming agent for it. The classic example is soap and water. Pure water will not foam. The addition of soap considerably lowers water's surface tension and bubbles become stable. This is the criteria for a good foaming agent, and the one selected for this experimental study with mesophase.

An apparatus was designed and constructed which measures surface tension of mesophase pitches using the maximum differential bubble pressure technique. This method overcomes several problems associated with previous apparatus constructed to make these measurements (pendent drop techniques). Data was taken on pure AR mesophase solvent-doped AR mesophase, and AEROCARB 60, 70, and 80.

The detailed report description, method, results and discussion are reported in Contributive Research and Development Final Report, Volume 6, Behavior of Mesophase Pitch In The Fabrication of Graphite Foams.

TASK: 9

TASK TITLE: Synthesis of Ordered Polymers

TASK OBJECTIVE: The SYSTRAN scientist shall investigate the synthesis of rod-like polymers which would be expected to exhibit strong conductive and semiconductive behavior. The effort shall include synthesis of the requisite monomers as well as study of polycondensation conditions.

SCIENTIST: Kevin L. Cooper, Ph.D.

DESCRIPTION OF WORK:

The synthesis as well as the thermal characteristics of segmented and tri-block polymers composed of an amorphous, glassy, poly(arylene ether keton) (PEK) engineering thermoplastic, and an anisotropic, liquid crystalline poly(benzothiazole) (PBT) were investigated. In particular, it was discovered that high molecular weight polymers could be synthesized that displayed excellent thermoxidative resistance as well as a softening or glass transition temperature.

In addition, a method for the synthesis of arlyene, 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. However, attempts to synthesize the pseudo-ladder poly(benzothiazole) PBT polymer were unsuccessful. The solubility of 1,5-dihydroxynaphthalene-2,6-dicarboxylic acid in polyphosphoric acid (PPA) was determined to be very low (1 wt%), limiting its reactivity, and hence, the corresponding molecular weight of the pseudo-ladder PBT polymer. Syntheses of several derivatives of the above monomer were also attempted, but were unsuccessful.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 3, Synthesis and Characterization of Poly(Arylene Ether Ketone)- Poly(Benzothiazole) Copolymers and Poly(Benzothiazole) Conducting Polymers.

TASK: 10

TASK TITLE: Polymer

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. A 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. 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. Recently, an 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 was prepared using blends of poly(p-phenylene benzobisthiazole) (PBZT) and polyamide having pendants terminated with sulfonic acid groups (ASPA). 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 not have a high entanglement 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.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 1, Synthesis of Rigid-Rod Polymers.

TASK: 11

TASK TITLE: Molecular Beam Epitaxy of Strained Layer Superlattices

TASK OBJECTIVE: Develop and apply techniques for MBE growth of strained layer superlattices of InGaSb/InAs and characterize these films as potential IR detector materials.

SCIENTIST: Michael A. Capano, Ph.D.

DESCRIPTION OF WORK:

The primary function performed during this project was to characterize Group III-V and Group IV semiconductor heterostructures using double-crystal x-ray diffractometry (DXRD), thin film x-ray diffractometry (TFD) and x-ray topography. X-ray topography was used to study strain relaxation in SiGe on Si(001). Group III-V heterostructures, including the systems InGaAs/InP, AlGaAs/GaAs, GaSb/GaAs and InAs/GaSb/GaAs, were characterized by DXRD to determine the epilayer composition and assess the general quality of the epilayers. Both DXRD and TFD were needed to determine whether the low-temperature GaAs (Lt-GaAs) layers were polycrystalline or single-crystalline. LT-GaAs layers were polycrystalline when grown on a GaAs(111) substrates but were single-crystalline when grown on GaAs(001) substrates.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 2, Molecular Beam Epitaxy of Strained Layer Superlattices.

TASK: 12

TASK TITLE: Intelligent Systems Design

TASK OBJECTIVE To examine application of intelligent systems techniques to the design of batch manufacturing processes.

SCIENTIST: Alley Butler, M.S.

DESCRIPTION OF WORK:

The present research project describes the development of an expert system which effectively

duplicated the professional judgement of a skilled tribologist in the selection of rolling element hearings. The research included the completion of a literature survey on the application of intelligent systems to computer aided design, a literature survey on university based research in feature based design, and research into the use of symbolic logic for reliability based design. Each of these is included in a separate appendix to ensure completeness of the report regarding the work accomplished.

Included in the work is a report on use of the Dempster-Shafer theory to represent evidence in an expert system for the selection of rolling element bearings. Much of the research conducted over the last three decades has focused on expanding the capability of Computer Aided Design/Engineering(CAD/E) systems, and this work continued in this trend by illustrating the use of the Dempster-Shafer theory to expand the computer's role in a CAD/E environment. In this study an expert system was created using Dempster-Shafer methods which effectively modeled the professional judgement of a skilled tribologist in the selection of rolling element bearings. A qualitative and symbolic approach was used, but access to simple quantitative models was provided to the expert system shell. The Dempster-Shafer theory was found adequate in all respects for replicating the expert's judgement; however, an understanding of the basic theory is required for interpreting the results.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 27, Computer Aided Design/Engineering of Bearing Systems Using the Dempster-Shafer Theory.

TASK: 13

TASK TITLE: Crystallography Discovery System for Material Design

TASK OBJECTIVE: To develop a self-improving system for analyzing TEM diffraction patterns and characterizing crystal lattices and structures as a basis for extending (through abduction, analogy and generalization) expert knowledge regarding fundamental relationships between crystals and material properties for use in automating the process of 'material design'.

SCIENTIST: Allen G. Jackson, Ph.D.

DESCRIPTION OF WORK:

Research into developing a self-improving computer based system for analyzing TEM diffraction patterns was conducted. The research was divided into multiple pattern problem, standardized cubic patterns and symmetries, and application of symmetry recognition. Single diffraction patterns can be analyzed by use of syntactic files containing equations related to the crystallography of the structure producing pattern. Qualitative aspects of the pattern such as the observed symmetry can also be used for analysis by appealing to the algorithm approach developed in an earlier effort. Separation of multiple patterns can be accomplished by determining the nature of the overlap present. Tilting to

specific diffraction conditions can be handled once the pattern is recognized and the zone axis identified. Rotation, mirror reflection, and twinning cases were examined, and an approach to this problem was developed.

Specific details of standardized diffraction patterns from cubic lattices were listed. Use of these standardized patterns in the self-learning environment was explored through the scaling of the patterns to fit the experimental patterns.

Symmetry in the cubic crystal system was explored in some detail and the symmetries obtainable from a two dimensional pattern were enumerated. The connection of these symmetries with the symmetry recognition algorithm produce an extension that allows quantitative information on the crystal system to be found.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 4, Crystallography Discovery System For Material Design.

TASK: 14

TASK TITLE: Crystal Orbital Investigations of Electrical Conductivity Mechanisms in Conjugated Polymers

TASK OBJECTIVE: Prediction of chemical structure modifications on conduction processes in polymers.

SCIENTIST: Jorge Medrano, Ph.D.

DESCRIPTION OF WORK:

This project was based on the application of the conceptual and computational tools of the Quantum Theory of Molecular Orbitals and the Quantum Theory of Crystal Orbitals. The goal was to make progress in the field of conducting polymers, with both the purpose of gaining insight into the conduction process inorganic polymers and finding some examples of very low bandgap materials. This was done at the semi-empirical level of the theory, using the programs MOPAC 5.0, MOPAC 6.0, and MOSOL.

Three main lines of research were undertaken. Firstly, an attempt was made to find some examples of polymers with very good intrinsic conductivity, i.e., a very low bandgap. And in fact some examples were found. Secondly, a line of research was started directed to achieve a better understanding of the role of quasi-particles such as solitons, polarons, and bipolarons in the conductivity phenomenon in organic polymers. And thirdly, a study was initiated of ways for obtaining the wavefunction of infinite systems incorporating some degree of electronic correlations.

The utilization of a semi-empirical approach, applied for the first time in these contexts, proved to be a very apt method, giving a good compromise between accuracy and computational cost. In some of the examples described in the report semi-empirical approach is the only one to render the calculation feasible due to the huge requirements of CPU time. That is the case for example, of the quasi-particle calculations.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 22, Theoretical Studies of Conductivity in Infinite Polymers.

TASK: 15

TASK TITLE: Synthesis of Processible Nonlinear Optical Polymers

TASK OBJECTIVE: To synthesis conjugated aromatic high molecular weight enyne and polyanthrylene vinylene polymers which are soluble in organic solvent.

SCIENTIST: Thomas Hall, Ph.D.

DESCRIPTION OF WORK:

This research directly addressed the Air Force's need for new third-order nonlinear optical (NLO) materials which can be used to fabricate electro-optical devices for advanced information processing and communication systems. Extended-chain and rigid-rod type polymers are attractive NLO materials because of their high degree of pi-electron conjugation. Both these types of polymers, however, are typically poor optical media due to their strong tendency to scatter light. Molecular composites of an organic polymer dispersed in an inorganic glass matrix have shown to improve the optical quality of materials over the pristine organic polymer. This research concentrated on the synthetic efforts to prepare two novel
molecular composites which incorporate a poly(anthrylene vinylene) and a poly(phenylene bisbenzothiazole), respectively, into a silica-glass matrix.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 26, The Synthesis of Novel Third-Order Nonlinear Optical Molecular Composites.

TASK: 16

TASK TITLE: Synthesis of Aromatic-Heterocyclic Polymers

TASK OBJECTIVE: To synthesize novel aromatic-heterocyclic polymers for nonlinear optical

applications.

SCIENTIST: B. Robert McKellar, Ph.D.

DESCRIPTION OF WORK:

This research 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—a block copolymer approach would include a TPBT block and a 6FPBO block.

Monomers necessary for the synthesis of TPBT and 6FPBO were prepared. TPBT and 6FPBO homopolymers of differing molecular weights and terminated with the appropriate end functional groups were synthesized by varying the proportions of certain monomers. Two different approaches were employed to synthesize block copolymers. The first approach involved reacting the two homopolymers. The second approach involved reacting TBPT homopolymers with 6FPBO monomers. In each experiment the products were extracted with tetrahydrofuran (THF) to remove 6FPBO homopolymer. The existence of the products as copolymers could not be conclusively demonstrated by thermal analysis; i.e. the Tg for these materials was not significantly greater than the Tg of 6FPBO homopolymer. In a controlled experiment more 6FPBO could be extracted from a physical blend (using encapped TPBT) than from a comparable copolymer reaction, but extraction was not quantitative.

The graft copolymer approach involved the synthesis of a thiophene polybenzobisthiazole (TPBT) with aryl ether pendant groups on the thiophene ring. The phenyl ring of the pendant provides 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 serve as electron donating substituents, which have been shown to enhance the χ^3 NLO response in model compounds.

A procedure was developed to synthesize 3-(2,6-Dimethylphenoxy)thiophene, 3-(2,6-dimethylphenythio)thiophene, 3-(2,6-dimethylphenythio)thiophene-2,5-dicarboxylic acid, 3-(2,6-dimethylphenythio)thiophene-2,5-dicarbonyl chloride in very good overall yield and purity. Model compounds were made by reaction with 2-aminothiophenol. Reaction of these monomers with 2,5-diamino-1,4 benzenedithiol dihydrochloride using a wide variety of conditions in polyphosphoric acid (PPA) and in polyphosphoric acid trimethylsilyl ester (PPSE) produced only low molecular weight polymer. The most important factor for these results is the instability of these thiophene monomers in PPA at elevated temperatures.

An additional project involved the synthesis of copolymers containing N-aryl Benzobisimidazoles. The N-arylimidazole moiety is of interest as the second dimension in potential two-dimensional NLO materials.

1,7-Diphenyl-2,6-di-[2-(5-carboxythienyl)]benzo[1,2-d:4,5-d']bisimidazole was synthesized in good yield and purity by a multi-step synthesis. A polymer reaction was conducted by reaction of this

compound with 2,5-diamino-1,4 benzenedithiol dihydrochloride.

The detailed project description, method, results and discussion are reported in Contributive Research and Development Final Report, Volume 13, Synopsis of Copolymers as Nonlinear Optical Materials.

TASK: 17

TASK TITLE: Episodal Associative Memory for Support of the Rapid Design System

TASK OBJECTIVE: To collaborate in the development of a memory for maintenance and organization of design information.

SCIENTIST: Kam Komeyli, M.S.

DESCRIPTION OF WORK:

This project continued the research and development of an Episodal Associative Memory (EAM) with storage and retrieval utilities for machined parts. EAM will be used in conjunction with a feature based design system (RDS) which provides means for design, fabrication planning, or inspection planning of mechanical machined parts. Parts are designed using a pre-defined feature set. Goal of the EAM in design stage is to guide the designer by retrieving from a design database, the design/designs which are most similar to the current design under construction. Similarity in design stage is a measure which is described by the type of features which make the design. Similarity measure can also be defined in other components of the RDS (i.e.,in manufacturing, inspection). EAM can also be used in manufacturing and inspection modules to perform the storage and retrieval tasks of most similar designs. Development during this effort concentrated on the translator, standardization, store, and retrieval modules of the EAM.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 20, Episodal Associative Memory.

TASK: 18

TASK TITLE: Properties of Laminated Ceramic Composites

TASK OBJECTIVE: Determine the mechanical properties of laminated model composites and evaluate the applicability of laminate theory.

SCIENTIST: Anuradha Venkateswaran, Ph.D., AdTech Systems Research

DESCRIPTION OF WORK:

This research was aimed at determining whether flaws in ceramic fibers can be tolerated provided their spacing is greater than a certain "critical" value. The model system chosen to study damage propagation in composites with and without fiber flaws is SiC(SCS-6)/Sodium Borosilicate glass.

Fiber-reinforced ceramic matrix composites, (CMC'S) are attractive candidates for high-temperature structural applications given their low density, chemical inertness and environmental stability, and significantly higher fracture toughness and reliability when compared to monolithic structural ceramics. Flaws in ceramic fibers, which serve as a reinforcement in ceramic matrix composites, can limit their usage to their fullest potential.

Owing to the difficulty in introducing controlled flaws into a fine diameter fiber such as Nicalon (available in bunched tows), monofilament SCS was selected as the reinforcement. It was decided to introduce flaws by scribing onto pre-wound filament tapes. Flaw-lines were scribed at 1" spacings, at a 45° angle over the SCS-6 tapes, using a diamond scribe. By shifting the origin of the scribe lines from tape to tape, over 8 tapes a degree of randomness was achieved in the composite. The 45° angle was chosen as intermediate between a 0° (flaws along fiber axis) and a 90° one which would severely bias failure in the composite. A 1" spacing was selected as being representative of typical test gage-lengths reported in such composites. Scribing was performed at intermediate pressures, sufficient to penetrate beyond the external C-coating, but insufficient to break the fiber during subsequent handling. Flaw depths were subjective, owing to the non-automated procedure, and their surface size ranged from 50 to $>100\,\mu$m, at 45°,depending on the pressure and the extent of rolling of the filaments.

Most of the single fiber tests were run on a screw-driven Instron (ATS) with a 500N load cell (Interface) at a cross-head speed of 0.02mm/sec. For the SCS-6 filaments the loads were high enough that a tab-free technique was found to work better than the standard ASTM D-3379-75 (1984) tabbing technique. Displacements were measured directly on the fiber surface using a LaserMike optical light source. For each test, fresh foil surface was used as the fiber cuts through the foil during the test.

For flawed fiber testing, several 7-8"lengths of fibers were arranged together such that their spacing was about that in the filament wound tapes and cellotape strips were applied at the top and bottom. 1" spaced flaws were scribed at 45°. For a 9-10 cm gage length this yields 3 flaws per fiber. Earlier experiments revealed that the distance between scribed flaws, provided it is large enough that flaw interactions do not occur, is not important as a strength determinant in SCS-6, and that strength is governed by the most severe flaw. Scribing was done such that the LaserMike flags could be positioned between the flaws.

The detailed project description, method, results & discussion are reported in Contributive Research & Development Final Report, Volume 30, Effect of Fiber-Flaws on Damage in SiC/Sodium Borosilicate Composites.

TASK: 19

TASK TITLE: Investigation of the Interactions of Carbon-Carbon Materials with Hydrocarbon and Inert Gas Mixtures

TASK OBJECTIVE: To model and experimentally verify the thermochemical stability and reaction kinetics of hydrocarbon and inert gas mixtures in contact with uncoated, uninhibited carbon-carbon substrates.

SCIENTIST: Sarwan S. Sandhu, Ph.D., University of Dayton

DESCRIPTION OF WORK:

The overall goal of this theoretical work was to establish a practical scheme for protecting a structural carbon-carbon composite from oxidation in a high temperature gas environment. Carbon-Carbon composites are structural materials consisting of a carbon matrix reinforced with carbon fibers. To exploit the outstanding elevated temperature mechanical properties of carbon, considerable effort has been devoted to overcoming its oxidation susceptibility via oxygen barrier coatings. Failure to simultaneously provide a coating material which is oxidation resistant and possesses adhesion, thermal expansion matching, and chemical compatibility with the carbon substrate renders such coating system partially or totally ineffective. Theoretical investigation of the idea of protecting a carbon-carbon material in a hostile environment by exposing it to gas mixtures in equilibrium with structural carbon was the subject of this research.

The investigation was conducted in four phases. In the first phase the principle of minimization of Gibbs free energy was employed to obtain information on solid carbon-gas equilibrium compositions at a number of temperature and pressure conditions. In the second phase, a mathematical model was developed to predict oxidation carbon mass loss from the interior surface of a cylindrical tube made of a carbon-carbon material in the presence or absence of protection provided by the inert nitrogen gas boundary layer flow. In the third phase, a mathematical model was developed to predict the oxidation carbon mass loss from the interior surface of a carbon tube with additional protection provided by the presence of carbon monoxide in the protective gas flow. In the fourth phase, the cylindrical geometry model differential equations and boundary conditions were formulated for the prediction of oxidation carbon mass loss from a carbon tube surface for the situation of augmented protection provided by slightly wet (with water) carbon monoxide in the protective boundary layer gas flow.

The information generated theoretically on the equilibrium gas mixtures was found to be in good agreement with that reported in the literature. The predicted carbon mass loss was reduced by a factor of three at 2000K for the case of protection provided by the nitrogen gas boundary layer flow along the surface of a carbon composite tube. A synthetic gas mixture of 30 mole per cent of carbon monoxide and 70 mole per cent of nitrogen flowing in free form of protective boundary layer along the tube surface shows additional reduction in the average carbon mass rate by 21% at 2000K.

The detailed project description, method, results, and discussion we reported in Contributive Research and Development, Volume 37, Carbon-Carbon Surface Oxidation Protection.

TASK: 20

TASK TITLE: Nonlinear Optical Characterization of Biopolymers

TASK OBJECTIVE: To characterize the chi(2) and chi(3) properties of biopolymers being developed in the materials in-house research programs.

SCIENTIST: Rama Vuppuladhadium, M.S.

DESCRIPTION OF WORK:

A novel technique was developed to study the third order nonlinear susceptibility coefficient, $\chi^{(3)}$, by utilizing the intensity dependent dispersion relation of surface plasmons. The third order nonlinear coefficient $\chi^{(3)}$ is a very important optical property of the materials because of its contribution to numerous nonlinear optical processes. The degenerate third order nonlinear susceptibility has shown a growing interest in all-optical signal processing. The nonlinear changes in the dielectric constants $\epsilon(\omega)$ also contribute to well known effects such as self-focusing, self-trapping, and self-bending of light and phase conjugation.

Surface plasmons are electromagnetic surface waves which propagate along the metallic surface with a maximum intensity at the surface and exponentially decaying into the space perpendicular to the surface. One can excite these surface plasmon by coupling the light through the prism (called attenuated total reflection) or through a grating. The strong enhancement at the surface is correlated to the strong reduction in the reflected intensity, indicating the complete transformation of the incoming light to surface plasmons. If the metallic film is further coated with nonlinear media, the degenerate third order nonlinear susceptibility $\chi^{(3)}$ causes a change in intensity of the waveguide mode, which results in the change in the resonant coupling angle. In this research, both the prism coupling and the grating method were used to measure the third order nonlinear susceptibility. Holographic sine wave gratings were made successfully with peak to peak amplitude of 5000 A and an amplitude of (peak to valley) 500 A, resulting in narrowest $\theta^{1/2}$ value. Having controlled the thickness of the non-linear material (in PMMA) and the intensity of the input laser energy, the measurement of $\chi^{(3)}$ was possible.

The detailed project description, method, results, & discussion are reported in Contributive Research & Development Final Report, Volume 38, Measurement of Third Order Nonlinear Susceptibilities by Surface Plasmons.

TASK: 21

TASK TITLE: Molecular Dynamics Calculations on Perfluoropolyalkyethers

TASK OBJECTIVE: To develop a fundamental understanding of the variation in viscosity with molecular structure for oligomeric fluoroalkylethers (with comparable molecular weight distributions), of the variation in viscosity-temperature properties with molecular structure, and of the solvent properties of these materials. These fluoroether materials are candidate high-temperature liquid lubricant base stocks for IHPTET.

SCIENTIST: Robert Zellmer, Ph.D.

DESCRIPTION OF WORK:

This project was undertaken to aid in the understanding of perfluoroalkoxy radicals through the use of ab initio computational chemistry methods.

Perfluoropolyalkylethers are considered as potential replacements for chlorofluorocarbons (CFC's) used for lubrication in gas turbine engines, hydraulic systems, and as coolants. In order to make the determination as to which material is "best", the various reactions that they can undergo and the resulting by-products must be studied. These by-products often contain radical species which are extremely difficult or impossible to study experimentally.

Ab initio Self-Consistent Field Hartree-Fock calculations using double-zeta, double-zeta polarized, and triple-zeta polarized basis sets were performed on the anionic and radical forms of molecules with the general formula C_nF_mO, where n=1,2,3and m=3,5,7. In addition, calculations on the cis and trans form of CF_3OH were also performed. Optimized geometries, normal mode vibrational frequencies, and zero-point energies were obtained. It was found that good results could be obtained with a basis set in which polarization functions are added only to the carbon and oxygen atoms. The results with this basis are comparable to those obtained with the fully polarized double- and triple-zeta basis sets.

It was also found that for all molecular species for which there are rotational barriers about a bond, that the trans species are always the lowest form of energy form. The rotational barriers for CF_3OH, C_2F_5O and $C_2F_5O\bullet$ are 1.0, 5.5 and 3.4 Kcal/mol, respectively.

In addition, the results of this study for the highest normal mode vibrational frequency of $CF_3O\bullet$ disagree with those of previous studies. This study predicts the high vibrational mode at about 1460 cm^{-1} to be due to CO stretching, while the two CF stretching modes are in range of 1400-1425 cm^{-1}. This is exactly opposite of the findings of the previous studies. It is felt that the present results are correct since this study used larger basis sets which include polarization functions. Also, the CO stretching

modes for the other molecules studied in the present have the largest C-X (X=O,F) frequencies, in agreement with the results found for $CF_3O\bullet$.

The detailed project description, methods, results and discussion are reported in Contributive Research and Development Final Report, Volume 41, Ab Initio Computational Studies of Perfluoroalkoxy Radical and Related Compounds.

TASK: 22

TASK TITLE: Microstructural Studies on a Gamma Titanium Aluminide Alloy

TASK OBJECTIVE To characterize the microstructures of the hot worked γ-TiAl alloy

SCIENTIST: Rama Nekkanti, Ph.D.

DESCRIPTION OF WORK:

The microstructures of a wrought gamma titanium aluminide alloy under various processing and heat treatment conditions were characterized to determine the optimum processing parameters to achieve a chemically homogeneous (within each phase) and microstructurally uniform structure. The microsegregation that is inherent in the cast microstructure due to a double cascading peritectic reaction seems to persist in the homogenized as well as in extruded and forged microstructures.

When the extrusion or forging operations were conducted in the temperature range 1050-1275°C (gamma processing), the 'as cast' lamellar colonies seemed to have only recovered but not recrystallized; their size and spacing were reduced by the amount of reduction ratio in one direction and correspondingly got stretched out in the orthogonal direction, thereby forming almost continuous bands in a fully recrystallized gamma phase matrix. The extrusions that were processed in the alpha+gamma phase field (1350-1425°C) also show a banded structure, but there is an increase in the lamellar phase volume with an increase in the extrusion temperature. The same effect is observed when the gamma processed material is heat treated in the two phase field. Additional deformation of an already extruded material brought the lamellar bands together thereby decreasing the diffusion distances, but the banding still persisted.

The above studies indicate that there is a large processing window for processing these materials and the microstructure can be manipulated with proper heat treatment schedule after the ingot breakdown operation.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 12,Microstructural Evaluation of a Gamma Titanium Aluminide Alloy.

Task: 23

TASK TITLE: Annular Cracking in Brittle Matrix Composites (BMC)

TASK OBJECTIVE: To solve a boundary value problem in the theory of heterogeneous elasticity that simulates an annular matrix crack in a BMC and use the solution to evaluate the crack-tip stress field and stress intensity factors as the crack approaches the fiber.

SCIENTIST: Autar Kaw, Ph.D.

DESCRIPTION OF WORK:

This study is relevant to the use of ceramic materials in many high temperature application engineering components. Their advantages of strength, low density, excellent corrosion and oxidation, resistance, and low cost are offset in stress applications by their brittleness and tendency to fail catastrophically. Brittle matrix cracks are seen to occur in fiber reinforced ceramics under a tensile load. These cracks signify the onset of permanent damage.

In this project, elasticity solution to the problem of an annular crack in a brittle matrix composite under a remote uniform axial strain and constant temperature change was found. Stress intensity factors in front of the crack tips and the stresses at the interface were studied to determine the nature of the crack growth in the composite. These parameters were studied as a function of the elastic moduli and the thermal expansion coefficients of the constituents, the fiber volume ratio, crack geometry, interface properties, under an applied remote axial strain and constant temperature change.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 11, Annular Cracking on Brittle Matrix Composites.

TASK: 24

TASK TITLE: MBE Autotuning Research

TASK OBJECTIVE: Conduct experiments on autonomous state space parameter acquisition for autotuning of MBE controller.

SCIENTIST: Jeffrey J. Heyob, M.S.

DESCRIPTION OF WORK:

This project quantified overall process control improvement by the Process Discovery Autotuner as applied to the Molecular Beam Epitaxy (MBE) process. The process control of interest was the MBE Knudsen Cell temperature control loop. The temperature control of the Knudsen Cells was found

to be critically important toward maintaining flux beam stability during the MBE growth process.

Maintaining the necessary temperature control of the Knudsen Cells required optimum tuning of the Eurotherm PID controllers associated with each of the eight Knudsen Cells mounted on the MBE system. Process first principles were autonomously extracted about each Eurotherm controlled Knudsen Cell using a robust qualitative process discovery technique called "Trapezoidal Tuning" and assembled as a knowledge base within a microcomputer. The knowledge base was then used in situ by the microcomputer to optimally tune the Eurotherm temperature control loops for all Knudsen Cell control requirements. This Process Discovery Autotuner methodology achieved 1.45% reduction of overall root-mean-square process error and a 17% reduction of overshoot error during process setpoint changes.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 5, Autotuning of Molecular Beam Epitaxy Process.

TASK: 25

TASK TITLE: Intelligent Process Automation

TASK OBJECTIVE: Process automation, measurement, and control with the new quality technologies.

SCIENTIST: Patrick H. Garrett, Ph.D.

DESCRIPTION OF WORK:

Improvements in process control have been significantly facilitated by advances in computer technology. The research performed on this project aids this advancement by developing two quantitative measures of process control system uncertainty including methods for their reduction, where their minimization is axiomatic for improving process performance.

The accuracy of the controlled variable in a process control loop was defined by the derivation of independent controller and process uncertainty metrics, and their minimization was described by integrating control system design with principles of the new quality technologies. The first provides accountability of the instrumentation uncertainty of controller device and system elements whose minimization is achieved by rescaling controller full scale to the current setpoint and process variable values as an equivalent to Taguchi's tolerance design of discrete components. The second represents the uncertainty of process first-principles compensation whose minimization is achieved by the experimental acquisition of insitu process parameters to define controller PID terms with greater accuracy than traditional tuning methods provide.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 15, Minimizing Variability in Process Control Systems

with Online Quality Technologies.

TASK: 26

TASK TITLE: MBE Growth Simulation Program Development

TASK OBJECTIVE: Complete study of AlGaAs/GaAs heterojunction materials and devices, and extend the research to InGaAs/InAlAs/InP material systems.

SCIENTIST: Peter Kosel, Ph.D.

DESCRIPTION OF WORK:

A computer software package, MBESIM Version 1.1,was developed for predicting the features of Molecular Beam Epitaxy (MBE) grown aluminum gallium arsenide-on-gallium arsenide materials for HEMT devices. This package can predict the features of a single MBE grown layer from the physical parameters of an MBE system and the physical laws of material growth and dopant diffusion. Verification of this software through fabrication and testing of HEMT test structures was also initiated. Both optical and electrical measurements were performed and early results showed that optical measurements of grown layers are not sufficient to predict the variation of parameters associated with the operation of HEMT devices. The most useful characterization probes for these materials was found to be (1) carrier profile measurements from Schottky barrier capacitors and (2) sheet resistances from Van der Pauw test structures. Hall mobility mapping is also considered important but construction of this test facility has not yet been completed.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 31,MBE Growth Simulation Program Development.

TASK: 27

The government canceled this task.

TASK: 28

TASK TITLE: Identification of Compatible High Temperature Systems

TASK OBJECTIVE: Select and verify thermodynamically compatible fiber/coating/matrix combinations for ceramic composites.

SCIENTIST: Sankar Sambasivan, Ph.D.

DESCRIPTION OF WORK:

The goals of this research project were directed toward understanding high temperature interfacial chemistry occurring in ceramic matrix composites (CMC's) based on Yttrium aluminum garnet (YAG). As a widely used material in optical devices, yttrium aluminum garnet (YAG) is well known for its desirable electronic properties. Recent studies indicate it is also a potential structural material especially as a composite constituent. It is also known to be chemically and mechanically stable with alumina.

This work was undertaken to study various aspects of chemistry as related to ceramic matrix composites (CMC's). A feasibility study was done to investigate the possibility of mechanically weakening the fiber/matrix interface in CMC's using dopants to preferentially segregate to the interface. Yttrium Aluminum Garnet (YAG) and alumina were chosen as the composite constituents and Sr, Ca, Zn, Sc and Ni were selected as dopants for the study. Amongst all the dopants used, Sr showed strong tendencies to segregate as well as weaken the YAG/alumina interface relative to the undoped material. In another study, thermochemical properties of YAG were determined using zirconia as a chemical potentiometer. The free energy of formation of YAG was determined as a function of temperature to give

$$\Delta G_f(kJ/mol) = -48.2(\pm 1.74)-0.023(\pm 9E\text{-}5)^{*}T$$

In a third study, a synthetic route was developed to produce homogeneous YAG powder using Y and Al isopropoxides as starting materials. Prior to mixing the two alkoxides, Y-isopropoxide was molecularly modified with ethyl aceto acetate to control the rate of hydrolysis and also to avoid the formation of Y-Al double isopropoxide. NMR and IR spectroscopies were used for structural characterization of the intermediates.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 45, Chemistry Related To Yttrium Aluminum Garnet/ Alumina Composite System: Interfacial Properties, Thermo-Chemical Stability and Sol-Gel Processing.

TASK: 29

The government canceled this task.

TASK: 30

TASK TITLE: Associative Memory Architectures

TASK OBJECTIVE: To evaluate and categorize associative memory architectures for use as an

Episodal Associate Memory.

SCIENTIST: Yoh-Han Pao, Ph.D., Case Western Reserve University

DESCRIPTION OF WORK:

This work constitutes a generalization of some of the practices in several research projects carried out in recent years. In each of these projects, we needed a computer-based 'intelligent' task-support system to be used in support of human task performers.

In each case, the computer system could have been developed in any one of the customary Expert System styles, involving production rules, forward or backward chaining of rules, search and so on. Instead, we adopted a different approach relying substantially on the functionalities of an episodic associative memory which we had developed previously, and which we had christened the Episodal Associative Memory (EAM).

The resulting methodology constitutes an amalgamation of the linguistic symbolic processing of established Artificial Intelligence practice and the 'all-things-considered' wholistic processing approach of artificial neural-net computing. We find that this alloying of the two styles leads to a system architecture well-suited to the integration of several intelligent system technologies.

In this effort, we described the role of the Episodal Associative Memory as the core of an Expert System and discussed its functions in the task of experience-based planning. It is seen that modification of previous plans consists of a gradient decent search in plan space aimed at reducing the difference between desired goals and the attainable goals. Errors in planning are dealt with by updating (or repairing) the memory. The plan is then automatically repaired.

The detailed project description, method, results, and discussion are reported in Contributive Research Development, Volume 40, The Episodal Associative Memory Approach to Expert Systems.

TASK: 31

TASK TITLE: Prototype Development of Episodal Associative Memory

TASK OBJECTIVE: To develop a prototype of an Associative Memory Using Object Oriented programming techniques.

SCIENTIST: Ron Cass, B.S., AI WARE

DESCRIPTION OF WORK:

This research described the application of a prototype episodal associative memory (EAM) to

support the knowledge based functions of the Rapid Foundry Tooling System (RFTS).

The Rapid Foundry Tooling System (RFTS) is a software system which facilitates the design of sand molds for cast aluminum parts. The task of patterning is a complex design task, which must be learned from experience. Thus, a memory-based approach to problem solving is well suited for application in the casting domain.

The episodal associative memory is constructed from object-oriented neural network capabilities provided by the Object N-Net functional library, a commercial product of AI WARE. The principle functions of the EAM are: clustering of designs based on similarity of features and identification of cluster membership for a given design.

The prototype EAM exhibits a number of interesting properties. By remembering past experiences and organizing them for efficient recall, the EAM can enhance the process of designing a casting. Cross-context reminding allows for ease of recalling designs which have only a few salient features in common.

The detailed project description, methods results, and discussion are reported in Contributive Research and Development, Volume 52, Prototype Development of Episodal Association Memory.

TASK: 32

TASK TITLE: Mechanics of Cracks at Interfaces in Ceramic Composites

TASK OBJECTIVE: To evaluate the stresses and energy release rates in materials containing cracks at interfaces between two different elastic materials.

SCIENTIST: Leslie Banks-Sills, Ph.D., Tel Aviv University, Israel

DESCRIPTION OF WORK:

Two methods were developed for calculating stress intensity factors at an interface between two linear, elastic materials. With both methods, a finite element analysis was required. The resulting displacement field was then employed to obtain the stress intensity factors. The first method employed both the J-integral and the displacements along the crack edge. The second method, which is more accurate, was based upon two conservation integrals. Two example problems were analyzed to examine the accuracy of both methods. Finally, a homogeneous and a glass/epoxy Brazilian disk specimen was analyzed for one crack length and several loading angles.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 28, Development of Methods for Determination of Interface Stress Intensity Factors.

TASK: 33

TASK TITLE: Investigation of Metal Matrix Processes

TASK OBJECTIVE: To provide a critical assessment of scientific techniques used in understanding, predicting, and controlling the manufacture of metal matrix composites by thermal and solidification processes.

SCIENTIST: Khairul Alam, Ph.D., Ohio University

DESCRIPTION OF WORK:

Advanced technological requirements for materials having high specific strength at elevated temperatures have been the driving force in development of composites. Composite materials, both Metal Matrix Composite (MMC) and Ceramic Matrix Composites(CMC) are under continuous development to fulfill this requirement. These composite materials are manufactured by using a matrix material in which a second material is disposed in the form of powder, whiskers of fibers.

The objective of this research was to assess the scientific techniques used in understanding, predicting, and controlling the manufacture of MMC's by thermal and solidification processes.

The manufacture of metal matrix composites (MMC) typically involves a number of thermal processes. These processes include heating, solidification, deposition processing, hot pressing, etc. The heating and solidification processes lead to thermal stress problems. There may also be associated degradation of the reinforcing phase during heating or solidification. In almost all processing of the composites, problems may arise in obtaining full densification or filling of the matrix material around the fibers. These processes which are being used at present were developed primarily by experimentation. The processing can be developed further by making full use of analytical and numerical modeling methods along with experimental studies of the process. This is particularly true of the novel deposition processes.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 58, Investigation of Metal Matrix Processes.

TASK: 34

TASK TITLE: Full Potential Total Energy Electronic Structure Calculations

TASK OBJECTIVE: To design and implement a full potential version of the LKKR program at the WL/MLLM (Materials Laboratory).

SCIENTIST: James M. MacLaren, Ph.D., University of Tulane

DESCRIPTION OF WORK:

The goal of this research was to provide an accurate fast method to compute the electronic structure for intermetallics such as TiAl, focussing on properties such as the planar fault energies, atomic relaxations and elastic constants.

This work resulted in improvements and extensions to the electronic structure theory of materials in two major theoretical areas. The first was the treatment of the full one-electron potential rather than the approximate spherical form. The implementation of the theory progressed to the stage that several sensitive tests were applied to check accuracy, computational speed etc. Further testing was however still required. The second was the theoretical modeling and prediction of properties resulting from the addition of low concentrations of impurities. Using the coherent potential approximations, the effects of disorder and ensemble averaging were included into a first principles theory for bulk materials and their interfaces.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 14, Electronic Structure Calculations of Intermetallics.

TASK: 35

TASK TITLE: Dislocation dynamics in Intermetallic Compounds

TASK OBJECTIVE: To perform experimental measurements of the dislocation dynamic properties in selected intermetallic compounds.

SCIENTIST: Edward M. Nadgorny, Ph.D.

DESCRIPTION OF WORK:

The objective of the research was to begin a fundamental experimental study of dislocation dynamics in intermetallic compounds, primarily for dislocations in Ni_3Al and NiAl single crystals. Although intermetallics have been investigated for a rather long time, we know very little, if any, about such fundamental properties of dislocations in these materials such as their mobility, effects of stress and temperature on the dislocation velocity, changes due to deviations from the stoichiometric composition, ternary-element effects, etc. These data are particularly important because of the limited toughness of intermetallics in general, which is one of the major impediments to the practical use of

these materials for structural purposes.

Depending upon the characteristic value of dislocation velocity and its stress-temperature dependence, at least two alternative theories can be suggested to explain the brittleness of intermetallics and predict possible ways to improve it. Some dislocation mobility experiments may well help to sort this out. But at the same time, it is impossible to perform such experiments without a lot of preliminary research on the crystal perfection, dislocation revealing techniques, specimen preparation and handling. The target of this project was to start this type of research and develop it to a necessary level.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 29, Dislocation Dynamics in Intermetallic Compounds.

TASK: 36

TASK TITLE: Associative Memories for Materials and Processing Research

TASK OBJECTIVE: Extend and apply associative memories to materials and material processing research.

SCIENTIST: Steven LeClair, Ph.D.

DESCRIPTION OF WORK:

Task-aiding technology is the augmentation, via computer, of the human ability to use experience in problem solving activities. The potential for "task-aiding" technology as applied to materials research and manufacturing (materials production) is both pervasive and economically significant. Of the many potential applications, the intersection of *Materials, Processing and Control Research* was the focus of this project. Each of these areas has realized significant improvements via computers in data collection, modeling, analysis, and decision making relative to task performance.

In tasks such as materials research or manufacturing, the expert benefits from knowledge of experience. The essence of this knowledge involves dependencies or relationships between domains such as materials, processing and control. Such interdependencies are often too incidental and erratic to be captured as an equation or a rule because they are often influenced by constantly changing conditions. Associative memory provides a means to organize these changing and infrequent conditions into patterns which can be expressed in the form of concepts.

A discussion on task-aiding addresses the more creative element of task performance (i.e. discovery) and explores the use of associative memory as a computerized tool to augment human memory. A brief review of material processing and current research was presented to establish context regarding the complementary use of associative memories with other computer technology for task-

aiding.

Current research in the automation of material processing is commonly referred to as "Intelligent Processing of Materials". The IPM challenge is to advance control theory and control technology in terms of system conceptualization (human representation of the problem), modeling (providing a more parametric representation of the process), and identification (real-time as well as pre/post-experimental measurement of process inputs and outputs).

The researcher believes that task-aiding by means of an associative memory, will be required to map theoretical knowledge of materials, process and control to the practice of material processing and vice versa. The memory will need to be associative to support the continual and evolving nature of material, process, and control knowledge. Human(memory)interaction with the computer memory will require the development of a vocabulary for providing and extracting the above knowledge-in effect communicating with the system.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development, Volume 46, Associative Memories for Materials and Processing Research.

TASK: 37

TASK TITLE: Fundamentals of Solid and Liquid Lubricants

TASK OBJECTIVE: The objectives of this task were to develop new and improved lubricants, both solid and liquids, for use in spacecraft applications and for the integrated high performance turbine engine technology program.

SCIENTIST: Scott D. Walck, Ph.D.

DESCRIPTION OF WORK:

Pulsed laser deposition (PLD) is a relatively new technique for the deposition of thin solid films for tribological applications at high temperature. It has several advantages over the other deposition techniques including excellent film adhesion, replication of the target chemistry, and low substrate temperature during deposition. It is also a very straightforward deposition process.

This work concentrated on developing suitable electron microscopy techniques for the microstructural and morphological investigations of thin films of interest to the tribology group. Morphological examination of as-deposited films was performed using the scanning electron microscopy (SEM). It was also used to study the microstructural changes of wear tested samples of TiC.

Transmission electron microscopy (TEM) was used to study the microstructure, morphology, crystallography, and chemistry of PLD thin films. For tribological purposes, two types of films are important, solid phase lubricants and hard phase coatings. The solid thin film lubricant provides lubricity by its physical properties, either providing easy shear planes or liquidating under high temperatures or pressure. Hard thin films provide adherent scratch resistant coatings which provide load support and low coefficients of friction.

The archetypical solid lubricant is MoS_2. Because of its hexagonal crystal structure of covalently bonded MoS_2 layers separated by weak bonds, MoS_2 is an excellent solid firm lubricant. The weak bonds allow the MoS_2 layers to shear giving good lubricity. They also allow the layers to bend which allows the material to conform to the sliding surfaces. The orientation of the basal plane is important with respect to the tribological performance of MoS_2. A basal orientation, basal planes oriented parallel to the surface, is preferred because it is the easy slide direction and it is less chemically active. MoS_2 is limited to use below about 350°C. PbO is a useful solid film lubricant above this temperature and provides its lubricous properties by liquating.

An example of a hard coating which is useful for tribological applications is TiC. TiC is one of several hard, refractory carbide and nitride phases that have been deposited using other deposition processes such as ion sputtering or chemical vapor deposition. An inherent problem with these techniques is that the substrate, which is often a heat treatable alloy, is required to be held at high temperatures during the deposition process. In many cases, the length of time at temperature can adversely affect the metallurgical properties or change the dimensions of the part to be coated. Pulse laser deposition easily produces stoichiometric, crystalline thin films of these materials at ambient room temperature. Although the PLD growth rate of these materials can be quite slow because of their refractory properties, the ability to grow the films at room temperature is a major advantage. The microstructure and morphology of these coatings are very important with respect to the desired properties.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to study thin film coatings of solid phase lubricants, MoS_2 and PbO/MoS_2 and the hard phase TiC. A modified sample preparation technique for preparing cross sectional TEM samples was developed for the MoS_2 and PbO/MoS_2 films. Films of MoS_2 deposited at room temperature were found to be amorphous, while those deposited at 300°C were crystalline, had a very fine grain size, and had the basal planes oriented parallel to the substrate within the first 12-15 nm of the substrate with an abrupt upturn into a perpendicular orientation further from the substrate. Films of PbO/MoS_2 deposited at room temperature were found to have two phases present, on amorphous and the other crystalline, while those deposited at 300°C were found to be single phased and highly oriented. A technique was developed for successfully obtaining the integrated peak intensities for the severely overlapped Pb-M, Mo-L, S-K characteristic X-ray lines. Room temperature and high temperature films of TiC were found to be fully crystalline TiC with grain size of 2-10 nm.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 44, Application of Electron Microscopy to the Study

of Pulsed Laser Deposition of Thin Films for Tribological Application.

TASK: 38

TASK TITLE: Microcrack Initiation and Growth in Metals

TASK OBJECTIVE: To evaluate the application of scattered acoustic waves to detect the initiation and growth of microcracks.

SCIENTIST: Michael T. Resch, Ph.D. and Mr. Yerrapalli Shekar, M.S., University of Nebraska-Lincoln

DESCRIPTION OF WORK:

In studies of the initiation and growth behavior of fatigue microcracks it is of paramount importance to detect the existence of the cracks as early as possible during fatigue cycling. A surface acoustic wave nondestructive technique was used to detect the natural initiation of surface microcracks in highly stressed regions of aluminum lithium alloy 2090 T8 during fatigue cycling. The experimental procedure involved excitation of sub-millimeter wavelength Rayleigh waves on the surface of each specimen using prototype miniature surface acoustic wave contacting wedge transducers during fatigue cycling in a servohydraulic testing machine. The presence of specular reflections from a nucleating crack superimposed on nonspecular reflections from microstructural features surrounding the flaw was observable without signal processing at a crack depth of approximately 125 micrometers. Subsequent processing of digitally acquired signals improved the minimum detectable crack depth by at least a factor of two.

Experiments were performed combining ultrasonic reflection and laser interferometric measurements of microcrack opening behavior on large sized Larsen-type fatigue specimens. Ultrasonic measurements of crack opening were observed to augment the information obtained from the laser-optical measurements. Additionally, identical transducers were utilized to generate Lamb waves in a titanium aluminide metal matrix composite laboratory specimen with a small central hole. Numerical calculations were performed in order to examine the phase velocities of several symmetric and antisymmetric Lamb wave modes in aluminum lithium and titanium aluminide plates. Ultrasonic detection of crack growth and opening behavior was accomplished during in situ monitoring of the specimens using transmitted and reflected Lamb waves. Finally, the frequency response and energy conversion efficiency characteristics of the contacting wedge ultrasonic transducers were investigated.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 17, Microcrack Initiation and Growth in Metals.

TASK: 39

TASK TITLE: Mechanics of Natural Composites

TASK OBJECTIVE: To investigate the structure of natural composites for potential innovation in the design of synthetic fiber reinforced composites.

SCIENTIST: Joseph E. Saliba, Ph.D. and Fred K. Bogner, Ph.D., University of Dayton

DESCRIPTION OF WORK:

This project was initiated to investigate the structural efficiency of the "bessbeetle" (Odontotaenius Disjuctus) as compared to typical "man-made" or synthetic composites. Just about every structure found in nature including bone, wood, mollusc shell, and insect cuticle is a composite. Nature is able to combine and organize relatively weak constituent materials into structures that are strong, stiff, tough, and lightweight. Constituent material selection is restricted for use in natural structures so unique designs and material combinations are used to compensate. The opposite is true for man-made composites, the selection of constituent materials seems endless but we are still limited by design and processing constraints. Therefore, man-made composites may benefit from the analysis and application of novel design concepts used by nature to possibly solve current problems and create new designs and structures for the future.

The specific objective of this task was to investigate the effect of ply orientation or stacking on the structural efficiency of the bessbeetle. To accomplish the specific objective the following tasks were undertaken:

- Compare symmetric to unsymmetric laminate when subjected to tension loading.
- Compare symmetric to unsymmetric laminate when subjected to pure bending.

A synthetic laminate was configured according to standard composites design practices. An orthotropic unidirectional T300 tape with circular fibers and 60% fiber volume fraction was used. The specific ply orientation of the symmetric man-made composite was $[0/+45/-45/90]_{2S}$. The natural laminate studied was unsymmetric with the individual plies made of the same orthotropic unidirectional T300 tape but with different ply orientation. Contrary to previous beliefs, the natural composite did not assume a balance of inplane and bending properties which in essence mimic the behavior of isotropic behavior. The results of efficiency of natural composite for inplane or tension loading did not show any noticeable advantages while the pure bending case resulted in higher values for the principal stresses in the unsymmetric laminate.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 23, Mechanics of Natural Composites Ply Orientation Study.

TASK: 40

TASK TITLE: Microstructural Effect on Small Fatigue Cracks

TASK OBJECTIVE: To determine the effects of microstructure on the growth of small fatigue cracks in titanium aluminide alloys.

SCIENTIST: Kakkaveri S. Ravichandran, Ph.D.

DESCRIPTION OF WORK:

This project comprised studies on some titanium alloys and recently developed titanium aluminides to provide an in-depth understanding of the mechanisms of growth of small surface cracks in these materials. These materials are prime candidates for various aerospace applications and hence an understanding of small crack behavior is of importance both for alloy design by microstructure control, and predications of life in fatigue.

The principal theme underlying this investigation was the measurement of surface crack lengths and aspect ratios during the growth of three-dimensional small surface cracks in fatigue using a laser interferometric and photomicroscopic system at the Materials Behavior Branch, Materials Directorate, Wright Laboratory. It was shown that such measurements could be made accurately on a number of candidate alloy systems comprising titanium alloys and newly developed titanium aluminide intermetallics. Fatigue crack growth rates could be accurately calculated and were correlated to data obtained on large cracks in the corresponding materials.

Measurements of shapes of three dimensional surface cracks continuously during fatigue crack growth were made in a near-alpha titanium alloy, Ti-6A1-2Sn-4Zr-6Mo. Crack aspect ratio measurements were made for cracks growing from electro-discharge-machined (EDM) notches of different geometries (shallow or deep). The experimentally determined aspect ratio variations during crack growth were shown to be in good agreement with the expected variations in aspect ratio. The fatigue crack growth rates of surface cracks, after incorporating the variations in aspect ratio in the calculations, agreed with large-crack growth data.

Fatigue crack growth behavior of small surface cracks in α_2 (Ti_3Al) based titanium aluminide alloys such as Ti-24A1-11Nb (at%) and Ti-25Al-17Nb-1Mo were also investigated in the Widmanstatten basketweave microstructural condition. The continuous variations in crack shape induced by microstructure were measured and accounted for in crack growth rate calculations. The growth rates of large cracks were found to be similar in both the alloys. The differences in small crack behavior were attributed to the differences in the microstructural environment through which the cracks grew.

A theoretical simulation of crack shape variations in a polycrystalline titanium alloy, Ti-8Al was made. It was shown that the variations in crack shape and the corresponding errors in stress intensity factor range (ΔK) calculations can be significant in small crack investigations. A large number of experiments were done on a coarse grained (200 μm) Ti-8Al alloy to measure crack aspect ratios using a laser interferometric system. The experimentally measured aspect ratios were found to agree closely

with the expected theoretical simulated pattern of crack aspect ratio variations. After incorporating crack shape data into growth rate calculations,much of the scatter in small crack data could be reduced and the small crack behavior is similar to that of large cracks.

Fatigue crack growth data of large cracks in Ti-24Al-11Nb revealed that crack growth rates are sensitive to stress ratio. Crack growth rates in the three microstructures investigated, show higher crack growth rates at high stress ratios even after closure correction. While the crack growth rates varied little between the microstructure, the variation of crack closure was found to be sensitive to microstructure.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 80, Fatigue Crack Growth Behavior of Small and Large Cracks in Titanium Alloys and Intermetallics.

TASK: 41

TASK TITLE: Optimal Control of Material Processes

TASK OBJECTIVE: To establish a scientific methodology for optimal control of metal deformation processes.

SCIENTIST: Dennis Irwin, Ph.D. and Sunil K. Agrawal, Ph.D., Ohio University

DESCRIPTION OF WORK:

In material processing such as forging, extrusion, and rolling, the relevant material properties are the grain size and the volume fraction. These properties depend upon the time histories of temperature, strain rate applied during the process. The problem of optimal material processing is to find the time histories of strain, strain-rate, and temperature such that the material achieves the desired grain size and volume fraction. The mathematical relationships between the control variables such as temperature, strain, and strain rate and the output variables such as the grain size and the volume fraction are well-described in the literature.

The goal of this project was to analytically study the internal properties of a material as it is subjected to different time histories of temperature, strain, and strain-rate. Three different path-planning schemes were tried: (a) locally optimal methods, (b) globally optimal methods, and (c) parameter optimization method. The simulation results obtained by these techniques indicated that the desired volume fraction and the grain size can be obtained with high degrees of success. These results can be quite appealing to metallurgists, research and industrial community. In summary, this preliminary study on optimal methods in material processing demonstrated feasibility of the technique and has potentials of further research.

In a second task on this project, an optimal strategy for strain, strain-rate, and temperature

trajectories for dynamic recrystallization was developed. A set of equations due to Yada describing the grain size and percent recrystallization were transformed and partially linearized in order to obtain a description which can be used with the theory of calculus of variations to obtain strain, strain-rate, and temperature trajectories. An optimality criterion based on physical considerations was presented and necessary conditions for its optimality were derived. It was demonstrated that for this particular choice of optimality criterion the optimal strain-rate trajectory is constant. A complete solution for the optimal strain, strain-rate, and temperature trajectories was derived.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 18, An Optimal Strategy for Strain, Strain-Rate, and Temperature Trajectories for Dynamic Recrystallization, and Volume 19, Optimal Control of Material Processes.

TASK: 42

TASK TITLE: Computation of Polymer Optical Properties

TASK OBJECTIVE: To perform calculations on polymer optical materials by molecular modeling methods.

SCIENTIST: Barry L. Farmer, Ph.D.

DESCRIPTION OF WORK:

Cyclic siloxanes with cholesteryl and biphenyl mesogens reveal a host of interesting structures and properties, depending, among other things, on the number of each type of mesogen on the cycle. Molecular modeling on these systems to date has been confined to the cyclic penta(methyl siloxane) having two cholesteryl and three biphenyl mesogens. The star molecules are somewhat smaller than the cyclic systems and the MD simulations are less onerous. The star also offers the possibility of investigating the dependence of material behavior on the length of the leader between siloxane core and the cholesteryl and biphenyl groups.

A molecular dynamics study of star siloxane molecules was undertaken. Siloxane stars having four biphenyl mesogens, four cholesteryl mesogens, or two of each, demonstrated the remarkable flexibility of the allyloxybenzoate leader group connecting the siloxane core and the biphenyl or cholesteryl moieties. In each case, three mesogens aggregated fairly rapidly in the in vacuo simulations, with the fourth mesogen eventually joining the aggregate as well. Cholesteryl mesogens in the 50/50 star seemed to form an especially long-lived association, showing little tendency to dissociate once formed.

The influence of intermolecular interactions on the biphenyl torsion angle was examined for the star containing four such mesogens. Oscillations over the barrier at 90 deg, which are prevalent when the mesogens are far apart, diminish when the mesogens are close together. The biphenyl rings then

reside in energy minima near 45 deg. Occasional transitions through coplanar confirmations were observed, but there was no indication of a tendency to remain at such torsion angles.

As an additional part of this task, two manuscripts were prepared titled "Molecular Dynamics of Rigid-Rod Polymers" and "Crystal Structures and Phase Transitions of Poly (p-phenylene) Oligomers".

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 43, Molecular Modeling of Non-Linear Optical Systems.

TASK: 43

TASK TITLE: Project Management/Administration

TASK OBJECTIVE: To provide support activities necessary to establish project task orders and overall contract administration.

PROGRAM MANAGER:Milton E. Zellmer

DESCRIPTION OF WORK:

The contributive research and development project required extensive management and administration activities that were not readily charged to a specific task. These activities fell into three general categories:

1. Those contract management administrative requirements to establish planning and control procedures that applied to the project as a whole. Examples are status reporting, project management meetings, and other general overall project reporting.

2. Those management activities required to establish each of the task assignments. These activities could not be charged to the task since the task was not yet approved during this phase.

3. Recording and reporting the performance and cost for the overall management and administrative activities.

This task provided project management/administration from 26 June 1991 through 25 June 1992.

TASK: 44

TASK TITLE: MBE Process Discovery Research

TASK OBJECTIVE: Conduct experiments on autonomous discovery of PID parameters for autotuning of MBE controller.

SCIENTIST: Jeffrey J. Heyob, M.S.

DESCRIPTION OF WORK:

The research was a control study applied to a process referred to as molecular beam epitaxy (MBE) which is used for the production of very thin, multi-layer optical and electronic devices. The reduction of flux variability in the MBE process demonstrates that the flux control system can be significantly improved by the implementation of performance-adaptive methods.

This task refined the "MBE Control" program that supports process control improvement of the Molecular Beam Epitaxy (MBE) process through the Process Discovery Autotuner. The process control of interest was the MBE Knudsen Cell temperature control loop and the associated Knudsen Cell fluxes. The temperature control of the Knudsen Cells was found to be critically important toward maintaining flux beam stability during the MBE growth process. Maintaining the necessary temperature control of the Knudsen Cells required optimum tuning of the Eurotherm PID controllers associated with each of the eight Knudsen Cells mounted on the MBE system. Process first principles were autonomously extracted about each Eurotherm controlled Knudsen Cell using a robust qualitative process discovery technique called "Trapezoidal Tuning" and assembled as a knowledge base within a microcomputer. The knowledge base was then used in situ by the microcomputer to optimally tune the Eurotherm temperature control loops for all Knudsen Cell control requirements. Previously, the Process Discovery Autotuner methodology achieved 1.45% reduction of overall root-mean-square process error and a 17% reduction of overshoot error during process setpoint changes. Further enhancements to the Knudsen Cell control-loop achieved an additional 67% reduction to Knudsen Cell flux deviation.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 36, Automated MBE Control Enhancement.

TASK: 45

TASK TITLE: Electronic Properties of III-V Antimony Alloys

TASK OBJECTIVE: Determine the electrical and optical properties of III-V semiconducting materials containing antimony, such as InGaSb.

SCIENTIST: Shanthi Iyer, Ph.D., North Carolina A & T University

DESCRIPTION OF TASK:

The object of this research investigation was to determine the quality of the layers grown by liquid phase electroepitaxially grown GaSb and GaInAsSb on (100) GaSb substrates using low temperature photoluminescence. The layers were grown by the investigator at North Carolina A&T University. Near band edge structures were studied in detail. The integrated intensity of the photoluminescence peaks were determined using the quantitative fit to photoluminescence specta. The identity of the various excitonic and acceptor related transactions were determined by studying the temperature and intensity dependence of the PL spectra. The presence of free exciton and the bound excitons with FWHM in the range of 1.7-5MeV indicated the good quality of the layers grown. The number of bound excitons and acceptor related transactions decrease with the shift in the quaternary alloy composition towards the lower energy. The band to band transition starts dominating for composition with lower band gap. Temperature dependence of the band gap shift follows the empirical relation of Varshni, band gap shift being comparatively smaller for the composition with the lower band gap.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 25, Photoluminescence Study of Liquid Phase Epitaxially Grown GaInAsSb on (100) GaSb.

TASK: 46

TASK TITLE: Pitch Reactor Design and Experiments

TASK OBJECTIVE: To design and build a process control system for a pitch reactor and to conduct initial experiments on the synthesis and centrifugal separation of mesophase pitch.

SCIENTIST: Rajeev Mehta, Ph.D., AdTech Systems Research, Inc.

DESCRIPTION OF WORK:

The advent of carbon fibers, with mechanical properties now approaching the theoretical limit imposed by the strength of carbon-carbon chemical bond, was the major stimulus to the development of composites. Carbon fiber-reinforced composites represent an attempt to incorporate the exceptional mechanical properties of fiber into a structural solid. Since carbon fibers are capable of carrying mechanical load at temperatures exceeding 2200°C, the operating temperature of the composite is controlled by the softening temperatures of the matrix constituent. Even the highest temperature polymer matrices cannot perform above 350°C. Metal matrices will tolerate higher temperatures but suffer from thermal expansion mismatch and chemical reaction with the fibers. Ceramic and carbon char matrices are brittle, leading to matrix cracking and delaminations.

The main hypothesis of this research project was that a new generation of composite materials, with

interconnected graphitic reinforcing ligaments, offers potentially significant improvements in specific mechanical properties over conventional fiber-reinforced composites while greatly simplifying the required fabrication processing of engineered materials. Such novel composites could, in principle, exploit the high intrinsic mechanical properties present in carbon fibers in a way which is much less dependent on the matrix constituent.

The temperature, gas flow rate, and pressure requirements were identified for the synthesis of mesophase pitch from isotropic pitch and for the processing of mesophase pitch foams. Based on these evaluations, a control system was designed for an autoclave reactor to control pressure and gas flow rate and to safely pyrolyze the by-products of these operations.

Highly graphitic carbon foams were processed from mesophase pitch, a carbon fiber precursor. The mesogenic pitch was expanded by an elevated temperature, with foaming effected by a variety of blowing techniques. Stabilization of the nascent foams was achieved by rapid cooling. The resultant pitch foams were converted to graphitic foam via oxidative stabilization followed by carbonization and graphitization. The foam structures were studied by fluorescent microscopy and scanning electron microscope, and were found to possess an open cell structure. Wide Angle X-Ray Scattering performed on the foams indicate that a high degree of graphitization is possible.

The suitability of various foaming techniques for the foaming of mesophase pitch material was studied. In particular, the technique of producing a micro-cellular foam by saturation of the material at a temperature below its softening point under high pressure and then desupersaturation at a temperature above its softening point at atmospheric pressure was studied. Attempts to produce a micro-cellular pitch foam by this route were unsuccessful. Solubility studies on nitrogen/pitch system showed that the solubility of nitrogen in pitch at room temperature is extremely low.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 34, Graphitic Foam Processing.

TASK: 47

TASK TITLE: New Nonmetallic Materials

TASK OBJECTIVE: Investigate new lubricant and elastomeric materials.

SCIENTIST: Stacy R. Robinson, B.A.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Education Fund Mathematics Collaborative Project "GEMMA". Under this program, Dayton area industries and the Wright Laboratory Materials Directorate establish eight week programs to familiarize local area math

and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

On this particular project molecular modeling was performed in support of the development of new lubricant and elastomeric materials. A 1,,2-dichloro-1,1,2-trifluoro-2-iodoethanemolecule was built using the Chem-x program. This program allows the scientist to build molecules, graph properties, calculate geometries, and many other concepts. Energies and geometries of this molecule were calculated on the Cray super computer. Programs used included Games, Gaussian 90, Gaussian 88, etc. These programs perform computational studies. The results are correlated with experimental results to compare the programs and to get as close as possible to the ideal result.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 47, Molecular Modeling of New Nonmetallic materials.

TASK: 48

TASK TITLE: Metal Matrix Composites

TASK OBJECTIVE: Investigate new metal matrix composites.

SCIENTIST: Tim W. Voegeli, MAT.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Mathematics Collaborative Project "GEMMA". Under this program Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

On this project the processing parameters affecting the compression and extrusion of titanium alloy(TiAl-G2) were examined. Parameters examined were temperature, stress, strain rate, and strain.

From stress data compared to variations in strain rate and strain at a constant temperature generated by ALPID software, equations were developed to express the relationships between parameters. These equations were then used to generate Load vs Stroke curves and compare accuracy, computer time, and number of iterations with curves from tabulated data. Both linear and polynomial equations were used to curve fit data and a power equation was used to relate stress with strain rate.

The equation for the Zener-Hollomon parameter, Z, was used to show how a change in strain rate affects the change in temperature. The Z parameter was also used to find an equation expressing grain size in terms of stress while holding temperature constant.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 9, Processing Effect in Compression and Extrusion of Titanium Aluminide Alloy.

TASK: 49

TASK TITLE: New Optical Materials

TASK OBJECTIVE: Investigate new polymeric materials.

SCIENTIST: Anita Conway, M.S.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Mathematics Collaborative Project "GEMMA". Under this program Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

On this project supporting the Material Directorate's investigation of new polymer liquid crystals, the photochromic behavior of Poly-L-Tyrosine was examined. The goal was to probe Poly-L-Tyrosine to see the conformation changes in a macromolecule of Tyrosine photochemical inducement, and model the compound. This amino acid shows reversal phase and the peptide added is a long leader group, flexible change, and has the ability to be photochromic.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 10, Study of Poly-L-Tyrosine and Photochromic Behavior.

TASK: 50

The government canceled this task.

TASK: 51

TASK TITLE: Processing and Characterization of Nonlinear Optical Polymers

TASK OBJECTIVE: To process by vapor deposition and to characterize nonlinear optical materials.

SCIENTIST: Hao Jiang, Ph.D.

DESCRIPTION OF WORK:

The study of non-linear optics (NLO) has grown rapidly over the last few years. The prospect of improved telecommunications devices, and in the longer term, optical computers, has ensured a steady flow of new NLO materials.

Polymers with extended conjugated backbones are being widely investigated as potential waveguide devices as the extended π systems in these polymers lead to high intristic values of third order non-linear response (χ^3). Among the most studied polymers are polythiophene (PT) and polybenzene (PB) largely due to their high χ^3. Unfortunately, these polymers are hindered by their uneasy processibility.

One new method which has recently begun to be exploited is the preparation of these polymer films by plasma deposition. Using this technique, thin, dense and smooth films, ranging from a few hundred angstroms to a few microns, of above mentioned polymers can be laid down under controlled conditions. This project involved research on poly(thiophene), poly(chlorothiophene), poly(bromothiophene), poly(3-hexylthiophene, poly(furan) and poly(benzene) films made by plasma deposition.

The research consisted of three parts: (1) Plasma vapor deposit (PVD) technique for nonlinear optical polymer materials, (2) Image contrast mechanisms and topological structures of Polyethylene(PE) single crystals: low-voltage high-resolution scanning electron microscopy (LVHRSEM) and atomic force microscopy (AFM), and (3) characterization of laser irradiated C_{60} and C_{70} "buckyballs"-toluene solutions and their containing glass or quartz cell damage.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 83, Processing And Characterization of Non-Linear Optical Polymers.

TASK: 52

TASK TITLE: Phase Transformation and Kinetics in Advanced Intermetallic Alloys

TASK OBJECTIVE: To establish phase-transformation kinetics in intermetallic alloys based on TiAl and Nb_3Al.

SCIENTIST: Sarath K. Menon Eachanattil, Ph.D.

DESCRIPTION OF WORK:

This project was undertaken to obtain an understanding of the various phase transformations in niobium base alloys, specifically those containing aluminum and titanium due to their importance as potential high temperature aerospace material. Attempts at alloy development were being carried out by several researchers and studies on Ti and other alloying additions to NB-Al alloys were being done. In the course of this work, five alloys viz.,Nb-9.89Al,Nb-17.47Al,Nb-15.6Al-10.45Ti, and Nb-13.25Al-21.40Ti (all compositions in at %) were investigated by metallography, XRD, EPMA, and TEM. Experimental work in the following areas was carried out:

(a) Initially, phase boundaries involving the bcc and the Nb_3Al phase were experimentally determined and isothermal sections of the Nb rich corner of the Ti-Al-Nb system established at 1923 K, 1423 K and 1273 K.

(b) The presence of absence of B2 phase was investigated and the regions of stability or metastability in the Nb-Al-Ti phase diagram established.

(c) The morphology and crystallography of the Nb_3Al phase in a variety of Nb-Al-Ti alloys were evaluated by transmission electron microscopy (TEM).

(d) The growth kinetics of plate shaped Nb_3Al precipitates forming in three alloys were determined and;

(e) A study of the pre-precipitation phenomena, in present case, ω phase formation in quenched alloys was also carried out.

This study showed that (a)the solubility of Al in Nb is considerably less than that previously reported, (b) the high temperature bcc phase in a wide variety of Nb-Al-Ti alloys undergoes an ordering transformation to produce B2 structure and (c) the ω phase also is produced during quenching even in Nb-Al alloys. The growth kinetics of the plate shaped Nb_3Al phase (with A15 crystal structure) was measured in three alloys in the gas temperature range 1273-1573K and it was found to be very sluggish. The observed crystallographic orientation relationship between the bcc matrix and the Nb_3Al precipitate phase could be described as: $\{012\}_{A15} \| \{111\}_{bcc}; <011>_{A15} \| <121>_{bcc}$. These studies indicate the possibility of producing single phase B2 alloys containing $\approx$ 40 at% Ti and $\approx$ 20 at% Al which with further minor alloying additions may offer a good combination of properties.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 59, Phase Transformations in Niobium-Aluminum-Titanium Alloys.

TASK: 53

TASK TITLE: Growth of Tri-allyl Thiourea Cadium Chloride

TASK OBJECTIVE: To grow and characterize the new nonlinear crystal tri-allyl thiourea cadmium chloride.

SCIENTIST: Uma B. Ramabadran, Ph.D.

DESCRIPTION OF WORK:

Nonlinear optical crystals of good quality and high frequency conversion efficiency were grown by the aqueous solution temperature reduction method. The widely used potassium dihydrogen phosphate (KDP) had been previously grown as a test material and subsequently the more recently discovered nonlinear crystals of L-arginine phosphate (LAP) were grown by a similar technique. The optimum temperature range for growth was found to be 40 - 30 degrees centigrade and rate of temperature decrease was determined to be 0.5 degrees centigrade/day. Small crystals of triallyl thiourea cadmium chloride can be obtained by evaporation of the saturated solution. These crystals were then characterized by measuring the electro-optic coefficients using a Mach-Zehnder interferometer and the piezoelectric coefficients using a Michelson interferometer. The electro-optic coefficients of KDP (γ_{63}) and Strontium Barium Niobate [SBN(γ_{13})] were measured to be 11.0 pm/V, 11.07 pm/V, and 51.96 pm/V respectively and were used as a calibration for the Mach-Zehnder setup. The γ_{13}, γ_{23}, and γ_{33} electro-optic coefficients of the new materials zinc tristhiourea sulphate were measured to be 2.6 +/- .01, 1.49 +/- .11, and 1.52 +/- .12 pm/V. Its deuterated analog had corresponding values of 2.64 +/- 0.14 pm/V, 1.67 +/- .14 pm/V and 1.52 +/- .074 pm/V. The piezoelectric coefficient of SBN was determined to be 30.37 +/- 1.7 pm/V and used as a calibration for the Michelson interferometer. The values of the d_{13} and d_{23} piezoelectric coefficients for ZTS and d-ZTS were measured to be .651 +/- .2 pm/V, 7.49 +/- .66 pm/V .71 +/- .06 pm/V, and 7.78 +/- .15 pm/V respectively. A separate effort involved study of the possibility of growing a new nonlinear crystal, triallyl thiourea cadmium chloride. The powder of the compound was prepared and it exhibited second harmonic generation.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 32, Aqueous Solution Growth and Optical Characterization of Nonlinear Crystals.

TASK: 54

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 Metals and Ceramics Division and to instruct MLL engineers and scientists in the use of AE.

SCIENTIST: Itzhak Roman, Ph.D.

DESCRIPTION OF WORK:

The applicability of utilizing AE as a mean of gaining better understanding of the deformation and fracture mechanisms that operate in advanced titanium based materials was examined. Several different combinations of materials and loading modes were employed in this study, namely, tensile testing of a monolithic titanium aluminide alloy, interfacial properties study of titanium model composites, tensile testing of a Ti-24Al-11Nb/SCS-6 composite and thermal fatigue testing of Ti-24Al-11Nb/SCS-6 composite.

The work completed in a previous phase of this study, consisted of room temperature testing of a monolithic α_2 alloy Ti-25Al-10Nb-3V-1Mo and initial interfacial properties characterization of two titanium model composites,i.e. Ti-6Al-4V/SCS-6 and Ti-24Al-11Nb/SCS-6. This work centered on further characterization of the composite interfacial properties.

The interfacial region between continuous SiC fiber and titanium alloy matrix, in monofilament metal matrix composites, was characterized extensively. The study utilized SCS-6 SiC fibers and two titanium alloys: Ti-6Al-4V and Ti-24Al-11Nb. The interfacial shear strength (ISS) was determined by two different techniques, indentation and fragmentation.

Results indicate that load is transferred from the matrix to the fiber through the bonding between fiber and matrix and by friction, which is due to residual compressive thermal stresses and surface roughness. Each fiber fracture produced a multiplicity of small pieces between adjacent larger fragments, and was accompanied by distinct intense acoustic emission with a characteristic waveform.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 33, Characterization of Interfaces in Model Titanium Base Composites.

TASK: 55

TASK TITLE: MBE Manufacturing Automation

TASK OBJECTIVE: To develop a control system which improves the manufacturing capability of MBE.

SCIENTIST: Oliver D. Patterson, M.S.

DESCRIPTION OF WORK:

The primary objective of this Molecular Beam Epitaxy (MBE) manufacturing research program was to improve the consistency and quality of materials grown with MBE. Although the selection of qualities most important to optimize depends on the type of thin-film being grown, the following qualities are generally important:

1) Layer Thickness
2) Alloy Concentration
3) Dopant Concentration
4) Impurity Levels
5) Smoothness of Material Layer Interfaces
6) GA_{As} or As_{Ga} Antisites (Ga occupies As location or vice versa)
7) Vacancies (Missing atom)
8) Dislocations (Missing line of atoms)
9) Oval Defects

Methods for improving the qualities #1,#2,#3, and #5 were addressed.

The improvement effort conceptually divides into three areas: improvement of flux control, real time control using an expert system and advanced sensor feedback, and material system modeling for the purpose of developing new recipes quickly. The focus of the first level is to improve the precision and tracking of the variables, flux, and substrate temperature. The second level consists of an expert system that uses sensors to monitor the status of the product in order to generate a process plan in real time. The third level features a continuously evolving neutral network model of the process which is used to recommend the recipe and command inputs to achieve a desired product goal. All three levels require models of the process which are updated using automatic process identification experiments. The three levels of the system are described and experimental data used to illustrate the impact of select modules. The system has potential to eliminate product variability to the accuracy of the sensor data.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 50, Progress Towards a Comprehensive System for Molecular Beam Epitaxy.

TASK: 56

TASK TITLE: Homogenization Studies on an Ingot Metallurgy Gamma-TiAl Alloy

TASK OBJECTIVE: To develop a generic understanding of the mechanisms and kinetics involved in second phase dissolution in intermetallics during homogenization.

SCIENTIST: Rama Nekkanti, Ph.D.

DESCRIPTION OF WORK:

Many of the near-gamma alloys being characterized at present are being synthesized via ingot metallurgy methods. It has been found that the resulting microstructures after such processing routes are often banded. Resulting from the double-cascading peritectic reactions that characterize the phase equilibria around the equiatomic titanium aluminum composition, the segregation has been found to be similar in extent in both binary multicomponent alloys. Because of the possibly adverse effect of such heterogeneities on the mechanical properties of these inherently brittle alloys, efforts were underway to define homogenization heat treatments to eliminate the banding.

The homogenization kinetics of a near-gamma titanium aluminide was determined by heat treating small differential thermal analyzer (DTA) specimens in a highly controllable, low thermal inertia differential thermal analyzer. The time for total dissolution of gamma grains varied by approximately two orders of magnitude for temperatures between 10 and 86°C above the alpha+gamma alpha transus. Comparison of these observations to the relative rates derived from a stationary interface type model indicated that the dissolution process is not limited by diffusion, but more likely by some form of interface reaction.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 35, Homogenization Kinetics of a Near-Gamma Titanium Aluminide Alloy.

TASK: 57

TASK TITLE: Interface Properties in Advanced Composites

TASK OBJECTIVE: To develop test and analysis techniques to determine interface properties in advanced aerospace composites.

SCIENTIST: Mark Waterbury, Ph.D.

DESCRIPTION OF WORK:

An automated digital deformation analysis (ADDA) system was developed that uses image correlation analysis to determine displacements and strains on surfaces. The system was implemented on a Macintosh™ microcomputer with images captured by an Eikonix 1410 digital imaging camera. The method determines the locations of reference points in images of the specimen before and after deformation and can make use of an optical fiducial grid to decrease the system sensitivity to surface degradation. Images are digitized from photomicrographs that can be made with optical or electron microscopy, provided that they are dimensionally stable, allowing measurements to be made over very short gage lengths. A test protocol to validate the ADDA system and investigate the influence of various error sources was developed.

Preliminary investigations into the single fiber fragmentation test applied to ceramic fiber reinforced intermetallic matrix composites were performed to prepare for an in-depth effort. Some of the fundamental differences between fragmentation in an intermetallic matrix and thermoset and thermoplastic matrices were identified. An approach to understanding the failure phenomena in Intermetallic Matrix Composites (IMC's) was determined.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 42, Development of an Automated Digital Deformation Analysis System and Single Fiber Fragmentation Testing in Intermetallic Matrix Composites.

TASK: 58

TASK TITLE: Microcrack Initiation Detection in Metals

TASK OBJECTIVE: To optimize techniques for the application of scattered acoustic waves to detect the initiation and growth of microcracks in metals.

SCIENTIST: Michael T. Resch, Ph.D., University of Nebraska-Lincoln

DESCRIPTION OF WORK:

Miniature contacting surface acoustic wave wedge transducers were designed and fabricated for the purpose of generating and receiving surface acoustic waves to experimentally detect the initiation and growth of microcracks in metals. These devices were optimized using well established principles of physical acoustics. In order to achieve additional optimization of the ultrasonic testing system, variable impedance matching networks were designed and fabricated in order to minimize reflected signals at the interface of the signal generation equipment and the transducer terminals. Measurements of the efficiency of these devices determined that these matching networks increase the global efficiency of the crack detection system by approximately 25%. Also, an automated technique was developed for measuring the complex impedance of the wedge transducers under computer control, including computerized data acquisition for waveform retrieval and analysis.

Evaluation of the ultrasonic detection system was achieved by developing a completely automated technique for detection of small cracks using reflected ultrasonic acoustic waves. This technique included remote control of the servohydraulic testing system and the ultrasonic testing system with a single microcomputer in addition to fully automated computerized data acquisition and storage of the ultrasonic signals. A simple threshold measurement of the maximum detected ultrasonic amplitude of reflections from the vicinity of the high stress region of the hourglass shaped specimens was used to detect the presence of naturally initiated microcracks. A significant improvement can be achieved by

using two dual element transducer arrays so that both sides of a specimen could be interrogated by a single set of ultrasonic electronic equipment. Finally, application of the technique was demonstrated by using the automated system to detect naturally initiated microcracks in hourglass shaped specimens of aluminum alloy.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 71, Microcrack Initiation Detection in Metals.

TASK: 59

TASK TITLE: Thermomechanical Fatigue in Metal Matrix Composites

TASK OBJECTIVE: To evaluate the fatigue behavior of titanium metal matrix composites under combined thermal and mechanical cycling.

SCIENTIST: Richard W. Neu, Ph.D.

DESCRIPTION OF WORK:

In this project, the framework for developing a mechanistic life prediction model for metal matrix composites (MMCs) was defined. Mechanistic thermomechanical fatigue life prediction models are important for several reasons. For one, they predict fatigue life under any general stress-temperature history experienced by the composite. Therefore, a comparison of the severity of different stress-temperature histories can be handled. Mechanistically-based models also can indicate why failure will occur under a particular stress-temperature history. This leads to a better understanding of the material behavior, which in turn identifies what aspects of the material need to be improved to sustain a given history.

This project consisted of two parts: development of a mechanistic thermomechanical fatigue (TFM) life prediction model for metal matrix composites, and experiments on SCS-6/ß21S, a titanium matrix composite with silicon carbide fibers. The mechanistic thermomechanical fatigue life prediction model accounts for the dominant damage mechanisms observed in metal matrix composites. These mechanisms were described by a damage model which accounts for the constituent stress and strains as well as the kinetics of the environmental degradation of the matrix and fibers under different applied stress-temperature histories. The model was able to successfully predict the thermochemical fatigue (TMF) life and the expected dominant damage mechanism of SCS-6/Ti-24Al-11Nb$[0]_8$ for a number of cycle types, including in-phase and out-of-phase TMF, and isothermal fatigue with and without stress holds. Experiments were conducted on SCS-6/ß21S for three different laminate orientations: $[0]_4$, $[0/90]_s$, and $[0/\pm45/90]_s$. Stress-controlled in-phase and out-of-phase TMF tests were conducted at 150°C and R=0.1. A rough correlation of the fatigue lives for the different laminate orientations was obtained by normalizing the maximum applied stress(S_{max}) by the ultimate tensile strength at the temperature

where S_{max} occurs. TMF lives can be predicted within a factor of three for out-of-phase loading, which is controlled by environment-assisted matrix cracking. There was more scatter in the in-phase lives, which could be attributed to sensitivity of the fatigue life on the fiber volume fraction.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 60, Thermomechanical Fatigue in Metal Matrix Composites: Mechanistic Life Prediction Model and Experiments.

TASK: 60

TASK TITLE: Microstructure/Property Relationships in Intermetallic Eutectics

TASK OBJECTIVE: Conduct thermomechanical processing to control the microstructure of advanced intermetallic eutectic systems and determine the microstructure/property relationships in these materials.

SCIENTIST: Sharvan Kumar, Ph.D.

DESCRIPTION OF WORK:

Two-phase "eutectic composites" are of interest for high temperature applications because the microstructures are thermodynamically stable, exhibiting no interfacial reactions and frequently resist coarsening upon exposure to elevated temperatures. An added advantage is that such composites are made in a single step thereby circumventing problems associated with the fabrication of conventional continuously reinforced composites.

A two-phase eutectic alloy of composition Cr-6.5 at% Hf was cast, homogenized and isothermally forged into a pancake using a height reduction of 3.5. The cast homogenized and forged microstructures were characterized via optical, scanning and transmission electron microscopy. The characteristic eutectic microstructure observed in the casting was broken down by the hot working operation. Specimens were machined from forging and subjected to a variety of heat treatments to understand the stability of the microstructure after hot working. These studies showed the C14 phase to be stable at room temperature and in equilibrium with Cr. A fine precipitate was observed in the Cr phase and was tentatively identified as C15 Cr_2Hf. Heat treatment at 1473K for 2h resulted in the transformation of some of the C14 phase into the 4H structure.

Compression specimens cut from the forging were evaluated in the temperature range 293K-1473K. The observed response is characteristic of BCC alloys. Four-point bend tests were conducted as a function of temperature and strain rate to obtain an appreciation for the ductile to brittle transition temperature. Notched bend specimens were tested as a function of temperature to obtain the variation

of fracture toughness with test temperature. Toughness was ~7MPa√m at 239K and increased almost linearly with temperature to ~15MPa√m at 873K. The resulting fracture surfaces were examined in the scanning electron microscope. The measured properties were correlated with the observed microstructures and an understanding was obtained for microstructural evolution during heat treatment of this alloy.

The detailed project description, method, results and discussion are reported in Contributive Research and Development, Volume 39, Microstructure-Property Relationships in a $CrCr_2Hf$ Alloy.

TASK: 61

TASK TITLE: Theoretical Analysis of Semiconductor Surfaces

TASK OBJECTIVE: Determine the values of kinetic parameters required for process modeling of Molecular Beam Epitaxy (MBE) by performing atomic scale simulations of semiconductor surface structures.

SCIENTIST: Shashikala Das, Ph.D.

DESCRIPTION OF WORK:

For the past several years the surface structures of binary polar semiconductors such as GaAs have been of great interest due to the important role they play in the epitaxy of thin film heterostructure materials and opto-electronic devices.

A semi-empirical self consistent molecular orbital program (MOPAC) and its solid state version MOSOL was used for determining the energetics of the surface atoms on the silicon and gallium arsenide (111),(100), and surface substrate. Total energy calculations performed for different cluster sizes to determine the difference between the binding energies of an arsenic atom absorbed on the (111) surface of GaAs at the hexagonal-closed-pack (T_4) and zincblende(Zb) sites indicated that the surface layer termination and the size of the cluster were very important in determining the binding energy accurately. The binding energies of As atoms at T_4 and Zb sites were found to be of the same order of magnitude when about six layers of GaAs were considered. A total energy calculation on large cluster indicated that the binding energy of three As atoms at the regular Zb surface sites is larger than the same 3 As atoms at the ($\sqrt{19}$ X $\sqrt{19}$) surface reconstruction site by a large amount (2.8ev) when six atomic layers are included in the calculations, supporting the recently proposed model for the ($\sqrt{19}$ X $\sqrt{19}$) reconstruction of the surface, which was based on scanning tunneling microscopy observations. The calculated sublimation energies for Si, Ga, and As atoms on surface were compared with the calculations of Krishnamurthy et. al. performed using Green function technique and are in good agreement for some lattice sites but are not so good for others.

The implications of these results for MBE simulations using the Monte Carlo method and the usual stochastic models were addressed. The activation energy for the Si surface atom diffusion and the energies of surface group atoms necessary for Monte Carlo simulations for the (111) surface of silicon were determined. The accuracy and limitations of the method were addressed. The work established that semi-empirical approaches of the kind adopted here are appropriate for such surface studies from consideration of both speed and accuracy.

The detailed project description, method, result, and discussion are reported in Contributive Research and Development, Volume 68, Theoretical Analysis of Semiconductor Surfaces: GaAs and Si.

TASK: 62

TASK TITLE: Deformation in Advanced Metallic Compounds

TASK OBJECTIVE: To investigate the extent and effect of localized deformation in advanced metallic compounds.

SCIENTIST: Sion M. Pickard, Ph.D.

DESCRIPTION OF WORK:

Continuously-reinforced titanium-based metal matrix composites (MMC's) have the advantages of improved specific strength and stiffness over Ni-base superalloys, and are capable of higher operating temperatures than are possible with monolithic Ti-based alloys.

Two Ti-based composites containing SCS-6 SiC fibers were characterized microstructurally and used as model systems in which to study the influence of fiber volume fraction (V_f) and cooling rate of residual stresses and strains developed after consolidation. A novel matrix etching technique was used to measure the axial fiber residual stress in the composite, and analysis of electron back scattered channeling patterns was employed as a means of measuring local plastic yielding in the matrix. In general, measurements of elastic residual fiber stress were in good agreement with analytical model predictions. However, the measured plastic strains were higher than those predicted when yielding occurs in the matrix during cooling due to CTE mismatch.

The detailed project description, method, results and discussion are reported in Contributive Research and Development Final Report, Volume 86, An Experimental Study of Residual Stresses in Ti Based SCS-6 Continuous Fiber Composites.

TASK: 63

TASK TITLE: Polymer Morphology

TASK OBJECTIVE: To determine the degree of order in pneumatic liquid crystalline rigid-rod and ladder polymer systems.

SCIENTIST: Daniel P. Heberer, Ph.D.

DESCRIPTION OF WORK:

A morphological investigation was conducted on two different families of intrinsically rigid rod materials. Propyl sulfonate groups were added to a sulfonated poly(benzobisimidazole) polymer in an attempt to create a "self-doping" system. The addition of the propyl sulfonate side groups had a pronounced affect on the material's solution and solid state behavior when compared to the poly(benzimidazole) homopolymer. The behavior was also a strong function of the computer-ion; the sodium salt exhibited an anisotropic liquid crystalline phase in water, while the free acid was insoluble in water and did not exhibit a liquid crystalline phase. The sodium salt exhibited an additional peak in the X-ray diffraction pattern which was attributed to a lamellar assembly of the polymer. The conductivity of the free acid was higher than that of the sodium salt, and the conductivity was increased when the sample was oriented.

The synthesis of copolymers of PBT (poly(benzobisthiazole)) and dihydroxy PBT was performed to increase the planarity of the polymer backbone by the creation of a pseudo-ladder structure and thereby increase the conductivity of the system. The addition of hydroxyl pendants changes the molecular packing in the crystalline sample. The (200) and the (010) planes were both affected by the copolymer composition, with the (200) plane increasing from 5.895 Å to 6.482 Å and the (010) plane decreasing from 3.539 Å to 3.404 Å upon going from the PBT homopolymer to the dihydroxy PBT homopolymer. The c-axis remained unchanged. The resulting changes in the crystalline packing, however, have little effect on the conductivity of the system with all conductivity values being in the very low range of 10^{-9}S/cm^{-1}.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 79, A Morphological Investigation of Intrinsically Conducting Rigid Rod Polymers.

TASK: 64

TASK TITLE: Molecular Dynamics of Grafted Rigid-Rod

TASK OBJECTIVE: To model the dynamical behavior of graft-copolymers composed of rigid-rod backbone with flexible coil pendents.

SCIENTIST: Steven Trohalaki, Ph.D.

DESCRIPTION OF WORK:

Molecular dynamics simulations of bulk systems of single-component molecular composites were performed in order to predict structure-property relationships and to help rationalize experimental results. The first system was a 'hairy-rod' molecular composite, a graft copolymer composed of a poly[*p*-phenylene benzobisthiazole](PBZT) rigid-rod backbone with flexible meta poly[aryl ether ketone](*m*PEK) pendant chains (the 'hairs'). A control simulation, consisting of unsubstituted PBZT rods, was also performed. The hairy-rod and control systems were simulated at two densities, 0.47 and 0.7 g/cm^3. The second molecular composite, simulated at a density of 1.0 g/cm^3, consisted of the same PBZT and *m*PEK subunits, but arranged as a block copolymer. The control simulation in this case consisted of *m*PEK homopolymer at the same density. The molecular-composite concept, conceived to circumvent solubility problems and improve compressive strength of PBZT, relies on an even distribution of rods in a coil-like matrix. In the case of the hairy rods, radical distribution and orientation-correlation functions as well as orientation-correlation volumes imply that the *m*PEK chains greatly reduce the correlation of rod orientation without altering rod spacing.

Ab initio molecular orbital geometry optimization was performed on several model compounds for methyl-substituted PBZT, a candidate for cross-linking via ion implantation and whose fibers have displayed enhanced compressive strength. Barriers to phenyl rotation were calculated for model compounds of unsubstituted and methyl-substituted PBZT, a rigid-rod polymer. Using the 6-31G* basis set, the barriers were calculated to be 4.0, 2.6, 2.3, and 2.6 kcal/mol for unsubstituted *o*-methyl, *m*-methyl, and *o*, *m*-dimethyl phenylbenzthiazole, respectively. The barrier calculated for unsubstituted benzthiazole is 3.6 to 5.3 times larger than those found from semi-empirical calculations on similar model compounds. Methyl substitution at the ortho position lowers the barrier by about one-third and shifts the barrier location from 90° phenyl torsion found for unsubstituted and *m*-methyl benzthiazole to a 180° phenyl torsion, i.e. a planar conformation with the methyl group near the sulfur. Methyl substitution at the *meta* position leaves the rotational potential virtually unchanged. Calculated bond lengths and angles of optimized conformations were generally in good agreement with those found from x-ray crystallography. Calculated torsional potentials imply that the discrepancy between theoretical and experimental torsions is due to crystal-packing forces.

Again using the 6-31G* basis set, intra-molecular hydrogen bonds were investigated for imidazole-substituted PBZT and for imidazole-substituted poly[*p*-phenylene benzobisthiazole](PBI) model compounds, both of which are models for pseudo-ladder polymers. Such ladder polymers have received attention as candidates for conductivity and non-linear optics applications. The differences in energy between isomers, where a hydrogen bond is expected in one but not in the other, were calculated to be 13.7 and 12.7 kcal/mol for the PBI and PBZT pseudo-latter model compounds, respectively. Repeating the optimization with the basis set augmented with diffuse functions on nitrogens and on hydrogens bonded to nitrogen yielded energy differences larger by only 0.1-0.2 kcal/mol. In addition to the hydrogen-bond energy, these energy differences contain a contribution due to the isomerization of imidazole moiety that has yet to be measured. In any case, these results imply that the pseudo-ladder conformation, i.e. the hydrogen bonded conformation, is considerably more stable than the rod-like confirmation.

The detailed project description, methods, results, and discussion are reported in Contributive

Research and Development Final Report, Volume 77. Molecular Dynamics Simulations of Single Component Molecular Composites Consisting of Flexible Coil and Rigid-Rod Subunits and Ab Initio Molecular Orbital Calculations of Model Compounds for Rigid-Rod and Pseudo-Ladder Polymers.

TASK: 65

TASK TITLE: Graphite Foam Processing

TASK OBJECTIVE: To identify a foaming process and to investigate the processing variables affecting the cell structure and mechanical properties of graphitic foams derived from pitch.

SCIENTIST: Rajeev Mehta, M.S., AdTech Systems Research

DESCRIPTION OF WORK:

Carbon fiber-reinforced composites represent an attempt to incorporate the exceptional mechanical properties of fiber into a polymer, metal, carbon char, or pitch matrix. The fibers act as the major load-bearing elements and the matrix serves to transfer load to the disconnected fiber network. However, there are two important drawbacks in carbon fiber-reinforced composite technology, namely the complexity of the fabrication process and the limiting properties of the matrix elements. The main hypothesis of this on-going research program is that a new generation of composite materials, with interconnected graphitic reinforcing ligaments, offers a simplified processing alternative to the conventional carbon-fiber reinforced composite technology, with the potential of significant improvements in specific mechanical properties.

Reticulated foams, which display such an interconnected ligament network, are readily synthesized from polymers, and represent the reinforcing architecture we sought. Due to their amorphous carbon morphology, however, these foams have relatively low moduli, much lower than one would expect in a aligned graphitic morphology. If the cellular graphitic ligament micro-structure is created from the thermotropic mesophase pitch, the ligaments of these reticulated foams, rather than being amorphous, should possess a morphology similar to that in advanced carbon fiber.

The objectives of this research were to describe three different ways of foaming mesophase pitch, and to demonstrate that a very high degree of graphitization can be achieved through high temperature treatment of these mesophase pitch foams.

The first technique used was the "microcellular foaming" technique. A "microcellular foam" is produced by first saturating a polymer with a gas under high pressure and then utilizing the thermodynamic instabilities that result when the temperature is raised and the pressure is reduced to produce the bubbles. The sudden instability instantaneously nucleates a myriad of bubbles with a subsequent uniform distribution. The bubbles are then allowed to grow to the desired size, at which

time the process is halted. The first foaming technique was attempted to obtain micro-cellular mesophase foams, i.e. with cell-sizes less than 10 microns.

The second foaming technique used was to employ a chemical blowing agent, barium salt of 5-Phenyltetrazole, as a source of gas. The foams obtained by the second technique were open-celled foams and the cell-sizes were fairly uniform (of the order of 100 microns).

The third foaming technique used for the mesophase pitch was to supersaturate the molten pitch at a high pressure and then to release the pressure accompanied by fast cooling. The foams obtained by the third foaming technique were reticulated foams.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development, Volume 48, Graphitic Foam Processing.

TASK: 66

TASK TITLE: Gas Layer Protection of Carbon-Carbon Composites

TASK OBJECTIVE: To model the oxidation behavior of Carbon structural materials in the presence of protective gas layers which are in thermodynamic equilibrium with the hot carbon surface.

SCIENTIST: Sarwan S. Sandhu, Ph.D., University of Dayton

DESCRIPTION OF WORK:

The principal objective of a theoretical investigation in the Materials Directorate was to find practical ways to reduce carbon oxidation mass loss from a low density (less than 2 gm/cm^3) carbon-carbon composite which exhibits outstanding elevated temperature, mechanical properties. The investigation on this project dealt with reduction of carbon oxidation mass loss from a carbon tube interior surface using a protective gas boundary-layer flow containing carbon monoxide. Transport of chemical species by convection in the axial direction and diffusion in the radial direction was modeled.

The gas phase removal of oxygen by reaction with carbon monoxide in the presence of water vapor was accounted for as oxygen diffuses towards the tube interior surface through the protective gas boundary-layer flow. The chemical species continuity equation coupled with the thermal energy equation was numerically solved for a non-turbulent flow to predict two-dimensional chemical species concentration and temperature profiles. Local and cumulative carbon mass loss rates were computed as a function of the tube axial distance.

Maximum local carbon mass loss rates were of the order of $3^{*}10^{-9}$ $gm/(cm^2\text{-}s)$ and $25^{*}10^{-9}gm/(cm^2\text{-}s)$, respectively, for the protective (i.e. carbon monoxide present in the boundary-layer flow at the inlet

to the carbon tube) and nonprotective (i.e. no carbon monoxide present in the boundary-layer flow at the tube inlet) cases at inlet parametric values of the average flow velocity of 100 cm/s, central flow oxygen and water mole fractions of 0.005 and 0.05, respectively, protective flow carbon monoxide mole fraction of 0.05, temperature of 1600K, and pressure of 1 atm.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 73, (Theory-Report II) Carbon-Carbon Surface Oxidation Protection.

TASK: 67

The government canceled this task.

TASK: 68

TASK TITLE: Material Behavior Modeling of Metallic Systems

TASK OBJECTIVE: To establish quantitative techniques for predicting microstructural changes of metallic systems during hot deformation processes.

SCIENTIST: Tim W. Voegeli, MAT.

DESCRIPTION OF WORK:

Scientific techniques from chaos theory have been found to have applications to certain dynamical systems. If the processing of metals is such a system then the methods recently discovered to describe chaotic systems can be used to better understand and describe their behavior.

The primary task was to establish quantitative methods for predicting microstructural changes of metallic systems during hot deformations processes.

Fractal analysis is the geometry used to illustrate the structure of chaotic systems. Computer programs demonstrating a variety of ways generating fractal shapes were investigated. Some of these methods include iterated function systems (IFS), the chaos game, Lindenmayer-systems (turtle graphics), and cellular automata. Concepts such as bifurcation theory, steady state attractors, sensitivity to initial conditions, and self-similarity are but a few characteristics of chaotic systems. Using the properties of chaos, it is possible to give both a qualitative and quantitative analysis of non-linear dynamical phenomena.

This project began to examine the underlying concepts of chaos theory, fractals, and their applications. To date, most applications have been in the areas of turbulence and mixing of substances.

If the processing of metals is found to match conditions of chaos then it is just a matter of time before the model is found to exhibit microstructural changes in a significantly more comprehensive manner.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 62,Quantitative Techniques for Predicting Microstructural Charges of Metallic Systems.

TASK: 69

The government canceled this task.

TASK: 70

TASK TITLE: Research on Optical Sensors for Molecular Beam Epitaxy

TASK OBJECTIVE: To determine the relevant process variables which can be measured by ellipsometry during the growth of device layers using MBE.

SCIENTIST: Sonya Cong, Ph.D., Technology Assessment & Transfer, Inc.

DESCRIPTION OF WORK:

MBE (molecular beam epitaxy) is a thin film deposition process where, under ultrahigh vacuum conditions ($\sim 10^{-11}$Torr), atomic or molecular beams react on the clean surface of single-crystalline substrate to form an epitaxial film. This technique enables the design and fabrication of novel materials and devices. During the MBE process, control of the property and structure for deposited film, such as alloy composition and thickness, is extremely critical. Optical techniques have been widely employed as real-time probes for the study of thin film depositions by MBE and other growth techniques.

In this project, real-time ellipsometry was used as the insitu sensor for the study and control of the MBE process. Ellipsometry is an optical technique which deals with polarized light. Due to its nondestructive and nondisturbing nature, ellipsometry is greatly favored as an insitu monitoring technique. By analyzing the change of polarization state of a polarized light upon its reflection from a sample surface, the dielectric property and structure of the sample can be assessed. Using ellipsometry measurements during MBE film growth, the film thicknesses, alloy composition and the layered structure can be determined instantaneously at each growth time. The ultimate goal is to send information of the instantaneous film status to the controlling computer which can, according to this information, make a decision on the adjustment of growth parameters required for a future time.

Although the main effort was focused on low temperature GaAs(LT-GaAs) thin films, other thin

film/substrate systems were also studied including InGaAs films on InP substrate and InGaAs films on GaAs substrate. An existing Geartner single wavelength ellipsometer was modified to include the spectroscopic capability.

In the research of LT-GaAs, real time ellipsometry was employed to achieve reproducible film properties and to study the microstructure of such films. LT-GaAs has been demonstrated to be a useful high resistivity buffer layer for subsequent growth of a variety of epitaxial device layers. It has proven difficult to reproducibly grow these films due to low ($\sim$250°C) substrate temperatures involved and the need for tight III/V flux control. Real time ellipsometry was used to reproducibly set the substrate temperature through a study of the As capping process on a GaAs surface. A hysteresis of $\sim$200°C occurred in the temperature at which As was deposited and subsequently removed. Subtle changes occur in the ellipsometric response in this temperature window which suggests minimal variation in the adsorbed As behavior on the GaAs surface. A point occurs in the ellipsometric response which characterizes that temperature at which As deposition begins for a given As overpressure. Using this signature, reproducible LT-GaAs films were grown and followed by ellipsometry. A uniform growth spiral was initially obtained indicating the formation of a homogeneous LT-GaAs layer. The ellipsometric response deviates substantially from the uniform growth spiral as the film thickness exceeds a critical value and may correspond to the formation of an amorphous or polycrystalline structure. Variations in the index for LT-GaAs verses growth temperature and As over pressure were determined from the growth spirals.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 85, Process Control of Molecular Beam Epitaxy By Real-Time Ellipsometry.

TASK: 71

TASK TITLE: Acoustic Microscopy for NDE

TASK OBJECTIVE: To assess the capability of acoustic microscopy for NDE of advanced materials such as metal matrix composites.

SCIENTIST: Peter B. Nagy, Ph.D.

DESCRIPTION OF WORK:

The most unique feature that distinguishes acoustic microscopy from all other types of microscopy is the origin of the contrast in the mechanical properties of the specimen. A low-frequency scanning acoustic microscope was designed and built for ultrasonic inspection of metals, ceramics, composites, and microjoints of these materials. The reflection-type microscope measures the Rayleigh wave velocity and attenuation of the specimens, therefore it is sensitive to surface or near-surface properties, only. In order to expand the field of application for the instrument, it was designed so that it could be used

as a conventional high-frequency C-scan imaging device in double-transmission or backscattering mode of operation as well.

The microscope operates in the 20-to-100 MHz frequency range. The finest scanning resolution is 0.5 mils (12.5μm) and the scanning area can be varied between 0.1"x0.1" and 2"x2". The image resolution is 200 x 200 pixels with 8 bit resolution, although the gray-scale resolution on the VGA monitor and the laser printer is limited to 6 bit. The microscope is controlled by a 486 AT personal computer equipped with a large-capacity hard disk for convenient data storage.

The instrument was successfully tested in both basic modes of operation. Initial results demonstrate that the reflection-type scanning acoustic microscope is particularly useful in studying weak charges in the micro structure which are accompanied by significant velocity variations(e.g., polycrystalline grains) while the C-scan imaging mode is more sensitive to scattering discontinuities(e.g., individual fibers embedded in a matrix).

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development, Volume 69, Acoustic Microscopy for NDE.

TASK: 72

TASK TITLE: Quasi-Particle Polymeric Systems Based on Air Force Poly(benzobisthiazoles) (PBX)

TASK OBJECTIVE: To explore the concept of in-situ generation of "quasi-particles", i.e., stable and mobile electrons (free radicals, diradicals/quinoid structures, and carbanions), and positive "holes" (empty pi-orbitals), in PBX polymers.

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

DESCRIPTION OF WORK:

The objective of this project was to prepare inherently conducting polymers. The incorporation of electroactive functionalities in the rigid-rod polymer backbone was investigated as a route to the preparation of inherently conducting polymers. The electroactive functionalities may be oxidized to generate a radical cation suitably modified to create a charged species, and the mobility of this species along the polymer chain could lead to its electrical conductivity behavior. To achieve this goal, the preparation of electroactive moieties such as, di-and triphenylamines and triphenylmethanols was undertaken. The report on the work describes the preparation and properties of the di- and triphenylamines based monomers, model compounds(benzothiazoles and benzoxazoles) and polymers. The preparation and the problems encountered in the synthesis of the triphenylmethanol monomers are also described.

The detailed project description, method, results, and discussion are reported in Contributive

Research and Development Final Report, Volume 88, Synthesis of Novel Triphenylamines and Triphenylmethanols for Inherently Conducting Polymers.

TASK: 73

TASK TITLE: Insitu Process Control Research

TASK OBJECTIVE: Implement autonomous state space parameter acquisition of process non-linearities, including required support elements, for Qualitative Process Automation research.

SCIENTIST: Jeffrey J. Heyob, M.S.

DESCRIPTION OF WORK:

The refinement of the "MBE Control" program resident on a Macintosh IIfx microcomputer progressed in several facets toward the improvement of the Molecular Beam Epitaxy (MBE) process.

MBE flux stability was addressed beyond its controllability through temperature by a proportion-integral-derivative(PID) control-loop. Flux data analysis gave support to a hypothesis that some of the residual flux instability might be due to power supply harmonics or powerline disturbances driving long term Knudsen Cell thermal oscillations on the order of ten minute periods and directly influencing flux stability. Preliminary tests were run to quantify this hypothesis by improving the stability of the PID temperature controller and power supply that controls the energy input to the Knudsen Cell thermal control loop.

Apple Computer's System 7 release and the corresponding "Think C" compiler upgrade to version 5 were installed in the MBE development microcomputers for the expanded multi-tasking facilities and support for interapplication communication (IAC). Multi-tasking and IAC will allow the MBE instrument interfaces, the Process Discovery Autotuner, beam equivalent pressure calibration, MBE growth control, and other supervisory processes to be developed as separate programs that communicate with each other. Individual program development promises shorter design cycles and simpler program troubleshooting.

Modular approach in the development of the MBE control system provides a protected environment for each program's unique and often complex data structures, and also provides a consistent data communication channel to any other programs required for data inter-action in the multi-tasking MBE control environment. The IAC connections between the various program modules are very flexible to allow making, breaking, and re-establishing data links with any combination of programs with as many as 128 simultaneous data links. Specific data flow through the system achieves better organization during special sequences of the MBE operation, such as during setup, tuning,

calibration, or growth, by having non-involved program modules idle.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development, Volume 70, Insitu Process Control Research.

TASK: 74

TASK TITLE: Nonlinear Optical Characterization of Biopolymers

TASK OBJECTIVE: To characterize the chi(2) and chi(3) properties of bipolymers being developed in the materials laboratory in-house research programs.

SCIENTIST: Rama Vuppuladhadium, Ph.D.

DESCRIPTION OF WORK:

A novel technique was developed to study the third order nonlinear susceptibility coefficient by utilizing the intensity dependent dispersion relation of surface plasmons. Surface plasmon method is suited for investigation of optical nonlinearities in ultrathin films, such as monolayer and multilayer systems. Surface plasmons are electromagnetic surface waves which propagate along the interface between a metal and a dielectric material such as organic films. The third order nonlinear coefficient $\chi^{(3)}$ is a very important optical property of the materials because of its contribution to numerous nonlinear optical process. The degenerate third order nonlinear susceptibility has shown a growing interest in all-optical signal processing. The nonlinear changes in the dielectric constants $\epsilon(\omega)$ also contribute to well known effects such as self-focusing, self-trapping, and self-bending of light and phase magnitude. This research developed a novel technique to measure both magnitude and sign of $\chi^{(3)}$ using the intensity-dependent dispersion relation of surface plasmons.

Surface plasmons propagate along the metallic surface with a maximum intensity at the surface and exponentially decaying into the space perpendicular to the surface. One can excite these surface plasmon by coupling the light through the prism (called attenuated total reflection) or through a grating. The strong enhancement at the surface is correlated to the strong reduction in the reflected intensity, indicating the complete transformation of the incoming light to surface plasmons. If the metallic film is further coated with nonlinear media, the degenerate third order nonlinear susceptibility $\chi^{(3)}$ causes a change in intensity of the waveguide mode, which results in the change in the resonant coupling angle. In this effort, the prism coupling method was used to measure the third order nonlinear susceptibility of PDA-4BCMU and Siloxane films. The results obtained from these films appear to be thermal rather than the electronic excitation. A Z-scan experiment was also set up to measure the $\chi^{(3)}$ of these films and the liquids.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 47, Measurement of Third Order Non-linear Susceptibilities of

Surface Plasmons.

TASK: 75

TASK TITLE: EO Polymer Research: Thermally Stable 2nd Order Materials

TASK OBJECTIVE: Synthesis of thermally stable 2nd order materials.

SCIENTIST: Ram Kannan, Ph.D.

DESCRIPTION OF WORK:

Chromophores for second-order guest host materials are continually being designed, synthesized, and evaluated with the expectations of improved second order non-linear optical performance. All second order chromophores consist of an electron donor and acceptor functionalities separated by several double bonds, as in 4-Niotroaniline. Since most of these containing traditional donors and acceptors separated by a polyene structure are not likely to meet the requirements of Air Force applications, particularly thermal stability at high temperatures, the polymer branch of Wright Laboratories/Materials Directorate initiated a program to explore the suitability of compounds possessing π-deficient heterocycles 2 as donors and acceptors respectively.

This research consisted of the synthesis of several pyridines and diazines containing thiophene nuclei. The evaluation of NLO properties on nearly 25 compounds was carried out. The available data indicate workable heterocyclic second order NLO chromophores. Pyrazines appear to be better acceptors and bithiophene a better donor relative to thiophene.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 87, Synthesis of All Heterocyclic Second Order NLO Chromophores.

TASK: 76

TASK TITLE: Optimal Control Techniques for Thermomechanical Processes

TASK OBJECTIVE: To investigate the application of modern control theory and statistical techniques to control microstructure during thermomechanical processes.

SCIENTIST: R. Dennis Irwin, Ph.D. and Alan R. Lindsey, M.S., Ohio University

DESCRIPTION OF WORK:

A material microstructure that can undergo plastic deformation is required in many engineering materials. The objective of the project was to determine a control law in terms of the physical variables of available processing equipment so that a desired material microstructure can be achieved. The microstructure requirement was one in which the material could undergo plastic deformation.

This process is broken into two steps: (1)given the microstructural specifications in terms of dynamic grain size and fraction recrystallization, find the optimal strain, strain-rate, and temperature trajectories to obtain the specifications and then (2)obtain the physical variables of the processing equipment necessary to achieve the trajectories.

A previous effort outlined a purely analytical approach to the trajectory optimization problem. There are several disadvantages to this approach. The first is that the derivation of necessary conditions for optimality is extremely tedious and must be rederived for every material type. A second disadvantage is that the resulting nonlinear differential equations hold little hope for analytical solution. Even if an analytical solution could be found, it would not be valid for a different material type. Hence, the analytical approach would involve a separate research effort different material type.

Since the analytical approach is ineffective, a hybrid numerical solution was proposed for generating optimal strain, strain-rate, and temperature trajectories for microstructural evolution. The approach is hybrid in the sense that symbolic manipulation codes are to be used for the derivation of necessary conditions for optimality and for manipulating the resulting necessary conditions into the form of second order nonlinear boundary value problems, which can then be solved using standard classical numerical techniques, such as nonlinear shooting algorithms. The method combines variational optimization techniques, symbolic manipulation, and classical numerical techniques for solving two point boundary value problems. The method was illustrated by application to a simplified microstructural optimization for plain carbon steel.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 82, A General Method for Numerically Determining Optimal Strain, Strain-Rate, and Temperature Profiles For Microstructural Evolution.

TASK: 77

The government canceled this task.

TASK: 78

TASK TITLE: Structural Polymer Research: Molecular Composites

TASK OBJECTIVE: Processing of hairy-rod molecular composites to improve tensile strength.

SCIENTIST: Utpal Vakil, Ph.D.

DESCRIPTION OF WORK:

Conceptually, molecular composites are materials comprised of flexible-coil matrix phase containing rigid-rod polymer reinforcements uniformly dispersed on a molecular level. Since physical blends of rigid-rod and flexible-coil molecules are thermodynamically unstable, these blends tend to undergo thermally induced phase separation during the processing steps. In order to restrict the extent of phase separation, a single-component "hairy-rod" graft copolymer of a rigid-rod polymer was developed.

Two batches were studied: (a) a hairy-rod copolymer with PEEKEK (polyetherether-ketoneetherketone), (rod/coil:30/70) and (b) a hairy-rod graft copolymer with STABAR (amorphous PEEK, polyetheretherketone), (rod/coil:30/ 70). The samples were processed into dogbone shaped materials and the tensile mechanical properties were determined. Although high molecular weight matrix resins were blended with the hairy-graft copolymers, the tensile strengths of the resulting blends did not exhibit any significant improvements.

Two fresh batches of the hairy-rod graft copolymer were made following the single step process. These materials were extruded in film form. The reason for extruding films from the one-step hairy-rod copolymer was to circumvent any processing difficulties associated with molding dogbone shaped samples. While the tensile strength of the film is greater than that of bulk specimens reported in earlier reports, the modulus is smaller than the value measured for bulk(dogbone) samples with 30 wt% rod content.

The tensile mechanical properties of the hairy-rod graft copolymers studied thus far have been relatively poor in comparison with results obtained earlier with physical blends of the rigid-rod PBT with nylon or STABAR. The results obtained suggest that the cause of the relatively poor mechanical properties for the hairy-rod graft copolymers may be due to inadequate adhesion within the matrix phase.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development, Volume 51, Structural Polymer Research: Molecular Composites.

TASK: 79

TASK TITLE: Modeling of NLO Materials Using Parallel Computers

TASK OBJECTIVE: To calculate the structure and properties of biologically derived nonlinear optical materials using massively parallel computers.

SCIENTIST: James A. Lupo, Ph.D.

DESCRIPTION OF WORK:

Massively parallel processors (MPP's) offer the prospect of significantly reducing the time required for large scale computational modeling of materials. This project investigated three major computational chemistry programs: GAMESS (an electron structure code), GROMOS (a molecular dynamics code), and PROTEAN2 (a molecular structure prediction code). For the problems examined, conventional sequential vector processors were often found superior to MPP's. This suggests considerable care is required in selecting a hardware platform for optimum performance.

The program GAMESS (General Atomic and Molecular Electronic Structure System) is a well known computational tool for theoretical chemists. Electronic structure calculations involving many atoms, with a consequent large number of electronic states, are numerically quite intensive. The GAMESS program has been ported to many different computer systems. This effort compared the execution times of the C_{60} geometry optimization model on a Cray X-MP with the same model executed on both 256 and 512 nodes of a Caltech Intel Touchstone DELTA massively parallel processor system. While several aspects of the problem ran much faster on the DELTA, the Cray proved to be a significantly better choice in terms of quickest total execution time.

The program UHGROMOS (University of Houston GROningen MOlecular Simulation) is a parallel version of GROMOS. It has the unique feature of being written in Pfortran, a FORTRAN preprocessor that adds parallel constructs to the FORTRAN language. This in principle, makes UHGROMOS portable to different MPP systems. The parallel performance of UHGROMOS was tested on an Intel iPSC/860 and on the Caltech Intel Touchstone Delta. Timing results were found to be nearly identical on the two machines. UHGROMOS parallel scaling behavior was found to be very poor, at least for the sizes of the problem of interest.

PROTEAN2 is a code which uses a double iterated kalman filter algorithm to predict molecular structure, given a set of known interatomic distances and angular constraints. The code is heavily dependent on basic linear algebra routines, which made it a good candidate for the data parallel programming model used by FORTRAN 90 on the Thinking Machines Inc. CM5. Good performance speedup was achieved over the performance on a single Cray Y-MP cpu. Parallel scaling, however, was very poor.

Project GROPE was conceived by Dr. Frederick Brooks, Jr. as a virtual reality system for chemists, allowing them to interactively manipulate molecules while receiving tactile feedback of the interatomic forces through a mechanical arm and viewing their motions in three dimensional stereographic display. DOCKER provides a graphical user interface to the system, three dimensional stereographics, and the ability to manipulate molecules with a mouse.

One particular application which requires high speed numerical support involves generating a virtual reality environment which allows interactive manipulation of chemical compounds. Stereographic images

are computer generated while a researcher provides input and receives force feedback through a mechanical arm. The DOCKER subsystem code from the University of North Carolina at Chapel Hill's Project GROPE was studied as the basis for such a system.

The DOCKER software was installed on a Silicon Graphics 4D/420 VGX system running IRIX 4.0.1. A CrystalEyes liquid crystal shutter stereo goggle system from StereoGraphics Corporation was installed to view the three dimensional display. This device alternates blanking the left and right eye, synchronized with the computer's display of left and right eye images, thereby giving the illusion of full color, three dimensional views.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 95, Modeling of NLO Materials Using Parallel Computers.

TASK: 80

TASK TITLE: Advanced Process Control Research and Development

TASK OBJECTIVE: Develop a structure of measured and manipulated variables that allows the decomposition of control tasks and the optimization of control problems for materials processes utilizing both modeling and experimental methods with advanced implementation technologies.

SCIENTIST: Patrick H. Garrett, Ph.D., and Douglas Moore, B.S., University of Cincinnati

DESCRIPTION OF WORK:

The advancement of technology has closely paralleled the capabilities for measurement and modeling throughout history. This is currently exemplified by manufacturing enterprises within which increasingly complex process representations require more complex measurement and control systems of unexampled accuracy and robustness.

On this project, a framework for integrating hierarchical control structures with axiomatically defined materials processes was presented concurrent with the development of control uncertainty measures and their propagation through a process to allow the prediction of online material variability and hence quality. Significant findings include: (1) that qualitative process control exhibits attributes of non-destructive testing with a probability of achieving goal states that can be completely determined from evaluation of the state transaction probabilities, (2) the accurate identification of process acquired first-principles parameter models for control compensator use is primarily limited by the implementation uncertainty of the control system devices they must transit, (3) implementation uncertainty is reducible

to essentially the sensor/actuator device errors through design optimization of the control system at the process environmental boundary, (4) sensor fusion can provide additional sensor/actuator error reduction through averaging achieved with multiple channels, and (5) an axiomatic process fenestration that permits a non-dependent mapping from environmental controlled variables to insitu process states to physical material properties also enables apriori determination of the required control system uncertainty to achieve specified material quality.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 61, Defined Uncertainty-Material Process Control.

TASK: 81

TASK TITLE: Damage Evaluation Using Acoustic Emission

TASK OBJECTIVE: To evaluate the development and propagation of damage in composite materials under thermal and mechanical cycling.

SCIENTIST: Itzhak Roman, Ph.D.

DESCRIPTION OF WORK:

Glass-ceramic matrices reinforced with ceramic fibers are candidates for replacing traditional structural materials in 21st century gas turbines and aerospace structures. These materials are intended for elevated temperature applications as they retain their high specific strength and stiffness and possess adequate toughness at high service temperatures.

A limited number of studies have characterized the mechanical properties of this emerging class of advanced materials at elevated temperatures in monotomic tension. Thus, the objective of this study was to conduct tension tests, at 25 and 1000°C, on a representative advanced high temperature ceramic matrix composite (CMC), while monitoring the acoustic emission (AE), produced during loading, to characterize the microscopic deformation and fracture mechanism. Specifically, the intent was to employ AE to identify the onset and extent of matrix cracking, as well as the relationship of stress-strain behavior to AE activity, for a CMC system tested at both ambient temperature and 1000°C.

The material used in this study was an advanced ceramic matrix composite of a barium-magnesium-aluminosilicate (BMAS) matrix reinforced with SiC(Tyranno-Si-C-Ti-O) fibers.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 63, Acoustic Emission Characterization of Damage Evolution During Tensile Testing of SiC/BMAS Ceramic Composites.

TASK: 82

TASK TITLE: Communications and Automation Software for Pulsed Laser Deposition (PLD)

TASK OBJECTIVE: Develop computer code in support of an effort to create an advanced process controller for a solid lubricant deposition process called Pulsed Laser Deposition (PLD). Establish communications between actuators and sensors of the PLD process and control software running on a Macintosh IFX computer.

SCIENTIST: David R. Tucker, M.S.

DESCRIPTION OF WORK:

This project, a continuation of work started on a previous contract, involving writing software for the pulsed laser deposition project. The pulsed laser deposition process places a thin coating of a solid lubricating material onto the surface item in a vacuum chamber. The process is monitored by a computer which also records various data.

Objectives of this project were to develop computer software in the LabVIEW and C languages for use in an advanced process controller, and investigation of optical filters which will be used in gathering data for that controller. The program which monitored the pulsed laser deposition process was improved and programs to manipulate matrices were developed for use in the advanced process controller. Three papers were written. Two concerned the interfaces from computer programs in the LabVIEW language written in C language. A third summarized the investigation into selection of the optical filters for use in the spectroscopy analysis. Examples from two LabVIEW programs were presented.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 74, Contributions to the Pulsed Laser Deposition Project: Prototype Modification, Code Interface Node Development, and Investigation of Optical Filters for Spectra Analysis.

TASK: 83

TASK TITLE: Electrical Characterization of Semiconductors

TASK OBJECTIVE: Determine the parameters associated with electronic properties of semiconductive materials.

SCIENTIST: Andrew O. Evwaraye, Ph.D.

DESCRIPTION OF WORK:

Silicon carbide is a material of choice for the fabrication of blue light emitting diodes, high temperature, high frequency and high power electronic devices.

Bulk silicon carbide single-crystal 6H-SiC wafers were characterized using capacitance-voltage (C-V), current-voltage(I-V), and deep level transient spectroscopy (DLTS) techniques. Ohmic contacts were formed on the wafers by sputtering Ni on the samples and annealing at 900°C for five minutes in an atmosphere of forming gas. Schottky diodes were then fabricated on the wafers by evaporating gold through a shadow mask. The C-V and I-V characteristics of these diodes were excellent. Deep levels were observed in these commercially-available single-crystal 6H-SiC wafers using DLTS. The concentration $N_T(x)$ of the defects was $1.7 \times 10^{14} cm^{-3}$ at the semiconductor interface. However, concentration profile of the defect showed that the defects were localized and that $N_T(x)$ decreased from the interface towards the bulk. Electric field enhancement of emissions from this defect was observed and the rate at which the potential barrier was lowered by the Poole-Frenkel effect was determined. These observed defects were removed by the growth of wet oxidation and subsequent etching of the wafers. It was therefore concluded that these defects were caused by residual damage from the polishing process.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 67, Electrical Characterization of 6H-SiC Single Crystals.

TASK: 84

TASK TITLE: Opto-electronic Polymers: Processing and Characterization

TASK OBJECTIVE: To process aromatic-heterocyclic polymers for evaluation of nonlinear optical activity and electrical conductivity.

SCIENTIST: Jar-Wha Lee, Ph.D.

DESCRIPTION OF WORK:

A novel process for the fabrication of optical quality thin films of rigid-rod polymers by coagulation from an isotropic solution was developed. This process consists of the following steps: (1) extrusion or doctor-blading of an isotropic rigid-rod polymer solution into a uniform thin solution layer, (2) relaxation of the solution in an atmosphere containing the vapor of a nonsolvent for an appropriate length of time, and (3) coagulation of the solution in a nonsolvent bath. Thin films of rigid-rod poly(p-phenylene benzobisthiazole) (PBZT) thus prepared do not show the large voids or line defects commonly observed in the extruded and subsequently coagulated PBZT thin films.

Optical quality thin films of rigid-rod polymers were prepared by rapid coagulation of extruded isotropic solution. Although these films contained the defects characterized as large voids, small particles, lines parallel to and lines transverse to the extrusion direction, they showed a high third-order nonlinear optical susceptibility of 4.5×10^{-10} esu and waveguiding property.

To elucidate the mechanism of void formation in the coagulated rigid-rod polymer thin films, the surface and the internal structure of various coagulated and then freeze-dried films were investigated by high resolution scanning electron microscopy. Results indicated that the void formation was due to a large scale incursion of coagulant during coagulation. The incursion of coagulant could be regulated by modifying the surface structure of the solution through relaxation in an atmosphere containing the vapor of a nonsolvent prior to the coagulation to fabricate void-free rigid-rod polymer thin films.

A processing window, based on the solution thickness and relaxation duration in a humid environment, was established for a 1 WT% Poly(p-phenylene benzobisthiazole) (PBZT) solution in methanesulfonic acid (MSA) to fabricate void-free PBZT thin films up to 6 μm in thickness at room temperature. Optical spectra and micrographs show that the PBZT thin films prepared by the current process compare favorably with those extruded and then coagulated in terms of low optical loss and fewer defects.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 94, Processing and Characterization of Optical Quality Rigid-Rod Polymer Thin Films.

TASK: 85

TASK TITLE: Fundamentals of Diamond Film Growth

TASK OBJECTIVE: The objectives of this task are to understand and optimize the role of hydrogen atoms on the growth of diamond films in order to obtain improved morphologies and growth rates.

SCIENTIST: Deborah L. Thebert-Peeler, M.S., University of Dayton

DESCRIPTION OF WORK:

Thin films of diamond-like carbon were grown by pulsed laser deposition. The growth mechanisms of diamond-like carbon were investigated. Previous work addressed the nature and speed of the particles ejected from graphite by pulsed infrared (1064nm) and ultraviolet (248nm) radiation, and the extent to which the kinetic energy of the ejected particles determines the character of the resultant films. This work continued the investigation of the incident particle kinetic energy on the character of amorphic diamond films grown by ultraviolet irradiation of a graphite target.

Films were grown with and without the more energetic, charged particles from the plume and were found to be virtually identical when evaluated by valence and core level electron energy loss spectroscopy, and raman spectroscopy. These data indicate that under these conditions the kinetic energy of the ablated particles is a more significant factor than is their charge state in the determination of carbon film properties grown by pulsed laser deposition.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 114, Fundamentals of Diamond Thin Film Growth by Pulsed Laser Deposition.

TASK: 86

TASK TITLE: Theoretical Analysis of Quantum Dots

TASK OBJECTIVE: Determine the electronic and optical properties of novel quantum dot structures.

SCIENTIST: Frank L. Madarasz, Ph.D., University of Alabama-Huntsville

DESCRIPTION OF WORK:

Within the last ten years, quantum structures with 2- and 3- dimensional confinement (wires and dots) have been fabricated through a variety of techniques. In general, quantum confined structures exhibit a rich variety of enhanced optical properties relative to those of bulk materials. This enhancement is due to the increase in the number of confinement directions, which result in the confinement of carriers to regions that are smaller then their characteristic size in bulk materials.

The reduction of dimensionally leads to new physics and to new phenomena with potential optoelectronic device applications. During this study, exciton and biexciton binding energies, wave functions, and oscillator strengths were calculated variationally for rectangular GaAs quantum well wires in an effective mass approximation. Coulomb interaction terms were treated exactly in their full three-dimensional form throughout the calculation, a more physically realistic procedure than employed in previous calculations which used effective one-dimensional potentials. The treatment was unique in the use of a two-dimensional Fourier expansion of the Coulomb potential, which removed the difficulty of dealing with the 1/r singularity and considerably reduced the computational effort. As an intermediate step, the linear absorption coefficients at the exciton resonance were calculated as a function of wire dimensions. Using the results of the exciton and biexciton calculation and following a previous approach to eliminate the dimensional dependence of the third-order nonlinear optical susceptibility, $\chi^{(3)}$, its magnitude for near-resonant excitonic absorption was estimated. $\chi^{(3)}$'s were obtained on the order 10^{-1}--1 esu for various wire dimensions.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 91, Theoretical Analysis of Quantum Dots.

TASK: 87

TASK TITLE: Micromechanical Modeling of Plastic Deformation of Advanced Materials

TASK OBJECTIVE: Develop micromechanical models of yielding and plastic flow for intermetallic alloys and porous metals and ceramics.

SCIENTIST: Henry Piehler, Sc.D.

DESCRIPTION OF WORK:

Micromechanical modeling of advanced materials was developed and used to characterize the plastic deformation by slip and twinning of γTiAl alloys and the power law creep of fcc metals deforming by climb of edge dislocations. These micromechanical models are extremely useful in explaining and often predicting the behavior of advanced materials during processing conditions and in service as well.

The micromechanical modeling of plastic deformation by slip and twinning in γTiAl was based on the use of Schmid's law (critical resolved shear stress criterion) to describe the onset of both slip and twinning. A fundamental assumption made in these micromechanical models is that the stress and strain states are uniform in each grain of the polycrystalline aggregate, i.e., there are no stress or strain gradients in individual grains.

Slip and twinning in γTiAl were described using critical resolved shear stress criteria to formulate isostress and isostrain micromechanical models. Slip was allowed to occur by motion of $a/2<110>$ ordinary dislocations plus $a<110>$ and $a/2<112>$ superdislocations; twinning in $a/2<112>$ directions. The operation of $a/2<110>$ and $a<110>$ dislocations was shown to be uncoupled in Bishop-Hill stress space, but both types of systems must be operated to accommodate an arbitrary imposed strain state. Procedures for constructing isostress lower bound yield loci using these critical resolved shear stress criteria were identified.

In order to characterize the consolidation of powder compacts deforming by power law creep, the creep of fcc metals by climb of edge dislocations was analyzed. One of the goals of this investigation was to determine whether the normality rule of plasticity, i.e., the strain vector is parallel to the gradient of the yield locus, holds for power law creep, in this case by climb of edge dislocations. Power law creep by climb of edge dislocations in fcc materials was first characterized using a critical resolved normal stress criterion, which results in pressure dependent climb loci and a dilatant creep strain which is normal to the pressure dependent climb loci. Criteria for pressure independent climb and constant volume climb strains were derived; the resulting constant volume climb strains are not normal to the pressure independent climb loci. Criteria for glide-climb interactions were developed for characterizing creep anistropy. The implications of these findings on constitutive modeling were addressed.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 113, Micromechanical Modeling of Advanced Materials.

TASK: 88

TASK TITLE: Project Management/Administration

TASK OBJECTIVE: To provide support activities necessary to establish project task orders and overall contract administration.

PROGRAM MANAGER:Milton E. Zellmer

DESCRIPTION OF WORK:

The contributive research and development project required extensive management and administration activities that were not readily charged to a specific task. These activities fell into three general categories:

1. Those contract management administrative requirements to establish planning and control procedures that applied to the project as a whole. Examples are status reporting, project management meetings, and other general overall project reporting.

2. Those management activities required to establish each of the task assignments. These activities could not be charged to the task since the task was not yet approved during this phase.

3. Recording and reporting the performance and cost for the overall management and administrative activities.

This task provided project management/administration from 26 June 1992 through 25 June 1993.

TASK: 89

TASK TITLE: Defect Levels in Wide Bandgap Semiconductors

TASK OBJECTIVE: Determine electronic and optical energy levels due to impurities, dopants, and intrinsic defects in silicon carbide.

SCIENTIST: Marek Skowronski, Ph.D.

DESCRIPTION OF WORK:

Silicon carbide possesses a set of properties which make it uniquely suited for application as material for high frequency/high power devices. The practical applications of SiC have been hampered by the technology which is far behind that of GaAs and silicon. Although practical devices made of SiC have been demonstrated in several laboratories, further progress depends on the development of crystal growth techniques. In particular, there is a need to produce crystals with high enough resistivities to be useful for device isolation in high integration circuits.

This research program concerned optical, electrical, and Secondary Ion Mass Spectroscopy characterization of bulk silicon carbide crystals grown by modified Lely technique. Of particular interest was the problem of electrically active impurities(both shallow and deep) and native defects and their effect on electrical compensation.

Samples for this study were obtained from Westinghouse Electric Science and Technology Center and from Cree Research Inc. Virtually all bulk SiC crystals were contaminated with transition metals including: titanium, vanadium, chromium, iron, and nickel. Titanium-related absorption was observed near the fundamental absorption edge of 6H polytype and interpreted as due to bound exciton. This observation proves that titanium behaves as an isoelectronic impurity and does not play a role in compensation mechanisms. Two new unidentified absorption features were detected for the first time. One is a wide photoionization band with the threshold at 0.75eV, another are two narrow lines between 0.62 and 0.6 eV. Both appeared to be caused by deep centers.

The Hall effect measurement verses temperature was performed on n-type crystals. The activation energy for carrier concentration corresponds to shallow nitrogen donors, and low mobility indicated scattering on macroscopic inhomogeneities in the crystals. Deep Level Transient Spectroscopy (DLTS) spectra on crystals with low carrier concentration ($10^{15}cm^{-3}$) exhibited two deep centers with peaks at 250 and 350 K. Their nature was not established.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 64, Optical and Electrical Characterization of Defects in Silicon Carbide Crystals.

TASK: 90

TASK TITLE: Genetic Algorithms for Materials Research

TASK OBJECTIVE: Investigate the development, integration, and use of genetic algorithms for conducting materials research.

SCIENTIST: Steven LeClair, Ph.D.

DESCRIPTION OF WORK:

The research reported herein involved the use of a specific type of a genetic algorithm (GA) which will be referred to as a 'Directed Evolution' (DE) algorithm. A genetic algorithm (GA) is a method of global optimization. Given some data set associated with an observed result, the task is to either find some function which best predicts or explains the results of the data or, in other cases, optimizes the behavior of a system (search strategy) based upon observations of past behavior. The DE algorithm is, roughly speaking, a slight generalization of a GA. Two important aspects of any *evolutionary* algorithm are its "survival of the fittest" selection operator, and its breeding/mutation operator.

This project addressed the topic of genetic algorithms in the context of materials discovery research. Fundamentals regarding genetic algorithms and their search strategy were reviewed to provide a foundation for subsequent discussion regarding applications. Potential applications range from the discovery of new material and properties to the synthesis of new materials and/or processes. The emphasis was on the use of genetic algorithms to search a large database of protein information for patterns which suggest rules regarding protein secondary structure. The specific Air Force interest in this particular application is in predicting and synthesizing the form of proteins as a substrate for growing non-linear optical materials.

The use of a genetic algorithm to discover the rules for predicting protein structure is an example of the growing area of knowledge discovery-the mining of existing and repetitively generated data for purposes of discovering facts which are of potential interest or significance. Typically, any system which addresses this task must exhibit some inherent data-driven search strategy which attempts to emulate the creative and/or analytic (pattern recognition) abilities of humans. Genetic algorithms utilize data-driven search techniques and are an ideal method for global optimization of large search problems.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 75, Genetic Algorithms for Materials Research.

TASK: 91

TASK TITLE: Manufacturing Research

TASK OBJECTIVE: To develop methods for design and control manufacturing processes.

SCIENTIST: Sharon Dutcher, M.E.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Mathematics Collaborative GEMMA". Under this program, Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business

problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

The primary task was to create a statistical mapping of data collected on the dynamic recrystallization of nickel during isothermal compression tests.

Ground work was laid to create a statistical mapping that will give a band or zone of reasonable or nominal data production. It will also allow generalization of the function for the data easier. From a materials point of view the band will allow acceptance or rejection of data that is really unique to the materials versus a random error happening.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 53, Manufacturing Research —Statistical Data Mapping of Isothermal Compression Tests.

TASK: 92

TASK TITLE: Control of Interfacial Bonding

TASK OBJECTIVE: To control fiber/matrix interface properties through boundary "poisons."

SCIENTIST: Sankar Sambasivan, Ph.D.

DESCRIPTION OF WORK:

In the yttria-alumina system, there are three stable crystalline phases, YAG(3:5), YAP(1:1) and YAM(2:1). YAG (3:5), yttrium aluminum garnet, has already been identified as a potential reinforcement for alumina matrices due to its high strength and creep resistance. As a composite system, YAG and alumina show strong interfacial bonding leading to low fracture toughness values for the composite. Therefore, interfacial tailoring is necessary to weaken the bonding between alumina and YAG.

This work was an extension of a previous investigation on chemistry related to yttrium aluminum garnet/alumina composite system. In this research, the following topics were addressed:

a) Energetics of formation of yttrium aluminates-the enthalpy, entropy, and free energy of formation of YAP was determined using zirconia as the chemical potentiometer. An analysis of the energies of formation of YAG and YAP based on their structural differences was performed.

b) Characterization of alumina/YAG composite system using analytical TEM-EDS spectra of the dopant in study was acquired from regions near and at the interface between alumina and YAG. Results obtained from the TEM analysis of the Sr and Zn doped materials seem consistent with SIMS analysis. However, in the case of Ni-doped material, the EDS spectra showed presence of Ni at the interface contrary to the SIMS results. Description of results obtained from all the characterization studies was presented.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 72, Chemistry Related to Yttrium Aluminum Garnet/Alumina Composite Systems Interfacial Properties and Thermochemical Stability-Part II.

TASK: 93

TASK TITLE: Photo Conductivity of Polymer Films

TASK OBJECTIVE: To measure and interpret the spectral response of the photoconductivity of polymer films.

SCIENTIST: Barney Taylor, Ph.D.

DESCRIPTION OF WORK:

There is great technological interest in the field of electrically conducting polymers. As a result, much research effort has been applied to the synthesis and characterization of such materials. They possess excellent mechanical and thermal properties and offer the possibility of good electrical conduction. Ladder polymers offer much hope for good electrical conduction due to multiple conjugation paths that allow carriers to bypass defect sites along one of the chains. A ladder polymer of current interest is BBL, which has been little studied to this point.

A laboratory was set up using standard apparatus to measure the photo-conductivity (PC) of the latter polymer BBL. Investigation of both pristine and thermally annealed samples showed the existence of a broad PC spectrum with shoulders on either side of the central peak. The intensity of the spectrum was found to depend linearly on the period of the chopped light used for synchronous detection of the PC current. The shoulders exhibited slightly different dependence than the central peak, leading one to expect that different physical mechanisms are responsible for the features. The photo-conductivity of the annealed samples showed a strong dependence on the time since annealing. Initially after anneal (several minutes at 350°C), the PC was several orders of magnitude greater than the pristine control sample. Over the course of a few days, the PC response dropped to a level where the photo-current was about two orders of magnitude greater than the control sample. This behavior follows the dc electrical conductivity for similar treated BBL samples.

The detailed project description, method, results, and discussion are reported in Contributive

Research and Development, Volume 66, Investigation of Photo-Conductivity in Ladder Polymers.

TASK: 94

TASK TITLE: Research Data - Gas Layer Protection Project

TASK OBJECTIVE: To establish an archive of research data collected during the execution of the experimental phase of the gas layer protection project and to generate appropriate documentation. The materials involved are high temperature carbon materials.

SCIENTIST: David S. Vail, M.S.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Mathematics Collaborative Project "GEMMA". Under this program Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

The objective of this project was to define and set up a data collection format for a carbon-carbon experiment being performed at the Nonmetallic Structural Materials Laboratory at the Wright Laboratories Materials Directorate.

Carbon-Carbon is being considered for use in air breathing engines of military airplanes because it possesses many qualities which make it desirable for such use. Carbon-Carbon is very lightweight compared to the materials now being used and it is also very durable with respect to other materials being considered. However, carbon and its composites are prone to high oxidation when exposed to high temperatures in an oxygen environment. The experiment was being conducted to determine a means to overcome or retard the oxidation process.

The task of formulating the data in a manageable and accessible manner was required to disseminate the information to all of those involved in the experiment. Some of the data acquired was that of pertinent literature, which was planned in a bibliography style format, so that quick references could be made. Other data that was documented was that of any presentation that would need to be made to concerned groups or individuals. The remaining and majority of the data to be collected was that of calibration and experiment protocol and of calibration and experiment data.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 54, Research Data-Gas Layer Protection Project.

TASK: 95

TASK TITLE: Processing and Characterization of Nonlinear Optical Polymers

TASK OBJECTIVE: To process aromatic-heterocyclic polymers into specimens suitable for evaluation of their nonlinear optical activity.

SCIENTIST: Jeffrey Bauer, B.S.

DESCRIPTION OF WORK:

Polymeric materials have been identified as a class of materials which hold great potential for nonlinear optical applications. Such applications will be vital in the development of electro-optic devices in the emerging field of photonics. Nonlinear optical processes are observable when the intensity of the incident light is sufficiently high to cause a polarization response that is nonlinear in character and that can act as a source of new optical fields with altered properties. The main objective of the synthesis and the processing of nonlinear optic (NLO) materials is to maximize the nonlinear effect so that it may be exploited in a photonic device which will require a minimum of incident intensity. Polymeric materials have great potential as NLO materials due to their large optical nonlinearities, low absorption, ease of fabrication, and chemical flexibility.

The objective of this research was to evaluate the efficiency of aligning nonlinear optical chromophores between polymer-polymer interfaces. Preliminary work indicated that spin-coating is successful in producing homogenous polymeric interfaces from polymeric solutions. This work also indicated that common circular glass slide covers are not viable as spin coating substrates due to their significant bowing, but that square glass slides offer a reasonable substitute. The effects of processing variables such as spread time, solution volume, and solution concentration on film quality and thickness were also evaluated. Attempts were made to further characterize these films by profilometry, ellipsometry, and spectroscopy (Ultraviolet, Visible, Near Infra-red, and Infra-red) with mixed success. Profilometry proved to be a useful tool in determining film thickness and was also developed as a surface contour mapping method, while the ellipsometric and spectroscopic methods needed further modification to be of significant use to spun films. The low absorbances observed in the spectroscopic techniques due to the thin film configuration hampered the detection of the chromophore molecules which also limits the possibility of developing a spectroscopic method to determine the alignment of the chromophore molecules (i.e. Polarized Spectroscopy).

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 65, Preliminary Investigation of the Alignment of Nonlinear Optical Chromophores at Polymer-Polymer Interfaces.

TASK: 96

The government canceled this task.

TASK: 97

TASK TITLE: Computational Models of Concept Formation

TASK OBJECTIVE: Investigate the development, integration, and use of incremental neural networks for constructing concepts based on frequency.

SCIENTIST: Yoh-Han Pao, Ph.D.

DESCRIPTION OF WORK:

The focus of this project was to discover concepts which can be used to inform a human designer of past problems and preferred good design practices in a feature-based design environment.

Tasks, such as signal interpretation, automatic target recognition, or process planning, are of the nature of deciding whether a given object is equivalent to a known prototype, canonical form, or structure in collections of such items. One of the central issues is that of re-description of raw precepts into concepts so that the object is described in the form suitable for comparison with the way objects are stored in memory. Another important issue is that of computational complexity. In this work the first issue in the form of concept formation was investigated. Progress on computational matters enabled implementation of the advances in concept formation.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 76, Concept Formation.

TASK: 98

TASK TITLE: Development of Intelligent Control Techniques for Materials Processing

TASK OBJECTIVE: Improve the quality and consistency of material produced from several material processes including Molecular Beam Epitaxy (MBE) and Chemical Vapor Deposition by developing a generic, computer-based control system and a methodology for applying it to materials processes. This system will use sensors to monitor the process and intelligently control it in real time. Ideas and perhaps code will be utilized from existing control systems in the Materials Directorate which control MBE and Pulsed Optimal Control Theory and Neural Networks into the control system if they show promise for improving manufacturing capability.

SCIENTIST: Oliver D. Patterson, M.S.

DESCRIPTION OF WORK:

Future electronic and electro-optic devices will rely more and more on materials grown in epitaxial thin-film forms. To achieve a substantial production level capability that can provide these low cost, reproducible, uniform, and tailorable thin-film structures will require advances in sensors of the growth process and integration of these sensors into an on-line real time process controller. Techniques such as Molecular Beam Epitaxy (MBE) and Metallorganic Chemical Vapor Deposition (MOCVD) do not currently utilize on-line process control and are subject to the variations and capabilities of the operator who sets machine parameters in advance of the growth run and hopes for a predictable product.

Ellipsometry, an optical sensing technique, is capable of providing a great deal of information on the status of the thin-film, however solving transcendental equations is necessary. Solving these equations in the normal manner, through an interactive search technique, requires more time than is available for real-time control. Artificial neural network technology was explored for mapping the inputs to the outputs of these transcendental equations so that solutions may be found in a timely manner. Experiments were run with several Multi-Layer Perceptrons and the design of the final artificial neural network was described.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 78, Application of Artificial Neural Network Technology to Ellipsometry Data Refinement For Real-time Control of MBE.

TASK: 99

TASK TITLE: Characterization of conjugated organic materials for possible nonlinear optical applications

TASK OBJECTIVE: To identify conjugated organic materials that may have large nonlinear optical response for applications in laser hardening.

SCIENTIST: Roderick Gray, B.S.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Mathematics Collaborative Project "GEMMA". Under this program Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

On this project various optical limiting experiments were performed on C60 and C70 in benzene (70% transmission) using a 35 pico second Nd-YAG laser at 532 nm. Silicon detectors were used for low input energy while pyroelectric detectors were used for higher input energies. Data was interpreted using computer graphing techniques. This work supported laser hardening projects.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 55, Optical Limiting Experiments.

TASK: 100

TASK TITLE: Synthesize characterization processing of bio-organic polymers for nonlinear optical applications

TASK OBJECTIVE: To synthesize polypeptides containing nonlinear optically active chromophones and to measure their nonlinear optical (NLO) response.

SCIENTIST: Mimi Mancham, M.S.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Mathematics Collaborative Project "GEMMA". Under this program Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

On this project polypeptides containing nonlinear optically active chromophores were synthesized and characterized. Using UV-Vis spectra, the percent modification of the polypeptide were calculated. The conformation of backbone of the substituted polypeptide was determined using CD spectrometer. An Alph Helix structure was determined for the poly-L-Glutamic substituted with 1-pyrenyl methanol. From the analysis of the products, it was found that coupling polypeptide with nonlinear active materials produces a polymer that retains the nonlinear optical characteristics of the attached groups.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 56, Synthesis and Characterization of Polymers.

TASK: 101

TASK TITLE: Fiber/Matrix Composite Materials

TASK OBJECTIVE: Determine fiber/matrix interface mechanical properties.

SCIENTIST: Susan M. Goffena, B.S.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Mathematics Collaborative Project "GEMMA". Under this program Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

The objective of this project was to synthesize pollucite and analyze the stability of the compound. Pollucite has several properties which indicate it may be useful for ceramic composites. It has a large crystal lattice which may indicate that it has a low creep rate.

The detailed project description, method , results, and discussion are reported in Contributive Research and Development Final Report, Volume 55, Pollucite Synthesis and Analysis.

TASK: 102

TASK TITLE: Effect of Debonding on Shear Modulus of Unidirectional Composites

TASK OBJECTIVE: To determine analytically the axial shear modulus of a unidirectional composite in which a symmetric debond is present at the fiber-matrix interface.

SCIENTIST: Fuh-Gwo Yuan, Ph.D.

DESCRIPTION OF WORK:

The mechanical properties of fiber-reinforces composites are significantly affected by the bond between various constituent materials at the microscale level, such as the interface between fiber-interphase or interface-matrix. In order to achieve optimal performance between strength and stiffness for composite development, the effect of weak bond or debonded interface condition on the mechanical properties of composite materials needs to be fully understood.

A theoretical analysis using finite element methods was applied to fiber reinforced brittle matrix composites in order to predict the influence of the debonded interface on "effective" elastic moduli of the composites. It was assumed the debond occurs at the interface and over the entire length of fiber. A geometry layout of the composite concentric cylinder model was considered in the analysis. The prescribed displacement and traction boundary conditions were imposed on the outer boundary of the

representative volume element (RVE). The results show that the elastic constants obtained from the composite cylinder model give much less degree of the unsymmetry. Furthermore, very little discrepancy about longitudinal shear moduli prevails between the two applied boundary conditions.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 49, Elastic Moduli of Fiber Reinforced Brittle Matrix Composites with Interfacial Debonding.

TASK: 103

TASK TITLE: Processing of Ceramic Matrix Composites via Tape Casting

TASK OBJECTIVE: To develop process models for fabrication of continuous fiber ceramic matrix composites via tape casting/vacuum not pressing.

SCIENTIST: Rollie E. Dutton, Ph.D.

DESCRIPTION OF WORK:

Ceramic composites can offer considerable improvement in various properties compared to single-phase ceramics. The potential for improved properties is, however, offset by the increased difficulties in forming ceramic composites with the required high density and controlled microstructure by conventional pressureless sintering. Commonly, hot-pressing or hot isostatic pressing have been used to fabricate ceramic composites with high densities. While these methods are effective, they suffer from a number of limitations; e.g., near net shape formation is difficult and fabrication costs are relatively high. It is therefore important to understand the factors that effect the densification of ceramic composites so that processing science can be better applied to the formation of these materials.

On this project, the modeling of the consolidation of ceramic matrix composites by sintering and hot pressing was illustrated by developing microstructural and continuum models which can be used to model the densification of a ceramic matrix containing continuous fiber reinforcements. The microstructural model is based upon the sintering equation and uses a stress intensification factor as an indication of the constraints to densification due to a changing microstructure (e.g., grain growth). The continuum model is based upon a modified yield function developed for compressible powder metallurgy materials. Uniaxial upsetting of powder compacts of varying relative densities was used to develop the necessary constitutive equations for the continuum (finite element method) model of matrix densification. The FEM model was validated by comparing the simulation predictions with experimental results published in the literature.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 124, Processing of Ceramic Matrix Composites Via Tape Casting.

TASK: 104

TASK TITLE: Fatigue and Environmental Effects on Titanium Aluminides

TASK OBJECTIVE: To study the role of composition, microstructure, and surface treatment on the fatigue and environmental resistance of titanium aluminide alloys and composites.

SCIENTIST: J. Wayne Jones, Ph.D.

DESCRIPTION OF WORK:

A study of the role of environment on microstructural damage accumulation processes was performed on two distinct materials systems subjected to different mechanical and thermal loading histories. In one case, microstructural evolution, environmental embrittlement, and crack initiation and growth were examined in a SiC fiber reinforced metastable beta titanium alloy that was subjected to isothermal exposure and cyclic thermal loading. In the second case the influence of microstructure on the mechanisms of fatigue crack growth at ambient and elevated temperature in a gamma titanium aluminide was examined.

The influence of thermal cycling and isothermal exposures in air on the residual ambient temperature strength of SCS-6/Ti-15Mo-2.7Nb-3Al-0.2Si (wt. %) metal matrix composites comprised of $[0]_4$ and $[0/90]_s$ laminates was determined. A maximum temperature of 815°C was used in thermal cycling and isothermal exposure. Temperature range, cycle count, maximum/minimum temperature, environment, and hold time at temperature were systematically varied. Post-exposure ambient temperature tension testing, scanning electron and optical microscopy, and fractography were performed on selected specimens to determine the degree of damage. A reduced residual strength was noted in thermal fatigue with increasing cycle count, maximum temperature, and hold time for all specimens tested in air. Isothermal exposures at 815°C also substantially reduced residual ambient temperature strength. Limited tests in inert environment produced considerably less reduction in strength than comparable tests in air. Damage processes include matrix cracking, fiber/matrix interface damage, matrix microstructural evolution, and matrix embrittlement and oxidation. Fiber orientations which allowed rapid ingress of oxygen lead to greater matrix embrittlement and resulted in more pronounced reductions in strength.

A microstructural and fractographic study was conducted of fatigue crack growth in case + HIP'ed Ti-48Al-2Nb-2Mn (at%) heat treated to produce a duplex microstructure. Tests were conducted in the temperature range 25 to 954°C under both load-shedding threshold and constant load crack growth conditions under a load range of R=0.1 and a frequency of 1.0 Hz. The final heat-treated duplex, two-phase microstructure consisted of equiaxed primary gamma grains and transformed grains of alpha-2/gamma lamellae. SEM fractography revealed the fracture processes in this microstructural condition to be predominantly: (a) translamellar fracture of transformed lamellar grains; and (b) brittle transgranular fracture of equiaxed gamma grains. The fatigue crack fracture surface morphology

changed very little as a function of temperature from 25 to 954°C. Additionally, there was only a modest dependence of the fatigue fracture behavior on ΔK at any of the test temperatures. There was, however, a slightly greater degree of interlamellar splitting and intergranular fracture at high ΔK values at elevated temperatures. The dominant crack growth processes exhibit fractographic features which are strongly dependent on the orientation of the alpha-2/gamma lamellae with respect to the macroscopic crack growth direction. In the interlamellar regions, the degree of interlamellar versus translamellar crack propagation was strongly dependent on the orientation of the lamellar colonies with respect to the crack propagation plane.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 136,Microstructural Damage Mechanisms in Thermal Fatigue of Titanium Composites and Fatigue Crack Growth of Gamma Titanium Aluminides.

TASK: 105

TASK TITLE: Opto-Electronic Polymers: Processing and Evaluation

TASK OBJECTIVE: To process aromatic-heterocyclic polymers in order to characterize nonlinear optical activity and electrical conductivity.

SCIENTIST: Ashwini K. Agrawal, Ph.D.

DESCRIPTION OF WORK:

Thin films of ladder polymer poly[7-oxo-7H,10H-benz(d,e)imidazo(4′,5′:5,6)-benzimidazo(2,1-a)isoquinoline-3,4:10,11-tetrayl)-10-carbonyl} (BBL), which were cast from an isotropic methanesulfonic acid solution of BBL, were characterized for electrical conductivity in the temperature range of 25-480°C. The electrical conductivity was measured *in situ* while the films were heated at a rate of 2°C/minute under vacuum. The in-plane conductivity of BBL films increased rapidly from below 10^{-10} S/cm at room temperature to 5×10^{-3} S/cm at 280°C and then increased slowly to a peak value of 5×10^{-2} S/cm at about 420°C. The out-of-plane conductivity of the films was comparable to their in plane conductivity at temperatures below 270°C, however, was lower by a factor of 10 than in-plane conductivity at temperatures above 270°C. This anisotropy in conductivity of BBL films was studied with respect to the film morphology determined by wide angle x-ray scattering studies.

The in-plane conductivity of BBL was also studied as a function of its film thickness to determine the contribution from surface conductivity in contrast to bulk conductivity. Three films of thicknesses 1.8μ, 4.6μ, and 18μ were measured for electrical conductivity under the identical conditions. Since the current through a film decreased in proportion to the relative decrease in the thickness of the film, no evidence of surface could be established. The calculated bulk conductivity for all three films was within experimental errors to one another.

Rigid-rod conjugated polymers are potential candidates for making efficient and stable light emitting devices. In this study, we also investigated photoluminescent properties of benzothiozole, benzoxazole, and ladder polymers. The feasibility of fabricating light emitting diodes (LEDs) using bisbenzothiazole polymers was also investigated. A few prototype LEDs were produced and studied for their light emitting properties.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 125, Electronic and Optoelectronic Properties of a Few Conjugated Polymers.

TASK: 106

TASK TITLE: NDE Materials and Processing Research

TASK OBJECTIVE: Identify and/or develop enhanced methods for quantitative extraction of flaw and/or material variations in advanced materials and processes using sonic, electromagnetic, radiographic, and optical nondestructive evaluation methodologies.

SCIENTIST: Renee Kent, M.S., University of Dayton Research Institute

DESCRIPTION OF WORK:

The characterization of ceramic matrix composites (CMCs) which are currently being investigated for elevated temperature structural applications is paramount to understanding and predicting the material behavior under its performance operating conditions. This characterization and investigation of the mechanical properties is often performed by means of destructive mechanical behavior testing. Typical tests include fiber push-in, fiber push-out, tensile strength, and fatigue testing.

Development and implementation of nondestructive testing technologies are currently being investigated in order to enhance understanding of the mechanical behavior of materials and to complement the information received from conventional destructive testing.

In this research study, conventional ultrasonics using shear wave back reflection and normal incidence C-scanning were used to assess the integrity of the fiber-matrix interfacial bond of selected ceramic matrix composites prior to and post fiber push testing. The results of the ultrasonics interrogation provide a quantitative basis for validation of the fiber push testing results.

Laser based ultrasonics was used to quantitatively determine the mechanical properties of specific

small diameter fibers which are used for reinforcement of composite material. Measurement of the velocity of shear wave and longitudinal wave propagation along the axis of a fiber provides an accurate measure of the elastic modulus and shear modulus of the material. Elastic modulus and shear modulus of SCS-6, BP Sigma, and Amercom TiB_2 coated fibers were determined and compared with values available in the literature.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 115, Investigation of Ceramic Composites Using Optical and Ultrasonic Testing Methods.

TASK: 107

The government canceled this task.

TASK: 108

TASK TITLE: Integration of Material, Process, and Design for Manufacturing Research

TASK OBJECTIVE: Investigate the development and integration of material, process, and design to conduct manufacturing research.

SCIENTIST: Gerald M. Radack, Ph.D.

DESCRIPTION OF WORK:

In order to have true concurrent engineering, it is necessary to integrate material property specification and material selection with process design and geometric design. The use of "features" within a computer-aided design (CAD) provides a good framework for achieving these goals. In order to handle general design problems, a CAD system must support complex geometries. In addition to form (geometric) features, material features can specify required materials properties within a region of a part. Both can be linked together with function features, which specify function of a portion of a part, e.g., "stiffener."

The primary effort on this task was to enhance an existing feature-based design system. The Rapid Design System (RDS) is an experimental artificial-intelligence based software tool for computer-aided engineering. The goal of the RDS project is to reduce design and process planning time, while improving quality. The intended application area of the RDS is discrete parts manufactured by machining processes.

The RDS is being developed as an internal research and development project by the U.S. Air Force Materials Laboratory, Wright Patterson Air Force Base, Ohio. A number of universities and outside

contractors have participated in the development.

There are four major "environments" within the RDS. They are:

- The *Feature-Based Design Environment* (FBDE) which is used to create a specification of the part's geometry. This is done by adding, modifying, or deleting features from the part model. The features handled by the FBDE are form features which give the nominal geometry of the part, and Geometric Dimensioning and Tolerancing (GD&T) features which specify the allowable deviation of a manufactured part from the ideal shape by the form features. The FBDE has the ability to do some constraint satisfaction.

- The *Fabrication Planning Module* uses the part specification (the collection of form and GD&T features) to produce a process plan for machining. The process plan includes tool selections, operation sequencing, tool paths, and feeds and speeds.

- The *Inspection Planning and Evaluation Module* (IPEM) uses the part specification to produce a process plan for inspection. Currently, only inspection by a 3-axis coordinate measurement machine is supported.

- The *Episodal Associative Memory* provides for retrieval of past designs based.

This effort concentrated on improving the FBDE. Several extensions to the Rapid Design System were presented to support research in concurrent design of product, process and material. These extensions fall into two categories: enhancements to the geometric model, and extensions to handle material and function specification. The enhancements to the geometric model comprise a way of positioning and orienting form features on curved surfaces, and a new feature type which can accommodate more general geometries than previous features. The extensions to handle material and function specifications consist of two new classes of features: material specification and function features. A material specification feature can be used to state the allowable range of a material property within a portion of the part's volume.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 81, Integration of Material, Process, and Design For Manufacturing.

TASK: 109

TASK TITLE: Experimental Conductivity Mechanism Determination

TASK OBJECTIVE: To determine the conductivity mechanism in rigid-rod and ladder polymers.

SCIENTIST: K.S. Narayan, Ph.D.

DESCRIPTION OF WORK:

Ladder polymers have far greater thermal stability and mechanical strength compared to the conventional doped conducting polymers like polyacetylene, polyaniline, and polythiophene. The electronic and optical phenomena in ladder polymers add to the multifunctional properties and are the reason for the rapidly growing interest in these systems. In this study, the thermally-induced characteristics in BBL were probed using dc conductivity, IR, and EPR measurements. Experiments conducted were: dc conductivity, IR-absorption, UV/Vis absorption, Electron Spin Resonance studies, steady state photoconductivity, and transient photoconductivity. Photoconductivity was described in terms of spectral response, electric field dependence, chopper frequency dependence, intensity dependence, temperature dependence, photocurrent and thermal heat treatment, transient photoconductivity, sandwich configuration, and infrared features.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 119, Electronic Properties of the Ladder Polymer BBL.

TASK: 110

TASK TITLE: Modeling of Temperature Transients in Materials Processing

TASK OBJECTIVE: To develop numerical models for temperature transients that occur during casting of VAR ingots and consolidation of foil-fiber-foil composites.

SCIENTIST: Khairul Alam, Ph.D.

DESCRIPTION OF WORK:

The development of temperature gradients and thermal stresses during the processing of ingots was investigated with special reference to brittle intermetallic materials such as titanium aluminides. Two different cases were considered - (i) stresses due to reheating of ingots and (ii) stresses due to cooling following vacuum arc remelting (VAR). Analytical solutions were derived to determine the influence of ingot diameter, heating or cooling rate, and thermal diffusivity and conductivity on temperature transients. The analytical solutions for the temperature field were used in conjunction with an elasticity analysis to determine the maximum thermal stresses that would be generated during ingot processing.

The consolidation of foil-fiber-foil plies is usually done by the HIP (hot isostatic pressure) process. In this process, foils and fiber mats are consolidated by the combined action of temperature and pressure in vacuum. During this process, the temperature variation in the plies may be quite large. A numerical model was developed to calculate the temperature transients in process.

The motivation in determining the temperature transients during VAR process is to predict the thermal stresses that occur in the process. These stresses can be large enough to crack the ingot. In the numerical modeling, the temperature transients for the heating of a simple ingot were first studied, and the thermal stresses evaluated. In the second phase, the temperature transients for the VAR process were modeled, and the thermal stresses were evaluated.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 105, Modeling of Temperature Transients in Materials Processing.

TASK: 111

TASK TITLE: Investigation of Novel Metallic Composites

TASK OBJECTIVE: To develop an understanding of the relationships between the composition and structure of fiber/matrix interfaces and composite properties.

SCIENTIST: Benji Maruyama, Ph.D.

DESCRIPTION OF WORK:

An investigation of composite matrix deformation in the neighborhood of the reinforcement is crucial to the understanding of the macroscopic mechanical behavior of metal matrix composites. Automated Digital Deformation Analysis is a strain mapping technique developed at the Wright Laboratory. It consists of digital imaging, deformation measurement and strain analysis in a highly automated fashion. In this work, enhancements were made in this program. Accomplishments include the development of a shadow mask gridding technique superior to the previously used optical lithography, design and acquisition of an optical imaging system, modification of the analysis software and gridding of a variety of sample geometries.

The sample gridding technique utilized optical lithography similar to that used in integrated circuit manufacture. It involved careful polishing of the sample surface, spin-coating the sample with a photoresist, exposing the resist using a contact mask aligner, developing the resist and etching the grid pattern into the sample via ion etching. This technique had several drawbacks.

Alternative gridding techniques were subsequently developed. The first is a shadow mask technique, the second is an adaptation of the Moiré grating technique. The shadow mask technique utilizes a nickel mesh with a grid pitch of 2000 lines per inch, corresponding to a 12.7 micron repeat distance. The mesh is approximately 2 microns thick, and has open square holes approximately 9 microns on a side. In general, a grid is applied to the sample by physical vapor deposition of a metal onto the surface through the mesh. The mesh shadows the deposition such that the sample grid pattern corresponds to the hole pattern in the mesh. This gridding technique can be modified to suit various

applications.

The Moiré grating technique was adapted from the Moiré Interferometry work done by David Mollenhauer of Wright Laboratory MLB. This technique uses a grating master, which consists of a flat glass substrate with an epoxy coating whose surface has undulations in height of approximately 0.3 microns, with wavelengths in the orthogonal directions perpendicular to the substrate normal of 0.8 microns.

At the beginning of the task, grid imaging was accomplished by taking polaroid optical micrographs of the sample surface in an ex-situ manner, i.e. the sample was removed from the deformation rig and imaged in a conventional light microscope. Next, the polaroids were digitally imaged using the Eikonix 1200 digital camera and Adobe Photoshop plug-in software. There are two main disadvantages of this technique. First, the inability to perform concurrent straining and imaging precludes the ability to image elastic strains, and necessitates the unloading and reloading of the sample each time it is to be imaged. Second, the two step imaging, polaroid followed by digital introduces extra sources of error and losses in resolution. This led to the design and acquisition of an imaging system for the ADDA program. It comprises a vibration-isolated optical workstation, mechanical stages to translate the optical microscope along three axes, an optical microscope with high-quality metallurgical objective lenses, the existing Eikonix digital camera, and a polaroid camera system as a secondary means of imaging. Initial trials using the optical workstation, the microstraining rig and a borrowed optical microscope demonstrated the advantages of vibration isolation as well as the feasibility of performing microstraining tests on the optical workstation.

At the start of the task, image analysis was accomplished via version 1.0 of the ADDA software written on the MacRail platform. Problems arose when images larger than 480x640 pixels were processed.

Modifications were made to the version 1.0 ADDA software written on MacRail version 7.2. These included restructuring the content and format of the output data, modifications of the user interface and grid layout procedure and modifications to make more efficient use of random access memory.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 127, An Investigation of Composite Matrix Deformation Via Automated Digital Deformation Analysis.

TASK: 112

TASK TITLE: Acoustic Microscopy for Nondestructive Evaluation (NDE)

TASK OBJECTIVE: To assess the capability of acoustic microscopy for NDE and material characterization of advanced materials.

SCIENTIST: Peter B. Nagy, Ph.D.

DESCRIPTION OF WORK:

A low frequency scanning acoustic microscope was previously designed and built within WL/MLLP for ultrasonic inspection of metals, ceramics, composites, and microjoints of these materials. The microscope operates in the 20-to-100 MHz frequency range. During this project, two new options were introduced to enhance image quality. First, the scanning resolution was increased from 0.5 mils (12.5μm) to 0.125 mils (3.125μm) by an interchangeable precision x-y stage of 1" x 1" scanning range. Second, the digitizing resolution was increased from 8 bit to 16 bit to accommodate more sophisticated image processing and displaying, and the operating software was modified to handle both old and new formats.

An automated *V(z)* option was developed to measure the local Rayleigh wave velocity of different materials within an approximately 1-mm-diameter spot. The procedure is semi-automatic under interactive control by the operator and there are four different data evaluation procedures one can choose from to optimize the measurement. The absolute accuracy of the technique is approximately 1.5% but comparative measurements can be done with much higher relative accuracy of 0.2%.

In order to expand the field of application for the instrument, it was designed so that it could be used as a conventional high-frequency C-scan imaging device in double-transmission or backscattering mode of operation as well. The instrument was successfully tested and used in different applications in both basic modes of operation. Results demonstrate that the reflection-type scanning acoustic microscope is particularly useful in studying weak changes in the micro structure which are accompanied by significant velocity variations (e.g., polycrystalline grains) while the C-scan imaging mode is more sensitive to scattering discontinuities (e.g., individual fibers embedded in a matrix).

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 112, Acoustic Microscopy for NDE.

TASK: 113

TASK TITLE: Microstructural Effects on Small Fatigue Cracks

TASK OBJECTIVE: To determine the effects of microstructure on the growth of small fatigue cracks in gamma titanium aluminide alloys.

SCIENTIST: Kakkaveri S. Ravichandran, Ph.D.

DESCRIPTION OF WORK:

Titanium aluminide alloys based on Ti_3Al intermetallic compound have attractive properties such

as higher strength at elevated temperature, higher modulus and greater oxidation resistance in comparison to conventional $\alpha+\beta$ alloys. Investigation of mechanical properties as a function of temperature is of interest to optimize composition and microstructure of these alloys.

Ti-25Al-17Nb-1Mo alloys possess attractive combination of strength and fracture toughness. In this research, tensile properties such as yield and ultimate strength, elongation and reduction in area were measured from tensile tests at temperatures of 25, 538, 649, and 760°C. The material used in this investigation was a vacuum arc melted and cast alloy of nominal composition.

Tensile tests were performed using specimens having threaded shoulder (diameter=12.7 mm) and a test section of length 25.4 mm and diameter, 5.0 mm. Tests were performed in air at a displacement rate of 0.002 mm/sec. Displacements were measured by quartz rod extensometers. The magnitudes of yield and ultimate strengths, and total elongation were estimated from the load-strain curves. The % reduction in area was estimated by measuring the specimen diameter before and after testing. After fracture, the final diameter of the fracture surface was measured at several orientations using an optical microscope. Due to limitations of load capacity of mechanical test machines and strain measuring extensometers, only tests at two different temperatures were performed in vacuum. It can be seen that yield strength and ultimate strength levels decrease as the test temperature is increased.

The yield and ultimate strengths of this material are slightly higher than reported in the review for alloys of this family. It was noted that the properties between vacuum and air did not exhibit significant difference. The small differences between the properties in air and in vacuum are of the order of experimental scatter. Further tests are necessary to ascertain this observation.

A survey of the results of fatigue crack growth behavior research on gamma TiAl alloys indicated that although all the alloys predominantly consisted of TiAl intermetallic compound, they also consisted of Ti_3Al compound, desirable for optimum strength and creep properties as well as ductility. The survey indicated that fatigue crack growth behavior exhibited wide variations in crack growth rates when comparisons were made to isolate the effect of a single variable, for example, a given microstructure morphology and temperature. These variations could arise due to the differences in processing methods, relative amounts of TiAl and Ti_3Al phases in a given microstructural morphology and the differences in the specimen geometry and test procedures employed.

An attempt was made in this research to begin investigations on small crack behavior in selected microstructural conditions of typical gamma TiAl alloys of interest to U.S. Air Force. The two TiAl alloys employed in this investigation were: Ti-45Al-2Nb-2Cr and Ti-46.5Al-3Nb-2Cr-0.22W. Both materials were received in the form of hot forged pancakes. Two different microstructures, namely, the duplex structure and the lamellar structure were generated by heat treatment for each alloy.

Small crack specimens were machined from the heat treated pancakes with the direction of growth of crack front at the depth of a surface crack coinciding with the radial direction in the pancakes. Compact tension specimens were also machined with the crack growth direction also in the radial direction. Fatigue precracking to initiate cracks naturally on the electropolished surface was performed

in a servo hydraulic machine equipped with two optical microscopes for insitu visual inspection of the fatigued specimen at periodic intervals.

At the beginning of the test program, inspection of the as-electropolished specimens revealed large preexisting cracks often of the size of a lamellar grain which could be seen even by direct visual examination. Such cracks were not found on the curvature sides of the test section of the specimens. A wide variation noted in fatigue lives at the same cyclic stress level could be due to the presence of large cracks on the side surfaces. Further studies are required to understand the nature of cracking and its relationship to machining procedures and microstructure.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 89, Tensile and Fatigue Crack Growth Behavior of Titanium Aluminide Intermetallics.

TASK: 114

TASK TITLE: Micromechanical Failure Mechanisms in Composites

TASK OBJECTIVE: To define the conditions causing damage initiation and subsequent growth of new damage in undirectional brittle matrix composites (BMC) under different loading conditions.

SCIENTIST: Som Soni, Ph.D., AdTech Systems Research

DESCRIPTION OF WORK:

The specific objective of this research was to employ an existing computer model, called the axisymmetric damage model, to solve for the micromechanical stress fields and energy release rates in a unidirectional BMC in the presence of initial annular cracks in the matrix. Subsequent growth, controlled by the local energy release rate, subsidiary failure mechanisms created along the interface, and finally, fiber damage was to be predicted as a function of the residual stress state of the composite and the imposed tractions. The effect of friction was to be incorporated in the model, as well as interface damage in which the crack opens under load. A user manual was also to be prepared for the updated computer code.

A preprocessor (PREP) was developed for the existing axisymmetric, thermoelastic response model of composites developed at the Air Force Materials Laboratory. The code, written in standard FORTRAN was developed to simplify the data input process and both the codes. The preprocessor and the analysis code are stand-alone and portable to other computer systems. Data may be entered either interactively or in a batch mode, through a file. A thorough description of the code and its use was

presented along with an example problem. The example problem consisted of a central fiber with a cylindrical region of matrix. The unit-cell contained an annular pressurized crack, partially extended into the matrix.

A User's Manual was prepared for the preprocessor (PREP) and submitted as part of the final report. The report also included an analytical analysis of stress fields in the free-free surface composite laminate.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 111, Micromechanical Failure Mechanism in Composites.

TASK: 115

TASK TITLE: Material and Process Models for Machining

TASK OBJECTIVE: Determine material models for use in advanced analysis of orthogonal cutting.

SCIENTIST: Oscar W. Dillon, Ph.D.

DESCRIPTION OF WORK:

Prior finite element analyses showed that the transition between the material to be cut and the chip that is being formed in orthogonal machining occurs very rapidly, in agreement with the classical picture where the flow direction of the material suddenly changes in a region of zero thickness. Therefore it was thought that it was worth while to study the "shear plane" region in more detail and on a finer scale.

This effort evaluated a material model for the analysis of the stresses, strain rate distribution, and temperatures that occur on the shear plane during orthogonal machining. A one dimensional model that imposed a uniform stress and a final strain of 2.5 was evaluated in detail. The cutting zone was assumed to contain either twenty or forty deforming elements. Rigid, but thermally conducting regions, are attached to each end of the deformation zone. The material was assumed to be of power law type in both the strain rate and strain. In an attempt at modeling the Chiem-Duffy behavior at very high rates, the exponent of the strain rate term was itself allowed to change at rates above 2,000/sec.

Results were obtained for 4340 steel at several speeds typical of normal cutting practice and to a lesser extent for commercially pure titanium. It was found that (for the assumed values of the parameters) the highest strain rates in the steel occur near the cutting zone exit location adjacent to the chip domain, while in the case of titanium they were at the entrance region or next to the work material at slow speeds. In both cases there was a significant build up in the temperature at the entrance to the cutting zone. Rather surprisingly, attempts at making the strain rate transition to zero in these regions by using more and smaller elements did not work very well.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 109, Orthogonal Machining Models.

TASK: 116

TASK TITLE: Development of a Concept Memory as a Methodology for Solving the Generalization Problem

TASK OBJECTIVE: To investigate and develop a system that can be used to perform feature sequencing in the domain of manufacturing using a concept memory.

SCIENTIST: Hilmi Al-Kamhawi, B.S.

DESCRIPTION OF WORK:

A system of algorithms was developed to efficiently (polynomial complete) design a sequence that optimally removes material. The process design is complicated by the combinatorial explosion of alternative solutions and interactions among process resources (machines, tool, and part orientation). Of more specific consideration is the generation of a process design for removing material which finds an optimal or near-optimal machining sequence involving conflicting criteria. The three predominant process criteria are safety, speed, and quality.

In designing the evaluation function a two-fold strategy was implemented. Penalties or positive value weights were imposed on sequences that violate safety criteria, e.g.,machining an edge cut before a hole that intersects the edge cut. 'Good' sequences were rewarded with negative value weights if they did not violate any of the safety, speed, or quality criteria. The evaluation function seeks to find the sequence with the most negative cumulative value. The usual priority for satisfying these criteria is: first safety, then quality, finally tool changes and distance.

Two Evolutionary programs were coded to exercise and compare alternative search strategies. Both programs employ the use of an assigned fitness function, inversion, and mutation as genetic operators. The first of the two is referred to as simply a Genetic Algorithm, and the second as an Evolutionary Simulated Annealing Algorithm.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 120, Solving the Problem of Feature Sequencing in a Feature Based Design System.

TASK: 117

TASK TITLE: Discovery Systems, Associative Memories and/or Genetic Algorithms for Concept

Formation

TASK OBJECTIVE: Investigate applications of discovery systems utilizing episodal associative memories (EAM) and genetic algorithms (GA).

SCIENTIST: Allen G. Jackson, Ph.D.

DESCRIPTION OF WORK:

Applications to materials research of various computer methods for discovery of processes and designs were explored. Methods examined included rough sets, concept memory formation, and concept formation algorithms. The most useful for discovery appears to be rough sets, because of its ability to sort through a multidimensional space and determine the relative importance of each variable with respect to an output. A tutorial style review of rough sets was presented based on papers available in the open literature.

Electro-optical data were used as a test data set to determine the usefulness of these methods for discovery. Rough sets was successfully applied to electro-optical data, succeeding in ranking variables correctly as verified by plots of the data. In addition, neural nets were briefly considered, but they were not pursued, because of the failure to simulate discrete conditions in the electro-optical data set.

Concept memory techniques appear to be promising for handling complex cases where simple concepts are inadequate to describe the relationships found. Russian literature concerned with automatic prediction of ternary compounds was reviewed, and useful information was extracted, particularly from the book by Gladun.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 126,Associative and Conceptual Memory Techniques.

TASK: 118

TASK TITLE: Model-Based Compensation of Shutter Opening Induced Flux Transients in Molecular Beam Epitaxy

TASK OBJECTIVE: Develop a model-based compensation algorithm to compensate for deterministic behavior. Use this algorithm to develop a module for the Materials Directorate's MBE Control System to minimize MBE shutter opening flux transients.

SCIENTIST: Steve Adams, B.S.

DESCRIPTION OF WORK:

During this task a robust control system for the reduction of the flux transient caused by a shutter opening on a Molecular Beam Epitaxy machine was developed and implemented. The first module, Automated Process Identification and Calculation Module, will run through a series of tests to obtain the transfer function of the system and the shutter opening disturbance. It will then calculate the least-squares fit to the test data and calculate the Flux compensation signal equation. The second module, Setpoint Compensation Module, will perform the necessary tasks to apply the setpoint signal to a proportional-integral-derivative (PID) controller. This control system determines the temperature setpoint modification needed to reduce the transient below 1.0% variation.

The process identification system will determine the characteristic of the disturbance and the transfer function of the system. From this data a compensation signal is calculated and applied to the setpoint temperature of the PID controller. A computer is used automatically to apply the setpoint signal to the PID controller. This compensator will be integrated into a MBE control system developed at the Materials Directorate of Wright Laboratory, Wright-Patterson Air Force Base, Ohio.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume Volume 129, Implementation of a Model-Based Compensation of Shutter Opening Induced Transients in a Molecular Beam Epitaxy Process.

TASK: 119

TASK TITLE: Development of Intelligent Control Techniques for Materials

TASK OBJECTIVE: Develop intelligent control techniques and methodologies for materials processing. Techniques will include Optimal Control, Qualitative Process Automation, and Neural Networks. Facilitate transition of the technology developed for the Material Directorate's MBE Control System to industry.

SCIENTIST: Oliver D. Patterson, M.S.

DESCRIPTION OF WORK:

In order to achieve real-time control of Molecular Beam Epitaxy, accurate and fast sensors are required. This task reviewed progress toward improving the speed and accuracy of thickness and composition information derived from ellipsometry measurements. Use of additional datapoints was shown to significantly reduce the effect of measurement error. Functional link and multilayer perceptron artificial neural networks were investigated for modeling the ellipsometry transcendental equations in order to reduce the time required to transform ellipsometry data into thickness and composition values.

The problem of the ellipsometry equations inversion was investigated mathematically and

numerically. Use of a combination of neural net and modified Newton's method to get sufficiently accurate results provided sufficiently accurate measurements. To make final conclusions, further numerical experiments are needed with more accurate data.

Two programs were written for numerical investigation of the problem. The first, called NEWTONAF, implements modified Newton's method and allows for numerical investigation of inversion of ellipsometry equations both with real and artificially generated data. The second, called TEST3, is designed for calculations of the film depth given input data and estimations of optical parameters of the film. Numerical experiments have shown that estimates of the optical parameters of the film are very sensitive to accuracy of the input data. It was found that there exist solutions of the ellipsometry equations with very close optical parameters and rather different values of the film depth. That feature, intrinsic to the equations, makes the problem of ellipsometry equations inversion a very difficult one and, maybe, leaves the only hope in the neural net solution.

Also explored was the use of neural-nets as efficient computational tools for providing estimates of optical material parameters, and for monitoring film thickness in the MBE process. Extensive training and testing of the nets was carried out. The neural net approach was critically helpful in establishing what appears to be a systematic (calibration) error in the experimental data presented for interpretation, as opposed to random errors.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 130, Application of Neural Network Technology to Ellipsometry Data Refinement for Real Time Control of MBE.

TASK: 120

TASK TITLE: Enhancement of the Molecular Beam Epitaxy Control System

TASK OBJECTIVE: Improve the robustness of the Molecular Beam Epitaxy (MBE) Control System so that its software can be easily modified and so that it can be installed on the MBE machines of several manufacturers. Assist in the design of software for processing the data from the Ellipsometer, an optical sensor being developed for the Self-Directed Control Module of the MBE Control System. Improve the robustness of the Automated Process Identification Module so that accurate models of the system can be obtained repeatably under the full range of conditions the MBE machine is under including near empty Knudsen Cells. Assist in the integration of the Model-based Shutter Opening Transient Compensation Module with the MBE Control System. Assist in the submission

of a patent for the MBE Control System.

SCIENTIST: Jeffrey J. Heyob, M.S.

DESCRIPTION OF WORK:

A "MBE (Molecular Beam Epitaxy) Control" program was developed which incorporates the Process Discovery Autotuner, Beam Equivalent Pressure calibration, flux compensation experiments, data logging, and other MBE set-up and growth functions. The relationship between flux and the multiple MBE Knudsen Cell temperatures required concentration on stabilizing the temperature of the Knudsen Cells. The volume of information needed to simultaneously stabilize all of these temperature control loops required computer automation of the process knowledge acquisition and utilization of this knowledge for optimum temperature control of the Knudsen Cells. The need for system customization, porting the system to new machines, and the ability to "drop-in" new instrument and sensor interfaces led to the implementation of modular programs and inter-application-communication (IAC).

The enhancement of the Molecular Beam Epitaxy Control System resident on a Macintosh IIfx microcomputer progressed in two facets toward the improvement of the Molecular Beam Epitaxy (MBE) process.

Work done to address MBE flux stability beyond its controllability through temperature by a proportion-integral-derivative (PID) control loop gave support to improving the stability of the PID temperature controller for the Knudsen Cell thermal control loop. The existing Eurotherm 825 PID temperature controller was compared with upgraded Eurotherm Model 818 and Eurotherm Model 905 controllers. The stability and overall performance tests favored the Model 905 controller with a sample-time five times faster than the original Model 825 controllers.

The multi-tasking and inter-application-communication (IAC) environment has allowed the MBE instrument interfaces and supervisory control modules to be developed as separate programs that communicate with each other. Individual program development has shortened design cycles and simplified program troubleshooting. This modular approach in the development of the MBE control system provides a protected environment for each program's unique and often complex data structures, and also provides a consistent data communication channel to any other programs required for data inter-action in the multi-tasking MBE control environment. The IAC connections between the various program modules are very flexible to allow making, breaking, and re-establishing data links with any combinations of programs with as many as 128 simultaneous data links. Specific data flow through the system achieves better organization during special sequences of the MBE operation, such as during set-up, tuning, calibration, or growth, by having non-involved program modules idle. The flexibility of the MBE Control System was demonstrated by its installation in a new system to automate Chemical Vapor Deposition (CVD) processes.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 84, Enhancement of the Molecular Beam Epitaxy

Control System.

TASK: 121

TASK TITLE: Self-Lubricating Metal-Matrix Composites

TASK OBJECTIVE: Determine wear lives of combinations of experimental, developed metal-matrix, self lubricating composites.

SCIENTIST: Somuri V. Prasad, Ph.D.

DESCRIPTION OF WORK:

The essence of this task was to explore the feasibility of developing self-lubricating aluminum metal-matrix composites for use in vacuum, dry, and humid environments.

The research involved the synthesis and tribological behavior of self-lubricating aluminum alloy metal-matrix composites (MMCs). The formulations comprised of tungsten disulfide (WS_2) and silicon carbide (SiC) particles dispersed in a commercial aluminum alloy (Al-0.40Si-0.75Mg) matrix. Composites were fabricated by a conventional powder metallurgy route involving blending, compacting, and sintering. In an effort to understand the lubricating mechanisms of pure tungsten disulfide, films of WS_2 were grown on stainless steel substrate using a pulsed laser.

Friction and wear tests were performed in a ball-on-disk configuration against a steel counterface. The test assembly was enclosed in a bell jar which permitted the tests to be performed in dry nitrogen and air. Tests on MMC surfaces were run for a duration of one million cycles. Wear scars and transfer films on steel counterface were analyzed by scanning electron microscopy and Raman spectroscopy.

The coefficient of friction of a typical aluminum alloy against a steel counterface 0.10SiC-0.03WS_2 MMC in dry nitrogen environment was 0.05, and in laboratory air (with relative humidity around 65%) it was 0.10. In both environments, transfer of aluminum to the steel counterface was absent. Tungsten disulfide platelets were not traced either in the wear debris or in the transfer film on the steel ball. Sliding of hexagonal tungsten disulfide platelets is not a probable mechanism of lubrication. The debris, which is spheroidal in shape, is different in chemical composition from any of the constituent phases of the MMC. Although the exact chemistry is unknown at this stage, formation of a new lubricous compound, as a result of tribochemical reactions, appears to be origin of lubrication in self-lubricating aluminum MMCs.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 139, Self-Lubricating Aluminum Metal Matrix Composites.

TASK: 122

TASK TITLE: Synthesis of Aromatic and Aromatic Heterocyclic Oligomers and Polymers for Third-Order Nonlinear Optical (NLO) Evaluation

TASK OBJECTIVE: The synthesis of novel aromatic and aromatic heterocyclic oligomers with unique arrangements of donor and acceptor aromatic rings.

SCIENTIST: Jay C. Bhatt, Ph.D.

DESCRIPTION OF WORK:

The Wright Laboratory Materials Directorate at the Wright-Patterson Air Force Base has been very actively involved in systematic structure-NLO property relationship studies. These studies have demonstrated that the third order NLO susceptibility depends on (i) nature of the heterocyclic chromophore, (ii) effective conjugation length, and (iii) 2-dimensional π-conjugation. The purpose of this research was to design and synthesize novel model compounds and polymers for γ^3 NLO properties. The focus was (i) to incorporate thiophene and related heterocyclic donor chromophores and attempt to optimize γ^3 values, (ii) to improve solubility/processability characteristics of the material, and (iii) to develop a structure-NLO property relationship for this series of compounds. Polyphenylquinoxaline was chosen as the backbone polymer because it can be obtained in high molecular weight by clean condensation polymerization reaction under mild conditions.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 140, Design and Synthesis of Polyphenylquinoxalines with Heteroaromatic Chromophores for NLO Material.

TASK: 123

TASK TITLE: Electrical Characterization of Semiconductors

TASK OBJECTIVE: Establish the important parameters associated with the electronic properties of semiconductor materials.

SCIENTIST: Andrew O. Evwaraye, Ph.D.

DESCRIPTION OF WORK:

Silicon carbide has unique physical and electronic properties that make it the material of choice for the fabrication of electronic devices. SiC devices can operate at high temperatures without being overwhelmed by intrinsic carrier conduction.

The successful development of device technology depends upon the ability to grow epilayers either by chemical vapor deposition (CVD) or by liquid phase epitaxy (LPE) on a suitable substrate. Silicon carbide epilayers have been successfully deposited on silicon substrate. However, such films have a high density of defects. Films grown on SiC substrates have a much higher quality and therefore the performance of the devices fabricated on such films is much improved. In order to produce semi-insulating substrates, silicon carbide must be doped, during growth, with impurities that will produce recombination centers in the bandgap. First we must know and identify the chemical impurities in bulk 6H-SiC that contaminate the system during growth.

The main task of this project was to characterize and identify the impurities in bulk 6H-Silicon carbide. Four major techniques were employed to study these impurity defects. These are (i) Deep Level Transient Spectroscopy (DLTS), (ii) Admittance Spectroscopy, (iii) Infrared Absorption Measurements, and (iv) Optical Admittance Spectroscopy.

The optical admittance technique is based upon the measurement of additional conductance and capacitance of a Schottky barrier while being illuminated. The measurement of the capacitance, C_p, and conductance, G_p, is based on the modulation of the space charge region by a sinusoidal voltage of frequency ω. This was the first time, as far as we know, that optical admittance spectroscopy was applied to n-type 6H-SiC crystals. The persistent photo conductivity and capacitance in 6H-SiC was reported for the first time.

Deep level transient spectroscopy (DLTS) was used to determine the thermal emission rates for electrons, e_n, the thermal activation energy, E_T, and the defect concentration, N_T. The measurements were made in the temperature range of 200 to 400K. No attempt was made to make measurements below 200K; there was a carrier freeze-out in these samples below 200K.

The technique of admittance spectroscopy, which is based on the measurement of conductance and capacitance of a junction, is not adversely affected by increased series due to freeze-out. Thus it is the appropriate technique for characterizing levels due to the shallow dopants. The admittance spectroscopy technique was used to study shallow levels in n-type 6H-SiC single crystals. A total of eight unintentionally doped n-type samples obtained from three different crystal growers were used in this study. Two of the samples were grown by the Lely method, the others were grown by the physical vapor transport process. We determined the activation energies, capture cross-sections, and the thermal emission rates for the shallow defect levels in n-type 6H-SiC. The E_c-0.11 eV and E_c0.08eV levels are associated with nitrogen at cubic centers (K_1, K_2) and the hexagonal (h) site. The 0.04eV and 0.03eV are too shallow to be due to nitrogen. They may be due to some other contaminants yet to be chemically determined.

The characteristic signatures of deep levels in n-type, 6H-SiC were also determined, that is, the emission rates, capture cross-sections, and activation energies, were measured by admittance spectroscopic methods. Deep level transient spectroscopy has been used to characterize deep impurity levels in n-type 6H-SiC single crystals, due to impurities un-intentionally incorporated into the lattice during growth IR signatures of vanadium in the samples were measured and correlated with the DLTS

results.

The DLTS technique was used to completely characterize a defect level observed in three samples. These samples were obtained from two independent crystal growers. The defect, which is at E_C-0.71 eV and has an electron capture cross-section of 5.63×10^{-20} cm^2, is a bulk defect. Infrared absorption measurements were also made on the wafers from which the diodes for the DLTS measurements were fabricated. A DLTS peak located at E_C-0.71 eV was observed in samples that showed the IR vanadium signature. On the other hand, the DLTS peak was not observed in samples that did not show the vanadium signature. It was therefore concluded that the observed defect at E_C-0.71 eV was due to vanadium contamination.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 106, Electrical and Optical Characterization of Bulk Silicon Carbide Single Crystals.

TASK: 124

TASK TITLE: NDE Technology Transition Development

TASK OBJECTIVE: Identify, analyze, and/or develop enhanced methods for technology transition of sonic, electromagnetic, radiographic and optical nondestructive evaluation (NDE) methodologies.

SCIENTIST: Matthew J. Golis, Ph.D., Advanced Quality Concepts

DESCRIPTION OF WORK:

This project was established within the NDE Branch (WL/MLLP) of the Materials Directorate of Wright Laboratory for the purpose of assisting in the evolving transition of Nondestructive Evaluation (NDE) technologies between the private sector and the Wright Laboratory. Project activities centered around three distinctly different types of tasks: (1) determination of the status of the Retirement for Cause (RFC) engine component inspection systems being used at the San Antonio Air Logistics Center (SA-ALC); (2) promotion of liaison activities directed at obtaining prompt technical responses to the NDE weephole inspection needs of the Warner Robins ALC; and (3) assisting in creating informational links between the branch's technical staff and private industrial and other agency sectors.

The status of the RFC systems in use at SA/ALC was determined through personal site visits, interviews with experts familiar with the RFC systems, and independent review and analysis of reports and recent performance data. Results indicated that the performance of these systems has met the expectations of the original reliability review team, but that on-going problems related to background noise, detection of cracking in tight corners and the development of generalized scan plans remain issues in need of future resolution.

The criticality of and the difficulties involved in inspecting cracking weep holes in the lower wing planks of C-141 fuel tanks was communicated to Wright Laboratory personnel following on-site visits to Warner Robins ALC and the field inspections conducted at Wright-Patterson AFB. Briefings were given to all interested personnel regarding the criteria being used to inspect for cracking and the difficult environmental setting within which inspections were being performed. As a result of these orientations and several advisory meetings, two weep hole inspection technology studies were quickly started within the NDE Branch.

Participation in several technology conferences took place in order to bring the activities of the NDE Branch to the attention of the private commercial sector. The session on NDE and the Federal Small Business Innovation Research (SBIR) program was chaired at the Fall 1993 meeting of the American Society for Nondestructive Testing (ASNT). Arrangements were made for an invited paper on the history and NDE developmental interests of the NDE Branch with emphasis on its use of the SBIR program to achieve various technology goals. Several other technical meetings were attended in order to identify possible NDE technologies which have the potential for adaptation to areas such as ceramics, composites, fasteners, and welded components. A formal critique was given to both Branch and Arinc project personnel regarding the effort to assess the performance of NDE methods used in the detection and sizing of corrosion attack on aircraft structures.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 137, NDE Technology Transition Development.

TASK: 125

TASK TITLE: Computational Predictions Using a Genetic Algorithm

TASK OBJECTIVE: To apply a knowledge based discovery system to the task of interacting with a Genetic Algorithm to do optimization of a non-linear problem.

SCIENTIST: Scott King, B.S.

DESCRIPTION OF WORK:

The activity of a protein is governed by its three-dimensional configuration; therefore, the key to understanding and determining protein function lies in structure analysis. However, the percentage of protein with known structure is very small relative to the number of sequenced proteins. An enormous campaign has been launched to narrow this gap by searching for a relationship between protein sequence and structure.

It is believed that proteins have evolved by means of random mutation of genes and natural selection. These mechanisms have been employed in an attempt to understand the relationship between the composition and shape of proteins. A Genetic Algorithm (GA), in conjunction with a rule based

inference engine, The Scholars Companion (TSC), was applied to this task on this project.

Combining TSC with a GA, we have a rule based system that can encourage the evolution of rules to answer questions. Using this system, a protein database was searched in an attempt to find empirical rules that predict the secondary structure of proteins based on their primary structure. Two disjoint sets of proteins were taken from the Brookhaven Protein Database; one set was used to train the population and the other to test how well the final population can predict protein structure.

In this study, a variety of GA's was applied to the task of predicting protein structure. One GA used consisted of a population of rules with actors and relations. This method was used to discover if the existence of certain amino acids in a window was adequate to predict the structure of the window. The results implied that there were many patterns that could predict certain structures of the whole protein. In a move to enhance the progress of the GA, a control engine was built. The DE consisted of a set of meta level rules that adjusted the environment of the GA. Slight improvements in prediction were achieved; however, the DE could not overcome the shortcomings of the protein GA. The final method considered every position in the window and attempted to predict a structure for each one. This method has not produced significant results, however it has demonstrated an ability to determine templates for the design of peptide segments with a certain structure.

The future appears to be in protein design, and not protein prediction. The GA has shown an ability to discover empirical rules for design.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 93, Discovery in Protein Structure with a Genetic Algorithm and TSC.

TASK: 126

TASK TITLE: Nonlinear Optical Characterization of Biopolymers

TASK OBJECTIVE: To characterize the chi(2) and chi(3) properties of biopolymers being developed in the materials laboratory in-house research programs.

SCIENTIST: Paul A. Fleitz, Ph.D.

DESCRIPTION OF WORK:

This research supported the study of new materials with potential applications for protecting sensors from high intensity light. One approach to sensor protection involves passive optical limiters.

Materials with large nonlinear optical properties are often used as passive optical limiters. For this reason, there is a significant effort to measure the nonlinear optical properties of organic materials. The objectives of this work were twofold. First, to characterize nonlinearity observed in new organic materials produced from both in-house and external sources. Second, to measure the nonlinear optical properties of these new molecular systems.

Z-scan technique was used to investigate the nonlinear optical properties of thin films produced by the plasma vapor deposition of benzene and also a series of conjugated organic molecules. The Z-scan technique is a simple, single beam technique to measure the nonlinear refraction and nonlinear absorption in materials. The results on the film indicate that the nonlinear refractive index of this material is less than $2x10^{-10}$esu. Nonlinear absorption has also been observed in these films, but the mechanisms responsible for this absorption are not known. For the organic molecules, the nonlinear refractive index was indistinguishable from the solvent contribution.

The nonlinear absorption for these materials was extensively studied. The molecules investigated were diphenyl acetylene, diphenyl butadiene, diphenyl butadiyne, 1,4-bis (phenylethynyl) benzene, bis (4-biphenyl) acetylene, 4,4'-bis(phenylethynyl) biphenyl. All of the materials investigated show nonlinear absorption. For two of the molecules, the nonlinear absorption is the result of a two-photon absorption process, and two-photon absorption cross-sections were measured. The remaining molecules exhibit two-photon absorption followed by linear absorption from the excited state.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 142,Characterization of Nonlinear Optical Properties Using the Z-scan Technique.

TASK: 127

TASK TITLE: Optimal Control Techniques for Thermomechanical Processes

TASK OBJECTIVE: To complete the investigation of modern control theory applied to the microstructural control of thermomechanical processes and to apply the results to the design of forging and/or extrusion dies.

SCIENTIST: R. Dennis Irwin, Ph.D.

DESCRIPTION OF WORK:

This research involved two major attempts to develop a general software system for calculating optimal strain, strain-rate, and temperature profiles for microstructural evolution in hot deformation processes. The first approach utilized a symbolic manipulation code as an automatic code generator. Functions to be used by existing MATLAB® codes that solve two point boundary value PROBLEMS are automatically generated by the symbolic manipulation code, in this case MATHEMATICA ®. This

approach proved to be unsuccessful, due to undocumented command line limitations in MATLAB®. However, the resulting software system organization was outlined so that, if future MATLAB® implementations correct the command line interpreter limitations, the software can be used for completely general optimal profile calculations.

Various alternatives to the use of MATHEMATICA ® and/or MATLAB® were considered. These alternatives included generating FORTRAN or C language functions; options which were rejected in favor of an approach involving the re-representation of the microstructural properties of interest as polynomials in several variables. The required MATLAB® functions were then generated manually. This process, which involved the calculation of several very complicated partial derivatives, was the single most time-consuming part of the overall software development. The calculations involved and the resulting MATLAB® functions were documented.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 143, Software Approaches for Calculating Optimal Microstructural Evolution Profiles.

TASK: 128

TASK TITLE: Micromechanics Based Constitutive Equations for Modeling of Composite Consolidation

TASK OBJECTIVE: To develop micromechanics-based constitutive equations for porous ceramic and metallic materials and incorporate these into finite element method (FEM) models of composite consolidation.

SCIENTIST: Shivaramaiah Shamasundar, Ph.D.

DESCRIPTION OF WORK:

A hybrid continuum-micromechanical constitutive model for the consolidation of porous media was developed. The model uses an elliptic form of expanding yield function. Relative density of the porous matrix is treated as the internal variable which is related to two intermediate variables apparent Poisson's ratio (process specific) and the relative microhardness (material and microstructure specific). The constitutive law is derived from the yield function assuming an associated flow rule and is implemented on a general purpose finite element simulation procedure.

The yield function and the constitutive model were applied to model the consolidation behavior of various ceramic and intermetallic powders in a range of processes including sinter forging, die-pressing, and hot isostatic pressing. Simulation results were compared with Materials Directorate inhouse

experiments and those available in the literature. A methodology for process optimization was proposed.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 153, A Hybrid Continuum-Micromechanics Based Constitutive Model for Consolidation of Powder Systems.

TASK: 129

TASK TITLE: Characterization of Ceramic Composites

TASK OBJECTIVE: To find economical methods for processing ceramic fiber-matrix composites

SCIENTIST: Michael K. Cinibulk, Ph.D.

DESCRIPTION OF WORK:

The overall goal of the research was to find relationships between the processing, microstructure, and structural properties of ceramic composites that yield useful insight towards the economical manufacture of composites with superior fracture toughness and creep resistance. The specific objectives of this task were to investigate the feasibility of using cleavable oxides as a fiber-matrix interphase in alumina-based composites, to achieve enhanced toughness and oxidation resistance.

Candidate materials were synthesized and screened on the basis of thermal stability of high-temperature oxidizing environments. Calcium hexaluminate was chosen as the prototype interphase material. A number of sapphire-fiber reinforced composites were fabricated having a calcium hexaluminate interphase and either alumina or yttrium-aluminum-garnet (YAG) as the matrix. The major processing goal of obtaining a highly textured interphase, with the basal (cleavage) planes of the coating oriented parallel to the fiber axis, was accomplished. Observations of crack propagation by cleavage in TEM foils suggest the ability of such a coating to protect the fiber from impinging matrix cracks.

Phase development of the sol-derived hibonite in powder and thin film forms was followed by X-ray diffraction and transmission electron microscopy (TEM). It was determined that if alumina is to be used in conjunction with sapphire fibers that a coating of phase-pure hibonite must be obtained prior to composite consolidation to minimize fiber-matrix interactions.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 146, Feasibility Study on the use of Cleavable Oxides as an Interphase in Alumina-Based Composites.

TASK: 130

The government canceled this task.

TASK: 131

TASK TITLE: Computational Material Modeling

TASK OBJECTIVE: To establish quantitative techniques for predicting microstructural changes of metallic systems during hot deformation processes.

SCIENTIST: Tim W. Voegeli, MAT.

DESCRIPTION OF WORK:

This project was an extension of earlier work. The primary objectives were two fold: (1) research the possibility of using fractal geometry to model grain structure of metals to describe morphological changes during a hot deformation process, and (2) examine the load and stoke data output of a hot deformation compression test to see if chaotic, periodic, or random information is present.

Grain models were accomplished using both matrix transformations and aggregations methods. Since matrix transformations will eventually completely fill the plane, these models could only be used after several iterations of the process. Aggregations will eventually reach a steady state and form grain boundaries. This second method, aggregation, seems more suitable for introducing "rules" that simulate material parameters.

Load and stoke data analysis was performed on a compression test using an aluminum-lithium alloy. Nonlinear forecasting of the load-difference data indicated chaotic properties at certain temperatures and strain rates. These temperatures and strain rates correspond to optimum processing conditions on known stability maps. However, the load-difference data showed remarkably similar frequencies at the same strain rate throughout the range of temperatures. It was concluded that this was the result of machine factors in the compression tests and not a result of material factors.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 123, Computational Material Modeling.

TASK: 132

TASK TITLE: Investigation of Advanced Metallic Composites

TASK OBJECTIVE: To develop an understanding of the relationships between the composition and

microstructure of matrices, the bonding at fiber/matrix interfaces, and composite properties in advanced metallic composites.

SCIENTIST: Lingang Xiao, Ph.D.

DESCRIPTION OF WORK:

The goal of this research was to investigate the failure mechanisms and processes of metal-matrix composites (MMCs) during mechanical loading using acoustic emission (AE) technique. Due to limitations of time, only acoustic emission from matrix materials was studied. However, the work conducted in this research was essential for establishing the basic "building block" for identifying the major failure mechanisms and processes of MMCs using AE technique.

In this study, in-situ microstructure observation on slip line and microfracture processes was coupled with mechanical deformation to investigate the acoustic emission of Ti-6Al-4V, a two phase alloy. The material was subjected to several different heat treatments to produce various microstructures and grain sizes. The dependencies of acoustic emission characteristics, such as the acoustic emission events amplitude, the rate of acoustic emission, location of the acoustic emission sources, and the total events of acoustic emission in each deformation test, on work hardening, grain size, second phase, and strain rate were explored. The presence of the second phase, ß, existing in either intergranular network or thin plates, was found to have little influence on the acoustic emission of this material. Furthermore, it was found that the dependencies of the acoustic emission characteristics on work hardening, grain size, second phase and strain rate could be explained in terms of the operation of Frank-Read dislocation sources.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 154, The Relationship Between Microstructure and Acoustic Emission in Ti-6Al-4V.

TASK: 133

TASK TITLE: Deformation in Advanced Metallic Composites

TASK OBJECTIVE: To investigate the extent and effect of localized deformation in advanced metallic composites.

SCIENTIST: Sion M. Pickard, Ph.D.

DESCRIPTION OF WORK:

Residual elastic stresses generated upon cooling from the processing temperature of continuously-

reinforced MMC's can lead to creep rates of the composite and reduce uniaxial yield stress. Residual tensile stresses also encourage the formation of matrix cracks about the fiber.

In this study, Ti 15/3 continuous SCS6 SiC Fiber reinforced composite was used as a model system in which to measure residual stresses by a matrix removal technique. The composite was evaluated both in the as processed condition and after uniaxial tensile deformation. Two different fiber volume fraction levels of Vf=0 and 0.35 were used in the study. The measured values of fiber residual axial strain were compared with model predictions using an elastic concentric cylinder model. The errors inherent in the residual strain measurement technique were critically discussed.

The effect of predeformation was found to greatly reduce the residual stress level. The measured values of residual stress were approximately 10% higher than the model predictions at both the volume fraction levels studied. This discrepancy can be accounted for by uncertainties in the coefficient of thermal expansion of matrix and fiber phases used in the calculations. The matrix removal technique for residual stress measurement was shown to be a potentially useful technique to apply to continuous fiber composites.

The detailed project description, method, results and discussion are reported in Contributive Research and Development Final Report, Volume 91, An Experimental Study of Residual Stresses in Ti 15/3 Continuous SiC Fiber Composites.

TASK: 134

TASK TITLE: Studies of Nonlinear Optical Material Designs

TASK OBJECTIVE: To investigate questions regarding use of nonlinear optical materials in various potential optical devices. Such questions will involve determining the optimum conditions for these new optical materials in thin film device structures.

SCIENTIST: Steven Cartwright, Ph.D.

DESCRIPTION OF WORK:

"Rugate" refers to the technique by which a type of filter is made. A rugate structure can be modeled as a set of very thin films where the individual indices of refraction vary approximately as a sine wave (or any other function). Using this model the characteristics of the rugate, including the internal electric field intensity, can be examined.

The approach utilized in this study was to calculate the electric fields directly from Maxwell's equations. This approach has the advantage that all parameters appear expressly and can be varied individually. The disadvantage is that simplifying assumptions must be made to render the problem tractable. Chief among these assumptions is that the index of refraction variations are sinusoidal. This

limits the analysis to only the simplest rugate structures. However, much can be learned from a simple case, and it is possible to add fields coherently (for the same wavelength) or incoherently (for different wavelengths) to construct much more complicated structures. In this analysis it was assumed that the index of refraction variations were small compared to the average index and that the materials used were not inherently absorbing. These restrictions are not severe and are usually made as well when using thin film programs.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 90, Analytical Model of the Internal Electric Field in a Rugate Filter.

TASK: 135

TASK TITLE: Control of Metal Forming Processes

TASK OBJECTIVE: To develop analytical models and control methodologies for hot deformation of high temperature materials.

SCIENTIST: Ramana V. Grandhi, Ph.D.

DESCRIPTION OF WORK:

This research program was established to develop a method for optimal control of process parameters for thermo-mechanical forging operations. The control objective is to obtain an optimum microstructure in the end product with the help of computer simulations and optimal control design of the forging process with the requirements on field variables such as strain-rate and temperature.

The research incorporated a design method where a state space representation of the deformation process was made based on the finite element model of the workpiece domain. The state equations were then solved using linear quadratic regulator theory to determine the optimal forging press ram velocity trajectory as well as initial temperature corrections for non-isothermal operations. Because finite element discretization can result in a large number of states, further research was done in reducing the order of the state space model without impacting the response of the full size system.

Validation of the process control methodology was accomplished via computer simulation using FEM program ALPID. Results of these simulations verified that state space control is an effective method for determining ram velocity and initial die temperature. Having developed the capability for determining optimal process parameters, the program can continue on through experimental verification.

The initial goal of the experimental verification phase was to demonstrate the ability of the integrated process control approach in the production of a highly complex part from alloys which are normally difficult to process. The candidate alloy for this particular task was titanium-aluminide (Ti-48Al-2V). The test article selected was the subscale integrated blade and rotor (IBR) turbine disk developed by Pratt & Whitney.

An equivalent axisymmetric model for the IBR disk was generated and used to determine the optimal press ram velocity schedule for the isothermal forging process. A velocity schedule for the initial stage of the forging process was generated using the state space representation with LQR control by three methods; full size state space control, reduced order model developed using balanced model reduction techniques, and single model control using the reduced order state space model. Results from all three methods compared well and provided results which were consistent with deformation modes and initial processing conditions where the ram velocity essentially remains constant as the flange (blades) are formed. It is clear that a single reduced order state space model can adequately represent the deformation process over an extended die stroke interval even when boundary conditions may be changing. For complex problems such as the IBR disk, the single model captures the flow trends and gives essential characteristics of deformation without using state space representation and LQR design at each time step.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 151 Control of Metal Forming Processes.

TASK: 136

TASK TITLE: Heat Transfer Analysis for High Temperature Materials Fabrication

TASK OBJECTIVE: Determine temperature nonuniformities in high temperature ($T \sim 2000°C$) tooling-workpiece systems used to fabricate advanced intermetallics and composites.

SCIENTIST: Vinod K. Jain, Ph.D.

DESCRIPTION OF WORK:

This research was divided into two parts. The first part of the work was concerned with the non-isothermal forging of titanium aluminide billets (TiAl) by creating near isothermal forging conditions. In order to achieve this objective, the TiAl billets were insulated, canned, and forged. In order to obtain defect free forging the insulation, can design, and processing conditions must be optimized. It was therefore required to analytically simulate the forging process and estimate the temperature distribution and metal flow behavior and correlate them with the microstructure.

Seven forging trials were performed to conventionally forge the titanium aluminide billets. The billets were insulated and canned in five cases, just canned in one case, and the last billet was forged

in as is condition. Simulation of the forgings was conducted using a visco-plastic finite elements analysis program Deform.

The second part of the task was concerned with the design and development of a die stack to be used at 2250°C for compressing ceramic matrix composites. The stack will be used on a 200-kip MTS machine in a high vacuum high temperature chamber. The work involved designing the cold and hot rams in addition to other components. The dies were attached to the hot rams and the cold rams were connected to the machine load cell and the actuator. Detailed drawings for fabrication of components of the furnace were provided.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 107, Heat Transfer Analysis for High Temperature Materials Fabrication.

TASK: 137

TASK TITLE: Neurocomputing Using Pattern-Space

TASK OBJECTIVE: To establish an architecture for memory based design in support of Semiconductor Wafer Growth using Molecular Beam Epitaxy.

SCIENTIST: Yoh-Han Pao, Ph.D.

DESCRIPTION OF WORK:

This project defined the architecture of a system which relies on experience and expertise to interpret the meaning of complex patterns of sensor readings, and in this manner provide support for decisions regarding control action. The experience and expertise are mostly cast in the form of neural-net memories and computing procedures. The design is general and this type of system can be used for the monitoring of many other types of processes, other than molecular beam epitaxy (MBE). However, to provide focus, and to illustrate specific points, concentration was on the use of optical ellipsometry for the monitoring of the growth of MBE deposited films.

The most important aspect of this architecture is that structures and procedures are not based on arbitrary rules (so-called expert system rules) but, rather, let data speak for themselves. In this way, when a *pattern* of non-uniformities and deviations are observed, one can estimate quite accurately what excursions in control or measurement techniques are likely to have been responsible for the deviations. The architecture supports not the usual 'Statistical Process Control' but rather intelligent interpretive statistical process control which points to one or more likely causes rather than a whole slate of possible causes. This architecture can be implemented in massively parallel processing manner and can handle complex process with large volumes of real-time data.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 116, Architecture of a Memory-based System for Monitoring Molecular Beam Epitaxial Growth of Semi-conductor Wafers.

TASK: 138

TASK TITLE: Mathematical Development for Pattern-Space Methodologies

TASK OBJECTIVE: To investigate the mathematical basis for the empirically observed excellent performance attainable with Function-Link net pattern-space methodologies.

SCIENTIST: Boris Igelnik, Ph.D.

DESCRIPTION OF WORK:

In this analytical effort, the mathematical basis for the empirically observed excellent performance attainable with Functional-link net pattern-space methodologies was investigated. It was shown that (i) a one-layer feedforward neural net of the Functional-link type is a universal approximator, (ii) approximation with arbitrary accuracy can be attained using only the optimization of external parameters, and (iii) random vector version of the Functional-link net is efficient utilization of the approximation capabilities of the net. Also obtained were: (i) explicit formulas for the neural net construction, (ii) estimates of accuracy of approximation, and (iii) new perspective representation of the neural net. The neural net of the Functional-link type was incorporated in the general pattern-space architecture as a high level encoding scheme.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 110, Mathematical Development for Pattern-Space Methodologies.

TASK: 139

TASK TITLE: Investigation of Advanced Metallic Composites II

TASK OBJECTIVE: To develop an understanding of the relationship between the composition and microstructure of matrices, the bonding at fiber/matrix interfaces, and composite properties in advanced metallic composites.

SCIENTIST: Daniel J. Tilly, Ph.D.

DESCRIPTION OF WORK:

Over the last several years a significant amount of work has been conducted on understanding the relationships between interfacial properties and bulk composite properties. One of the most important factors in the process of developing these relationships is the ability to readily evaluate the interface. The slice compression test has the potential to provide statistically significant amounts of data in regard to the state of the interface. This project established procedures to perform the slice compression test on metal matrix composites. The first step of the process was to put in place the capabilities to perform the test. This consisted of determining procedures to produce materials, identifying a test set up which collects as much information as possible about the debond event, and finally, collecting the appropriate data.

Some of the more significant findings concerning the procedures were: the establishment of a copper alloy (360 Brass) as the best combination of properties for use as a soft anvil material; results of tests on samples with varying thicknesses indicate that thickness effects may be avoided by using samples in the 4-5mm range. A sample preparation procedure was developed which significantly reduces fiber protrusions (95% of fibers protrude out <0.4fm).

Both analytical and numerical models were initiated. These models will identify trends in the data and verify test assumptions, thus advancing understanding of both the interfacial response and test. The large scale numerical model results indicate a uniform stress develops at the composite/soft anvil interface. The analytical model is based on the shear lag theory. The interface was described with the shear strength (τ) criteria in this model.

Testing of model materials (Ti64/SCS-6 and Ti64/SCS-0) to produce a database of interfacial properties was initiated. With the above procedures in place a coherent evaluation of fiber/matrix interfacial properties of advanced Ti-matrix composites can be conducted.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 155, Development of the Macro-Indentation Shear Strength (MISS) Method for Testing Composite Interfacial Properties.

TASK: 140

TASK TITLE: Materials Response for Optimized Forging of TiAl

TASK OBJECTIVE: To characterize and model the hot deformation behavior of a TiAl alloy.

SCIENTIST: Henry J. Rack, Ph.D., et.al., Clemson University

DESCRIPTION OF WORK:

This project consisted of two major tasks, Thermal Stability of TiAl Alloys (Task 1) and Constitutive Modeling (Task 2).

In Task 1, titanium aluminide alloy samples for optical microscopy were prepared by mechanical polishing and etching for 5 to 10 seconds in Kroll's reagent. Back scattered scanning electron microscopy samples were similarly prepared by mechanical polishing, with final preparation involving electropolishing. The high temperature phase stability of these alloys was determined using calorimetric differential thermal analysis (CDTA) and high temperature x-ray diffraction (HTXRD). High transformation temperatures were determined during heating and cooling at rates of 5, 10, 20, and 40 K/min. The heat flow, normalized per unit mass, and its first derivative with respect to temperature, were recorded. High temperature x-ray diffraction studies were undertaken to complement the calorimetry by identifying the phases present at elevated temperature.

Thermal analyses, x-ray and microscopic examination showed that the phase stability observed in Ti-(45-48)Al-x(Nb, Cr) TiAl alloys depends critically upon alloy content and temperature. Increasing temperature, decreasing total interstitial content, increasing Al content and increasing ß alloying content all decrease the stability of α_2, increasing the stability of ß and γ phases.

Task 2 showed that Dynamic Material Modeling (DMM) can be utilized to describe the high temperature, high strain performance of (α_2 + γ) lamellar Ti-49Al-2V at temperatures below the eutectoid transformation temperature. Stable flow is associated with dynamic spheroidization of the lamellar microstructure, unstable flow being associated with lamellar kinking, flow localization, and shear cracking.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 152, Materials Response for Optimized Forging of TiAl.

TASK: 141

TASK TITLE: Project Management/Administration

TASK OBJECTIVE: To provide support activities necessary to establish project task orders and overall contract administration.

PROGRAM MANAGER:Milton E. Zellmer

DESCRIPTION OF WORK:

The contributive research and development project required extensive management and administration activities that were not readily charged to a specific task. These activities fell into three general categories:

1. Those contract management administrative requirements to establish planning and control procedures that applied to the project as a whole. Examples are status reporting, project management meetings, and other general overall project reporting.

2. Those management activities required to establish each of the task assignments. These activities could not be charged to the task since the task was not yet approved during this phase.

3. Recording and reporting the performance and cost for the overall management and administrative activities.

This task provided project management/administration from 26 June 1993 - 25 June 1994.

TASK: 142

TASK TITLE: Long-Term Stability of Orthorhombic Matrix Composites

TASK OBJECTIVE: To develop an understanding of the long-term microstructural stability of continuously-reinforced titanium-matrix composites, with matrices based on the orthorhombic Ti_2AlNb phase.

SCIENTIST: Ian W. Hall, Ph.D.

DESCRIPTION OF WORK:

Intermetallic alloys have great potential for applications in airframes and aircraft engines because they may offer combinations of mechanical properties superior to those of conventional metallic alloys. Among the numerous intermetallic systems under development, those based upon titanium and aluminum are of particular interest since their relatively low density gives them attractive specific properties.

Originally, attention was focused upon intermetallic alloys based upon Ti_3Al and TiAl, referred to as alpha-2 (α_2) and gamma (γ) aluminides respectively. Attempts to improve the ductility of these intermetallics included the use of alloying additions and niobium was found to be highly effective in this respect. Subsequently, a new aluminide phase based upon the composition Ti_2AlNb was identified and early work showed it to be orthorhombic in crystal structure. This work led to the development of a new class of titanium aluminide intermetallics, the so-called orthorhombic alloys. While these alloys appear to have very attractive properties there was a major lack of fundamental metallurgical information concerning the phase stabilities, phase transformations, and their equilibrium phase diagrams. It was beginning to be appreciated that their microstructures are very strongly influenced by interstitial content, especially oxygen and nitrogen, and that variations in concentration of a few hundred ppm can substantially alter the relative fractions of each phase present.

Prior work by the scientist on this project provided insight into the microstructures present in ~2mm thick Ti-23.2Al-24Nb sheet. This follow-on research was undertaken in order to resolve some of the questions concerning the differences in microstructure between the sheet and the foil of the same alloy in order to facilitate interpretation of the results from the composite.

Intermetallic foil material had previously been processed by diffusion bonding into 5 ply consolidated panels; these were 'neat' panels and contained no fibers although they were processed in a similar manner to composite panels. Tensile and metallography specimens were cut from these panels and subjected to heat treatment. Because of the time constraints, only samples treated for 1000 hours were examined by TEM. Specimens for transmission electron microscopy (TEM) were prepared from material in each of these conditions and the plane of the specimens coincided with the plane of the foil. The specimens were examined principally in a JEOL 2000FX TEM at 200keV, and Energy Dispersive X-ray Spectroscopic Analysis (EDS) was performed using a Tracor Northern TN-5500 system. Results indicated that the final stable microstructure present in Ti-23.2Al-24Nb after very long times at temperatures below the beta transus will consist of the orthorhombic and disordered beta phases.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 108, Long-Term Thermal Stability of a Ti-23.2Al-24Nb Intermetallic Alloy.

TASK: 143

TASK TITLE: Spectroscopic Ellipsometry Enhancement

TASK OBJECTIVE: Continuation of the enhancement of existing ellipsometry single wavelength to spectroscopic capabilities. These will be used in the study of molecular beam epitaxial growth monitoring of III-V semiconductor materials.

SCIENTIST: Sonya Cong, Ph.D., Technical Assessment & Transfer, Inc.

DESCRIPTION OF WORK:

In this search, real time ellipsometry was employed as an in situ sensor for the process control of molecular beam epitaxy (MBE). The effect of transients in the molecular beam flux during semiconductor film deposition was studied by real time ellipsometry. Preliminary results indicated a trend similar to the results using other techniques. A real time ellipsometry control algorithm was developed to extract film parameters such as alloy compositions and thicknesses from the ellipsometry measurements. Finally, the ellipsometer with a single wavelength was modified to perform spectroscopic analysis.

A molecular beam is produced by evaporating the material from liquid phase in an effusion cell. A shutter is placed in front of the effusion cell to turn on and off the molecular beam. To produce well controlled and uniform film structures, it is essential to have constant molecular beam fluxes. However, a flux variation occurs upon the opening of shutters, and is referred to as the flux transient. The flux transient was observed and studied using a BEP ion-gauge. In order to study the effect of flux transient on the growing film, real time ellipsometry was applied to monitor the growing sample. A series of experiments were designed: 1) growth of a AlGaAs layer on a GaAs substrate as a reflecting layer, 2) growth of a GaAs film on top of the AlGaAs/GaAs structure, and 3) extraction of the film thickness and growth rate of the GaAs film with real time ellipsometry. Since no compositional variation can exist in the GaAs films, the growth rate of the film is proportional to the flux of gallium. Thus through the determination of growth rate, flux transients can be studied. A preliminary experiment was carried out in this study. A clear trend of a decrease in the growth rate was demonstrated during the initial growth segment. The scattering in the growth rate was partly caused by the lack of accuracy in the deposition time recording. Follow-up experiments were proposed to increase the accuracy of the measurements and to determine the influence of shutter opening frequency, cell temperature, and cell equilibrium.

In order to close the loop using ellipsometry MBE process control, three steps need to be completed: 1) obtain the ellipsometry raw data; 2) extract film parameters, such as alloy composition, substrate temperature, and film thicknesses, from the raw data; and 3) compare the film parameters with their target values and generate a control signal. The first was accomplished and tested in previous research by the scientist. In this project, the second step, by far the most important and difficult one, was studied.

Owing to the complexity of transcendental ellipsometry equations, an iterative method such as least square is required to extract the film parameters from measured data. Least square is one of the most commonly used methods of solving equations where analytical solutions are not available through data fitting and iterations. To examine the least square method for solving ellipsometry equations, simulated values (Δ, ψ) were used as measurements to allow efficient study of the problem. The simulated measurements contained a random component added to the exact (Δ, ψ) values on the order of 0.01 degree. This approximated the error in the true experimental environment and allowed the real film properties to be known.

A 20Å thin film segment was broken into 4 and 10 equal thickness intervals with simulated measurements taken at each thickness. These simulated measurements were then used to determine the film parameters using the least square method. The software performing the least square calculation was developed during this research.

In this term of the research, effort was focused on the implementation of spectroscopic ellipsometry. Several steps were necessary to complete this conversion. First the light was aligned to be perpendicular to the Glan Thomas polarizer. Secondly, the change in amplitude of the AC component of the signal was modified by passing the detected signal through a preamplifier. To overcome this problem, the rotation speed was reduced decreasing the magnitude of this effect and the computer program included an eda correction to account for this change. Finally, the detector side was

positioned and aligned to be perpendicular to the beam. It was found that an aperture on the detector side caused some scattered light which acted as an increased background during the measurement. This effect was accounted for with the eda correction. After these modifications data was obtained from C-Si and a SiO2/Si samples.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 121, Process Control of Molecular Beam Epitaxy.

TASK: 144

TASK TITLE: Aromatic-Heterocyclic Oligomers and Polymers for Opto-Electronic Evaluation

TASK OBJECTIVE: The synthesis of novel aromatic-heterocyclic oligomers and polymers for evaluation as electronic conductors on nonlinear optical materials.

SCIENTIST: Girish S. Patil, Ph.D.

DESCRIPTION OF WORK:

The objective of this research was the synthesizing of highly conducting polymers using a novel approach - Symmetric Ground State Systems (SGSS).

An integral part of a conducting polymer is a conjugated backbone. When these polymers are doped with either electron acceptors (p-type) or electron donors (n-type) electrical conductivity is observed to increase by several orders of magnitude. However, doped polymers have some disadvantages associated with them. One of the disadvantages is that these polymers tend to lose their conductivity with time. Also, in the conjugated systems due to the bond alteration band gap develops between the conduction band and the valence band. Conductivity is inversely proportional to the band gap i.e. larger the band gap, poorer the conductivity. In order to raise the conductivity one must then attempt to lower the band gap. This in turn can be achieved by reducing the bond alteration.

Symmetric Ground State System (SGSS) seems to be the answer to this problem. SGSS systems are systems where the ground state of the molecule is represented by two identical structural forms which make equal contribution toward the true structure. In addition, the double bond in one structural form should be a single bond in the resonate form.

In this effort, the choice of target molecules, synthetic strategy employed for making them, and the problems encountered in the process were described. Several polymers were synthesized, namely: benzophenone-4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid chloride, 4,4'-bis(4-methoxybenzoyl)benzophenone, and 4,4'-bis(4-methoxybenzyl)diphenylmethane.

The detailed project description, method, results, and discussion are reported in Contributive

Research and Development Final Report, Volume 171, Conducting Polymers: Symmetric Ground State Systems Approach.

TASK: 145

TASK TITLE: Theory of Electromagnetic Wave Propagation in Nonlinear Optical Films

TASK OBJECTIVE: To model the behavior of electromagnetic waves in nonlinear optical thin films.

SCIENTIST: David S. Moroi, Ph.D.

DESCRIPTION OF WORK:

Recently there has been considerable interest in second harmonic generation (SHG) in nonlinear film waveguides for possible use in the fabrication of compact short-wavelength coherent light sources. If the infrared (IR) radiation generates light in the visible region by frequency doubling, a number of important applications are possible.

No exact solution to Maxwell equations for the electromagnetic fields in a nonlinear $\chi^{(2)}$ medium are known to date. There are two well-known approximations for these solutions—plane wave approximation and slowly varying amplitude approximation (SVAA). The latter is an improvement over the former.

The purpose of this work was threefold: (1) to examine the validity of SVAA applied to the problem using the method of multiple scale (MMS), (2) to obtain the dispersion relations for the propagation constants of the confined TE and TM modes, and (3) to obtain accurate solutions for the electromagnetic fields in a nonlinear $\chi^{(2)}$ film waveguide.

Results of this effort showed that, with the help of the method of multiple scale, slowly varying amplitude approximation is valid for calculating the electromagnetic fields in a nonlinear $\chi^{(2)}$ medium. The dispersion relations for the propagation constants are obtained for the confined TE and TM modes in a nonlinear uniaxial film waveguide in which the optic axis lies in the x-z plane. The corresponding eigenfunctions are also obtained. The differential equations for the amplitudes of various TE modes are obtained in terms of their eigenfunctions.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 118, Theory of Electromagnetic Wave Propagation in Nonlinear Optical Films.

TASK: 146

TASK TITLE: Axiomatic Design of Multi-Stage Hot Rolling Processes

TASK OBJECTIVE: To evaluate the feasibility of Suh's axiomatic approach to design complex deformation processes such as multi-stage hot rolling.

SCIENTIST: Jay S. Gunasekera, Ph.D.

DESCRIPTION OF WORK:

Conceptual Design is a critical activity which greatly determines the constraints and parameters to be further analyzed and optimized, and thereby significantly influences the life cycle performance and costs of products and processes. The challenge of conceptual design has been traditionally accomplished through various empirical rules which have been derived from many years of experience. The thermo-mechanical processes like extrusion have been used for decades in industries but their operating conditions have traditionally been determined by trial and error.

Mathematical modeling and control of microstructural characteristics during these processes is still in its infancy even though the last decade has seen burgeoning studies on this subject. The objective of this work was to apply the axiomatic approach to the conceptual design of extrusion, capable of producing products having the desired properties and dimensions with controlled microstructure.

The overall design methodology, based on the Axiomatic Design, presented in this study gives a way of designing the whole thermo-mechanical process from the microstructure point of view. The whole process design and the die design were undertaken based on the final product characteristics, in this case it is the final microstructure of the material. This design methodology which has been successfully utilized for the design of the extrusion process can be extended with some modifications to the other thermo-mechanical processes, such as rolling and forging.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 122, Axiomatic Design of Multi-Stage Rolling Processes.

TASK: 147

TASK TITLE: Investigation of Vapor Deposition Processes

TASK OBJECTIVE: To study fundamental transport parameters of vapor deposition processes for the development of an intelligent control strategy.

SCIENTIST: M. Khairul Alam, Ph.D.

DESCRIPTION OF WORK:

Chemical Vapor Deposition (CVD) can be used to deposit a variety of materials, including metals, oxides, carbides, nitrides, silicides, borides, etc. An example of a fiber coating CVD reactor is a cylindrical reactor through which the fiber is moved while gaseous reactants flow around it. On this project, the fundamental transport parameters of a monofilament CVD reactor were investigated for use in an intelligent control strategy. Current process control for vapor deposition processing is based on experiments, and trial and error methods. An analytical model was developed to identify the basic parameters of the process.

Analysis was carried out for a simplified system where the fluid flow was considered to be plug flow (uniform velocity). The reactor was assumed to be isothermal. The reactant was in low concentrations in a background gas. The reactant was assumed to react on the surfaces in the reactor. The resulting model can be used to simulate the CVD process and to examine the influence of the important transport parameters in the reactor. By using these control parameters from the solution of the governing equations, it is now possible to make the control strategy more generic, efficient, and effective.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 117, Investigation of Vapor Deposition Processes.

TASK: 148

TASK TITLE: Fractal Studies in Manufacturing Research

TASK OBJECTIVE: To investigate the feasibility of using fractals to model material phenomena during metal forming processes.

SCIENTIST: David C. Carr, B.S.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Collaborative Project "GEMMA". Under this program, Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

The effort on this task was to examine the data from compression tests of an aluminum-lithium alloy for indications of chaotic behavior, and to develop a model, using fractal geometry, for the molecular deformation of the grain structure of the alloy during forging or extrusion processes.

Thirty compression tests were run in which the temperature ranged from 300 degrees Celsius to 500 degrees Celsius. The strain rate varied from .001 to 1. The time varied from 900 seconds to one/tenth of a second. The test data was compiled into special files which could be fed into a new forecasting program. The forecasting program was designed to indicate chaotic, periodic, or random behavior inherent in a data table. The results of some of the tests seemed to indicate a possibility of chaotic behavior. However, it was decided that the observed results were being caused by machine "noise" and were not necessarily indicative of chaotic behavior.

The modeling was successful in that the Fractal Geometry could be used to give reasonable looking pictures which resembled the grain structure in the Al-Li.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 96, Aluminum-Lithium Data Analysis.

TASK: 149

TASK TITLE: Special Studies in Manufacturing Research

TASK OBJECTIVE: To develop methods for design of metal forming processes.

SCIENTIST: Sharon Dutcher, M.E.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Collaborative Project "GEMMA". Under this program, Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

The effort on this task was to study material under processing conditions. Materials processing is viewed many different ways. It is looked at graphically, physically, numerically, and by a stability map. The primary task was to analyze and then present it in a new and different way—aurally.

Aluminum lithium data from hot compression tests, EEG data from the same person under different conditions, and function data from a spreadsheet were collected and converted to MAC compatible ASCII form. The data was converted to musical frequencies and duration using a data converter program written in Think C. The data was played using a music generator program written in Think C, and musical tunes were created from the sound generator.

The detailed project description, method, results, and discussion are reported in Contributive

Research and Development Final Report, Volume 97, Musical Metal.

TASK: 150

TASK TITLE: Physical Science Studies in Manufacturing Research

TASK OBJECTIVE: To investigate approaches for discovery systems that use knowledge from physical science to control and improve manufacturing operations.

SCIENTIST: Erin E. Dooley, B.S.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Collaborative Project "GEMMA". Under this program, Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

The effort on this task was to monitor a genetic algorithm (GA) software program and analyze a protein data base for preferred protein structures such as helices, sheets, and coils. The program consists of training and test sets to accurately predict amino acid sequences and preferred structures. The GA generates rules and these rules evolve to make better predictions. The GA has had moderate success and is under constant revision.

One element of the GA is a protein data base that contains information such as amino acid sequences, atomic coordinates, protein function, secondary, tertiary, and quaternary structures, and the protein's biological surface. The files were expanded by searching for homologies in structure and function from an existing data base known as the Brookhaven Data Base. The files were modified, inserted into the GA data base, categorized, and will become part of new training and test sets.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 98, Building Proteins.

TASK: 151

The government canceled this task.

TASK: 152

TASK TITLE: Processing Ceramic Composites

TASK OBJECTIVE: Conduct studies that will assist in the commercial fabricating of ceramic fiber-matrix composites for structural purposes.

SCIENTIST: Ruby L. Bryant, M.S.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Collaborative Project "GEMMA". Under this program, Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

The effort on this task was to produce a high temperature composite ceramic for use in jet engines. Pollucite is a monolithic compound being studied for use in jet engines because of its high lattice energy, high refractoriness, chemical inertness to molten metal, and relatively low coefficient of thermal expansion. It may be purchased commercially but also may be synthesized in the laboratory.

On this effort, pollucite was successfully made from cesium carbonate solution added to alumina and silica sols. The resulting sol was highly viscous. The product was homogeneous pollucite as determined by powder x-ray after 1200°C heat treatment.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 99, Investigation of Pollucite for Composite Ceramic Applications in Jet Engines.

TASK: 153

TASK TITLE: Synthesis of Biomaterials with Nonlinear Optical Properties

TASK OBJECTIVE: The synthesis of Polypeptides and proteins that have novel optical and nonlinear optical properties.

SCIENTIST: Carol S. Noffsinger, B.S.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Collaborative Project "GEMMA". Under this program, Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

The effort on this task was to develop a method for making optically clear thin films by means of self-assembled charged layers. Self-assembled thin films were created on silanized glass slides. The silanization process was simplified by using ethanol at room temperature instead of hot alkanes.

Using cleanroom techniques, silanized glass slides were coated with alternating layers of polyglutamic acid and poly-l-lysine. Since one layer was a polyanion and one was a polycation, the layers self-assembled. Presence of the layers was verified by the use of UV spectroscopy and the scanning electron microscope. Silanized slides were then coated with alternating layers of a negatively charged dye and poly-l-lysine. The first dye used was Congo Red. The presence of dye and polymer layers was verified by UV-VIS spectroscopy and IR spectroscopy. Silanized slides were also coated with alternating layers of Cu phthalocyanine and poly-l-lysine. The same verification techniques were used for the Congo Red system.

It was shown, by this technique, that multilayered thin films could be built up using a simple room temperature dipping technique. Optical clarity was a problem with the polyglutamic acid, but could probably be overcome with the use of a different polypeptide.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 100, Self-Assembled Thin Films.

TASK: 154

TASK TITLE: Scanning Electron Microscopy of Materials

TASK OBJECTIVE: Observe and document the microstructure of a variety of materials through the use of a scanning electron microscope

SCIENTIST: Pete R. Kramer, B.S.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Collaborative Project "GEMMA". Under this program, Dayton area industries and

WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

The effort on this task was to use Scanning Electron Microscopy (SEM) to analyze fracture in carbon-carbon composites and liquid crystal films.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 101, Scanning Electron Microscopy of Materials.

TASK: 155

TASK TITLE: Investigation of Natural Organic Microstructures

TASK OBJECTIVE: Develop a database of structural features present in a variety of naturally occurring organic materials.

SCIENTIST: Nancy A. Wilson, B.A.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Collaborative Project "GEMMA". Under this program, Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

The effort on this task was to use Scanning Electron Microscopy (SEM) to analyze fracture in carbon-carbon composites and liquid crystal films.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 102,Investigation of Natural Organic Microstructures.

TASK: 156

TASK TITLE: Fractography of Carbon-Carbon Composites

TASK OBJECTIVE: Determine the critical flaw size and/or geometry associated with shear failure of carbon-carbon materials.

SCIENTIST: Tom L. Fourman, M.E.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Collaborative Project "GEMMA". Under this program, Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

The effort on this task was to use Scanning Electron Microscopy (SEM) to analyze fracture in carbon-carbon composites and liquid crystal films.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 103, Fractology of Carbon-Carbon Composites.

TASK: 157

The government canceled this task.

TASK: 158

TASK TITLE: Experiments in Pattern Theory

TASK OBJECTIVE: Evaluate Wright Laboratory developed software for pattern finding capabilities which can be developed to control and improve manufacturing operations.

SCIENTIST: Kelly A. Burgeson, B.S.

DESCRIPTION OF WORK:

This research project was developed in support of the Dayton-Montgomery County Public Education Fund Collaborative Project "GEMMA". Under this program, Dayton area industries and WPAFB organizations establish eight week programs to familiarize local area math and science teachers with typical day-to-day applications of their sciences. The teachers work on real business problems during this period, and develop plans for incorporating real life applications into their teaching programs at the elementary and high school level.

The effort on this task was to correlate data to assist in the Partition Figure of Merit (PFM) evaluation, which is a project to determine the most robust decomposition process for extracting patterns

from a function.

Pattern Theory (PT) is a robust process for extracting "patterns" from a function. Its applications involve machine learning, image processing, and pattern recognition. "Patterns" are extracted from these functions by using a computer program FLASH, Function Learning and Synthesis Hotbed. This (PFM) project was concerned with finding ways to speed up the decomposition process using less memory. In support of this effort, a search through several disks was made to find certain dcp data files that contain the best DFC for the bench mark functions. The files that could not be found were regenerated. Correlations between the three different figure of merits (child cardinality (CC), grandchild cardinality (GCC), and the V2a decomposition plan) runs generated by FLASH were calculated.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 104, Partition Figure of Merit Evaluation.

TASK: 159

TASK TITLE: Damage Evolution in Ceramic Matrix Composites

TASK OBJECTIVE: To evaluate the development and propagation of damage in composite materials under thermal and mechanical cycling.

SCIENTIST: Shin S. Lee, Ph.D.

DESCRIPTION OF WORK:

Two areas of research were performed on this project: 1) fatigue damage and mechanisms of Nicalon/CAS-II, and C/SiC, and 2) evaluation of short- and long-term mechanical performance of four CMC systems under various mechanical and environmental loadings.

Fatigue damage in composites consists of various combinations of damage modes such as matric cracks, fiber-matrix separation, delamination, void growth, and fiber breakage. The mechanisms, mode, and distribution of fatigue damage in composites depend upon many characteristics such as fiber, matrix, and the fiber/matrix interphase/interface properties, stacking sequence, configuration of component geometry, fabrication techniques, environment, and loading history. A detailed characterization on causative sequence, and the influence of environmental effects on fatigue damage mechanisms in two CMC systems, [0/90] Nicalon/CAS-II, and 2-D [W] C/SiC was conducted.

In order to obtain a range of fiber/matrix interphase properties and bond strengths in Nicalon/CAS-II specimens, the specimens were heat treated at three different temperatures, 900°C, 1000°C, and 1100°C in air for 100 hours before testing. All fatigue tests were conducted under load control. For room temperature test strain measurements were made using a standard clip-on extensometer. For elevated temperature tests, strain measurements were made using a high temperature

extensometer with alumina rods. Thermocouples were mounted on specimens tested at elevated temperatures to monitor temperature distribution during each test. Damage and failure modes caused by cyclic tension at room temperature were characterized by several non-destructive methods. Both virgin and tested specimens were sectioned in longitudinal and transverse directions for characterization. Non-destructive methods including (1) X-ray radiography, (2) optical microscopy, (3) scanning electron microscopy, and (4) surface replication, were used to identify damage and failure modes.

The results indicate that changes in fiber/matrix bond strength affect not only the direction of matrix crack propagation but also the load transfer mechanisms between fiber and matrix, which has direct influence on the development of secondary matrix damage. Furthermore, as a result of strong fiber debonding strength, propagation of quasi-brittle matrix cracks in a self-similar manner was found in the specimens with post-processing heat treatments. Enhanced oxidation of carbon fibers was identified as the mechanism responsible for the premature failure of 2-D [W] C/SiC which manifested itself as a significant reduction of fatigue life at 1000°C.

In the second task, the main goal was to evaluate short- and long-term mechanical performance of four CMC systems, KAISER, HITCO, LANXIDE, and GEN-4 for insertion as engine components. A test matrix was carefully designed to fulfill the task. Monotonic tension tests at 23°C, 1000°C, and 1100°C were first conducted to obtain a baseline information and short-term mechanical performance of the four systems. The characterization of long-term performance was carried out by isothermal fatigue, and creep rupture tests at different selected stress levels. Environmental stability testing was carried out by salt fog interrupted elevated temperature tests at 1000°C.

All four systems exhibited very attractive room temperature mechanical performance, and short-term mechanical performance at elevated temperatures. However, different degrees of degradations of long-term performance were observed at elevated temperatures. In addition, reduction of long-term performance due to salt fog exposure indicated that three of the four systems, except GEN-4 suffered strength reduction. It may imply that the fiber used in the three systems, Nicalon fiber, may experience serious stregnth degradation caused by salt fog exposure.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 170, Damage Mechanisms and Mechanical Performance of Fiber Reinforced Ceramic Matrix Composites.

TASK: 160

TASK TITLE: Processing of Foam from Mesophase Pitch

TASK OBJECTIVE: To explore the feasibility of creating a high temperature graphitic reinforcement from a mesophase pitch precursor by examining the impact of foaming gas solubility on the nucleation and growth of bubbles.

SCIENTIST: Debashis Dutta, Ph.D., Wright Materials Research

DESCRIPTION OF WORK:

This project involved the processing and characterization of microcellular graphitic foams from a carbon fiber precursor, anisotropic pitch. It has been predicted that foams with interconnected strut networks of aligned graphite crystallites will have attractive mechanical properties. The elongational stress during the blowing process is expected to align the mesogenic units of pitch along the struts, producing a morphology resembling that of carbon fibers. The objective of these processing studies was to obtain open celled foams with strut cross-sectional dimensional scale on the order of traditional graphite fibers (7-10μm).

Microcellular pitch foams were processed with homogeneous and heterogeneous nucleation techniques. The pitch foams were then oxygen stabilized, carbonized, and graphitized over a range of conditions. Typically, the cell sizes were of the order of 70 μm and the struts 5-10 μm. The appropriate processing conditions for obtaining this foam morphology were identified. The effect of saturation pressure on foam porosity was studied. The porosity of the foams increased with increasing saturation pressure. Polarized light microscopy showed alignment of the graphitic planes along the strut axes. The graphitized foams were found to be mechanically strong.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 164, Processing and Characterization of Graphitic Microcellular Foams from Anisotropic Pitch.

TASK: 161

TASK TITLE: Sintering Processes During Manufacture of MMCs and CMCs

TASK OBJECTIVE: To develop simple models of sintering during consolidation of metal and ceramic matrix composites (MMCs and CMCs).

SCIENTIST: Rollie E. Dutton, Ph.D.

DESCRIPTION OF WORK:

Simple micromechanical models of the sintering of metal and ceramic matrix composites were developed. The models are based on the sintering equation and use a stress intensification factor as an indication of the constraints to densification due to the presence of a second reinforcing phase. A similar model for creep processes during densification was also developed. These models can be utilized to estimate the relative magnitude of the creep rate to the densification rate during pressure assisted sintering of metal and ceramic matrix composites.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 128, Sintering Processes During Manufacture of MMCs and CMCs.

TASK: 162

TASK TITLE: Deformation Behavior of Unit and Twinning Dislocations in TiAl

TASK OBJECTIVE: The objective of the work is to characterize the deformation behavior in several gamma titanium aluminide alloys with different aluminum contents, deformation temperatures and microstructures.

SCIENTIST: Vijay K. Vasudevan, Ph.D.

DESCRIPTION OF WORK:

The objectives of this work on TiAl alloys were to study by transmission electron microscopy (TEM): 1) the evolution and morphology of 1/2<110] unit dislocations as a function of temperature and Al content, 2) the composition and temperature dependence of twinning, and 3) the fine structure of dislocations in Ti-56Al single crystals deformed at temperatures between ambient and 600°C. Work was performed in each of these areas.

Recent theoretical modeling work at the Materials Directorate of the 1/2<110] dislocations has suggested that glide friction stresses are large for the screw and 60° orientations and small for the 30° and edge orientations. Consequently, both screw and 60° segments, being less mobile, might be expected to be the dominant orientations observable in the deformation microstructure. In samples deformed at room temperature on the project, the 1/2<110] dislocations generally showed both the presence of double kinks delineating long screw segments and many pinning points at the intersection of the kinks. These pinning points may be jogs created by intersections with other dislocations. At higher deformation temperatures, namely, 600°C, the 1/2<110] dislocations become very straight. Explanations for these morphological changes were given in a paper submitted to the journal *Acta Metallurgica et Materialia*.

TEM observations of dislocations in a Ti-53Al [010] orientation single crystal deformed at room temperature were also conducted. In particular, a moderate density of 1/2<110] unit dislocations was observed. These dislocations appeared predominantly as long screw segments with terminating 60° components. Thus, it appeared that the screw and 60° orientations have lower mobility, i.e. higher friction stresses, compared with other orientations, which agrees well with the predictions of the theoretical modeling.

Twins and stacking faults in a Ti-48Al alloy deformed at room temperature were observed. The stacking faults were analyzed and it was found that these are bound by 1/6<112] dislocations of the

same type. TEM observations of twin intersections and associated dislocation structures were also conducted. The results indicated that two types of intersections, Type I and Type II, were present. In the first, the intersection was parallel to a <110] direction and in the second to a <101] direction. In the latter case, many 1/2<110] dislocations were observed emanating from the twin-twin intersections. The associated crystallography and dislocation reactions were analyzed. Studies of the changes in the nature of twinning with Al content and temperature were also conducted, and a paper based on these various results was prepared for submission to the journal *Materials Science and Engineering*.

In previous work at the Materials Directorate, several orientations of single crystal specimens of a Ti-56Al alloy were compression tested at room and elevated temperatures, and a flow stress anomaly was observed in all orientations tested. As part of the present task, dislocations in an [010] single crystal prestrained at 500°C and restrained at room temperature were also examined.

Detailed characterization of dislocations in an [001] oriented crystal deformed at 600°C was performed. A thin foil prepared parallel to the operative {111} slip plane was obtained and the dislocations were characterized by weak beam electron microscopy.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 138, Deformation Behavior in Unit and Twinning Dislocations in TiAl.

TASK: 163

The government canceled this task.

TASK: 164

TASK TITLE: MBE Growth Model

TASK OBJECTIVE: Develop predictive capability for MBE growth parameters

SCIENTIST: Donald R. Thomas, M.S.

DESCRIPTION OF WORK:

The molecular beam epitaxy (MBE) growth chambers used in the Materials Directorate work group are controlled and monitored by a computer control process system developed by the Materials Process Design Branch (MLIM). This control process system, called the Intelligent Process Module (IPM), generates huge files containing the data collected while controlling and monitoring the MBE growth chambers. Reducing this data to a manageable size and modeling the MBE growth process were

the two main objectives of this research project.

In order to develop a predictive growth model, data collected during the MBE film growth must be extracted from its original data files and transformed into a usable format. A commercial neural network computer application is being used to develop the growth models, so the MBE growth data must be converted to a format readable by the neural network application. Computer software was developed on this project to reduce the original data files to a manageable size, and then to interactively search the reduced files for data matching user-defined criteria. Additionally, this software allows the user to add data to the data files which describes *ex-situ* measurements made on the MBE grown films.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 158, Development of Molecular Beam Epitaxy Growth Modeling Software.

TASK: 165

TASK TITLE: Microstructural Aspects of Fatigue Damage in Titanium Aluminide Alloys and Composites

TASK OBJECTIVE: To study the role of microstructure on the mechanisms of fatigue and environmental damage processes in titanium aluminide alloys and composites.

SCIENTIST: J. Wayne Jones, Ph.D.

DESCRIPTION OF WORK:

The fatigue crack growth behavior of the forged gamma titanium aluminide alloy, Ti-46.5Al-3Nb-2Cr-0.2W (at%), was investigated. Fatigue crack growth processes were investigated by combining microstructural studies with extensive fractographic analyses of failed specimens. Microstructure was controlled by heat treatment to produce a duplex microstructure consisting of equiaxed alpha grains and lamellar grains and a fully lamellar microstructure. Fatigue crack growth studies were conducted at room temperature, 600°C and at 800°C. Crack growth resistance of the lamellar microstructure was found to be superior to that of the duplex microstructure. In general, crack growth resistance depended significantly on microstructure, explaining, in part, the differences in behavior between the duplex and the fully lamellar microstructure. Fatigue crack growth in the duplex microstructure was dominated by cleavage-like crack advance in the equiaxed gamma grains. In the fully lamellar microstructure, with a colony size significantly larger than that of the duplex alloy, three modes of crack advance, intralamellar, interlamellar and translamellar, were observed. Colony orientation relative to the nominal crack growth direction exerted a strong influence on propagation mode. At room temperature, significant interlamellar and intralamellar crack advance occurred creating an extremely tortuous crack path. At elevated temperatures, less interlamellar and intralamellar crack growth occurred and there was a corresponding decrease in the crack path tortuosity.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 231, Fractographic Aspects of Fatigue Crack Growth in Gamma Titanium Aluminides.

TASK: 166

TASK TITLE: Processing and Poling of High Temperature 2nd-Order Electro-Optical Polymer Films

TASK OBJECTIVE: The production and electric poling of polymer films of high optical quality containing high optical quality containing high temperature 2nd-order nonlinear optical chromophores.

SCIENTIST: Jar-Wha Lee, Ph.D.

DESCRIPTION OF WORK:

In this research, a novel process technique was developed and used to fabricate optical quality rigid-rod polymer thin films. The objective was to improve the optical quality of PBZT thin films leading to the measurement of intrinsic $\chi^{(3)}$ of PBZT. Optical quality thin films of rigid-rod polymers were prepared from 1 to 3 wt% PBZT/MSA solution and characterized by utilizing a UV/Vis/NIR spectrometer. The results indicated that the film optical loss decreased with increasing the solution polymer concentration. The coagulated film optical loss was in the range of 4500 dB/cm at a wavelength of 600 nm. It was also found that much better optical quality thin films can be obtained by using solid state coagulation process. The coagulated film optical loss, at 600 nm, was reduced to a value of 1900 dB/cm. Furthermore, examination of the solid state coagulated colorless rod polymers, DMT-PBZT and BCO-PBZT, indicated that a very low optical loss film can be fabricated. This result strongly suggests that the measured PBZT film optical loss was mainly due to absorption.

For the second order polymer film preparation, thin, uniform 6F-PBO-3 films were successfully spin-coated on a conductive indium tin oxide (ITO) glass slide and silicon wafer in a class 100 clean room facility. The solvent was removed in three different procedures in order to find the best sample condition for poling and wave guiding experiment. The preliminary result indicated that the films dried under ambient condition have better quality in term of the film resistivity and optical loss. The more detail investigation was planned for future work.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 159, Processing and Characterization of Optical Quality Hetero-Cyclic Aromatic Polymer Thin Films.

TASK: 167

TASK TITLE: Modeling of NLO Materials Using Parallel Computers

TASK OBJECTIVE: To calculate the structure and properties of biologically derived nonlinear optical materials using massively parallel computers.

SCIENTIST: James A. Lupo, Ph.D.

DESCRIPTION OF WORK:

This project continued the investigation (started on a previous project, Task 79) of parallel processing of two major computational chemistry programs: PROTEAN2 (a molecular structure prediction code, and GROMOS (a molecular dynamics code).

The parallelization of the PROTEAN2 molecular structure prediction code was completed for the Thinking Machines, Inc. CM5. Benchmark and parallel performance analysis results were presented and compared with results obtained on a Cray C90 using multiple processors in autotasking mode. The choice of an optimal machine was shown to be dependent on the size of the model studied.

The parallel Fortran preprocessor, PFortran, was ported to the Intel Paragon, and was used to run the GROMOS molecular dynamics program. Benchmark and parallel performance analysis results were presented and compared with previous performance figures obtained on the Caltech GAMMA (Intel iPSC/860) and Caltech DELTA machines.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 144, Modeling of NLO Materials using Parallel Computers.

TASK: 168

TASK TITLE: Design of New Materials I

TASK OBJECTIVE: Optimization for Polymers, Surfaces, and Biomolecules: The evaluation of the global energy minimum or most stable conformation of large molecular structures, particularly biopolymers being developed in the materials laboratory in-house research programs.

SCIENTIST: Zhiqiang Wang, Ph.D.

DESCRIPTION OF WORK:

Biopolymers of defined secondary and tertiary structure derivatized with chromophores may be well suited for use as nonlinear optical materials. Indeed, polypeptides may provide the flexibility of

controlling backbone structure, thereby providing temporal stability to attached chromophores. Thus, it is of importance to understand the effects of the chromophore on the resulting polypeptide in such molecular systems. Although detailed molecular dynamics calculations of polypeptide-bound chromophores have provided insight into the effects of chromophore substitution, and have aided synthesis efforts, these simulations explain only local effects. The design of polypeptide-bound chromophores thus requires the development of new optimization techniques for determining a *priori* the global energy minimum of such molecular systems.

In this project, the Adaptive Simulated Annealing (ASA) algorithm was applied as a global optimization approach to the conformational search of biomolecules, using a ECEPP/2 (Empirical Conformation Energy Program for Peptides) potential. As applied to Met-enkephalin, the optimization resulted in a conformation of Met-enkephalin with energy 13.84 kcal/mol, very close to what has been previously reported. A dominant right-handed α-helical conformation was also found for 14 residue (L-Alanine) in a limited searching range. These results showed that the algorithm might be an efficient and robust algorithm for conformational analysis.

The geometries and vibrational frequencies of the pyran molecule and a number of its variants by ring dissociation at the C-O bond (2,4-pentadienals) were studied using Density Functional Theory (DFT) (VWN, BLYP), and Hartree-Fock (6-31G(d), MP2//6-31G(d)). All the BLYP, 6-31G(d) and MP2//6-31G(d) geometry optimizations predicted the most stable configuration of pyran to be an open form different from what was predicted in a previous Hartree-Fock 3-21G level calculation, while VWN predicts that the closed ring form of pyran is the most stable isomer. The DFT calculations of the vibrational frequencies of 2,4-pentadienal were in good agreement with the IR results, that favor the most-stable conformer identified by energy calculations on this project.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 191, Computer Simulation of Molecular Structure: Global Optimization and Density Functional Theory.

TASK: 169

TASK TITLE: Design of New Materials II

TASK OBJECTIVE: Optimization for Polymers, Surfaces and Biomolecules: The evaluation of the global energy minimum or most stable conformation of large molecular structures, particularly biopolymers being developed in the materials laboratory in-house research programs.

SCIENTIST: Paul N. Day, Ph.D.

DESCRIPTION OF WORK:

The goal of this work was to aid in the discovery, synthesis, and processing of optical materials through the use of computational chemistry. The computational modeling of nonlinear optical properties, other molecular properties, and reaction energetics of spiropyran and related compounds is of interest in the development of optical limiters and optical switches. Because these compounds are prepared in solution, traditional quantum chemistry calculations, which model a molecular in the isolated gas-phase, are not always appropriate. This effort consisted of the development of an effective fragment potential program for modeling solvent effects in ab initio quantum chemistry calculations, and the modeling of spiropyran and related molecules by quantum chemistry.

The effective fragment potential program included the incorporation of the interfragment electrostatic interaction energies, theoretical development of and incorporation of the polarizability in the generalized multifragment case, incorporation of a water-water exchange repulsion potential term to be used in multifragment problems in aqueous solution, and derivation and incorporation of the gradients for all these contributions to the energy. The computational modeling includes a detailed description of the reaction coordinate and reaction energetics for the pyran ring-opening reaction, calculation of nonlinear optical properties of pyran and nitrochromene, and modeling of the solvent effects on these systems. Ab initio quantum chemistry calculations were carried out on the full spiropyran system, and the equilibrium geometry for it and the open-ring merocyanine were found.

The models for microsolvation and bulk solvation indicate that solvation has little effect on reaction energetics, but a big effect on nonlinear optical properties. This indicates that the effective fragment potential program, which should allow for a more realistic simulation of solvation, should be valuable in the calculation of nonlinear optical properties of materials in solution.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 162, The Computational Modeling of Nonlinear Optical Materials in the Gas-Phase and in Solution: Quantum Chemistry Calculations on Spiropyran and Related Compounds.

TASK: 170

TASK TITLE: Fundamentals of Diamond Film Growth

TASK OBJECTIVE: The objectives of this task are to understand and optimize the role of hydrogen atoms on the growth of diamond films in order to obtain improved morphologies and growth rates.

SCIENTIST: Deborah L. Thebert-Peeler, M.S., University of Dayton

DESCRIPTION OF WORK:

Thin carbon films were grown by pulsed infrared (1064nm) and ultraviolet (248nm) radiation with

and without H° available to the substrate during growth. Previous work addressed the nature of carbon films deposited using these same wavelengths. It was found that 248nm radiation could be used to grow diamond-like carbon on room temperature substrates without any H° present. Films grown with 1064nm radiation on substrates from room temperature to 1000 C were all graphitic regardless of the H° available to the growing surface. This work continued the investigation of the effect of H° on the character of carbon films grown with these wavelengths; increasing the H° flux to the growing film and accelerating the charged particles from the plume onto the substrate. Films were grown with neutrals only and with the charged particles from the plume accelerated and not, with and without H°, and were found to be virtually identical when evaluated by valence and core level electron energy loss spectroscopy, and raman spectroscopy for each wavelength. These data indicate that growth of diamond-like carbon by pulsed laser deposition is fundamentally different than film growth by chemical vapor deposition processes for these wavelengths. In addition, these data further endorse the previous conclusion that under these conditions the kinetic energy of the ablated particles is a more significant factor than is their charge state in the determination of carbon film properties grown by pulsed laser deposition.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 213, Fundamentals of Carbon Thin Film Growth by Pulsed Laser Deposition: The Role of H°.

TASK: 171

TASK TITLE: Modeling Electronic and Optical Materials Systems

TASK OBJECTIVE: To develop mathematical models that describe the response of electronic and optical materials to external stimuli.

SCIENTIST: John Hurley, Ph.D.

DESCRIPTION OF WORK:

Optimum device applicability requires a thorough understanding of the properties and behavior of a structure's constituent materials. This has generally been approached primarily through characterization techniques in the form of transport and magnetization measurements. Most studies, to date, have focused exclusively on the macroscopic behavior of materials without much emphasis on the microscopic properties that map desired behavior. In this study, a conceptual overview of current theoretical and experimental studies used to define the critical current distribution of high temperature superconductors was presented. The methodologies were emphasized as they related to type-II thin film structures grown by pulsed laser deposition (PLD) on vicinal $LaAlO_3$ substrates. Hysteresis and harmonic analyses revealed results consistent with previously measured thin film Y-Ba-Cu-O structures.

The contributions of grains and their respective boundaries have generally been minimized or altogether eliminated in traditional studies, especially in those using a critical state model. The studies treat type II thin films as single crystal films, which theoretically allows the elimination of contributions due to the dimensions of the grains which decouple at high fields. The benefits of using finite element analysis to incorporate grain boundary morphology and kinetics into modeling schemes to enhance the predictability of critical current distributions in these structures were examined and discussed.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 192, Modeling Electronic and Optical Materials Systems, Part I: Modeling Critical Current Distributions of Thin Film High Temperature Superconducting Structures.

TASK: 172

TASK TITLE: Polymer Electroluminescence

TASK OBJECTIVE: To demonstrate electroluminescence in rigid-rod, ladder, and aromatic-heterocyclic polymers.

SCIENTIST: Ashwini K. Agrawal, Ph.D.

DESCRIPTION OF WORK:

Since the discovery of electroluminescence in conjugated polymers, various research groups have investigated the phenomenon in poly(p-phenylene vinylene) and polythiophene based polymers. The wide interest in the area is based on the fact that conjugated polymers may provide many advantages over the organic molecules in their application as light emitters. Conjugated polymers may show high device stability, good charge transport, high quantum efficiency of electroluminescence, and may be easily and inexpensively used to produce large area display panels. However, none of the conjugated polymers investigated to date satisfy all of the requirements for practical applications. One of the potential candidates for LEDs is rigid-rod conjugated polymers poly(p-phenylenebenzobisthiazole-2,6-diyl) (PBZT). PBZT is a mechanically strong, thermally stable polymer with good optoelectronic properties.

In this research, a single layer light emitting diode (LED) device was fabricated using a rigid-rod conjugated polymer poly(p-phenylenebenzobisthiazole-2,6-diyl) (PBZT) as an active electroluminescent layer. Indium tin oxide (ITO) coated glass and magnesium:silver (Mg/Ag) pads, respectively, were used as hole injecting and electron injecting contacts. A broad band electroluminescence centered at about 650 nm was observed from the device at an onset voltage of 2.5 volts. Similarity of the electroluminescent spectrum to photoluminescent spectrum of PBZT suggests that the electroluminescence originated due to recombination and radiative decay of injected charges within the PBZT layer.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 131, Light-Emitting Properties of Poly(p-phenylenebenzobisthiazole-2,6-diyl) (PBZT).

TASK: 173

TASK TITLE: Polymeric Ceramer Precursors

TASK OBJECTIVE: The synthesis and preliminary characterization of organic polymers as ceramer precursors.

SCIENTIST: Jom Pin Chen, Ph.D.

DESCRIPTION OF WORK:

Organic-silica hybrid materials prepared via sol-gel processing can have desirable properties, such as hardness, optical clarity, scratch and abrasion resistance, and thermal stability from silica, or toughness, flexibility,and weight lightness from organic components. However, one of the most difficult problems for producing xerogel hybrid materials is the large shrinkage and cracking during drying. A wet gel with weak interparticle bonding and uneven micropores is most likely to have cracking. The problem can be minimized to some extent by using extensive aging to increase the strength of the interparticle bonds, slow drying rate, and enlarging the pore size to reduce the stresses. In an attempt to understand the structure-processing relationship, hybrid xerogels prepared from alkyltrialkoxysilanes and alkylbistrialkoxysilanes were investigated.

Diethylphosphatoethyltriethoxysilane and 3-methoxypropyltrimethoxysilane were chosen as precursors for gels. By following the typical sol-gel processing and assuming the complete hydrolysis and condensation, hybrid xerogels were produced. However, cracking during drying occurred as usual.

Two types of bistrialkoxysilanes were prepared. The reactions of 3-isocynatopropyl-triethoxysilane and 3-aminopropyltrimethoxysilane or 3-aminopropylmethyldiethoxysilane gave alkoxysilanes which were converted to xerogels. Crack-free, colorless, transparent thick films of the xerogels were obtained. However, cracking occurred when monoliths were prepared.

Reaction of biphenyl tetracarboxylic dianhydride (BPDA) and 3-aminopropylmethyl-diethoxysilane in anhydrous THF at room temperature gave an amic acid with two reactive diethoxysilane groups. The amic acid in THF was mixed with various amounts of tetramethoxysilane and water to give a clear solution which turned to gel in 80 min. A tough, transparent thick film, amic-acid--silica hybrid xerogel, was obtained after the removal of solvent at room temperature. After heat treatment at 200°C, a more dense, tough, optical clear material, imide--silica hybrid xerogel was developed. The experiment indicated that a small molecule with reactive alkoxysilane groups can undergo cross-linking with tetraalkoxysilane to give tough hybrid materials, and the properties of hybrid materials might be tailored

by using various amounts of tetraalkoxysilane or by using various silane coupling agents. However, the preparation of crack-free monoliths was very difficult.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 133, Preparation of Organic-Silica Hybrid Materials Via Sol-Gel Processing.

TASK: 174

TASK TITLE: Microwave Properties of High-Tc Superconducting Films

TASK OBJECTIVE: To determine the microwave properties of high T-c superconducting (HTS) films and structures and to relate these properties to other film properties.

SCIENTIST: Eric K. Moser, Ph.D.

DESCRIPTION OF WORK:

Advanced microwave systems require high-temperature superconducting films with good microwave properties. The in-house HTS research program in the Materials Directorate at Wright Laboratory optimizes properties of thin films of the HTS material $YBa_2Cu_3O_7$ (YBCO) deposited on $LaAlO_3$ substrates, through investigation of pulsed laser deposition process. Enhancements to the thin film characterization capabilities are desired in the form of microwave surface resistance testing facilities, surface profiling, and facilities for testing the properties of weak-link junctions intended for electronic applications.

This task involved efforts to advance these characterization capabilities, establishing improved microwave testing facilities, performing Atomic Force Microscopy (AFM) measurements on HTS samples, and completion and initial testing of the junction testing systems. AFM results reveal differences in YBCO films grown under varying deposition conditions and enhanced nucleation gained by depositing YBCO on off-axis $LaAlO_3$.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 135, Microwave Properties of High-T_c Superconducting Films.

TASK: 175

TASK TITLE: NDE Materials and Processing Research

TASK OBJECTIVE: Identify and/or develop enhanced methods for quantitative extraction of flaw

and/or material variations in advanced materials and processes using sonic, electromagnetic, radiographic, and optical nondestructive evaluation methodologies.

SCIENTIST: Renee M. Kent, Ph.D., University of Dayton

DESCRIPTION OF WORK:

The material properties of the fibers used to reinforce ceramics and metals in the production of toughened composite materials are critical to an analysis and prediction of the behavior of the composite under its performance operating conditions at elevated temperatures. It is imperative to develop quantitative methodologies to accurately determine the fiber behavior and characteristics under such conditions.

However, the brittle nature and small diameter of typical reinforcing fibers makes accurate measurement of the fiber properties difficult. Elevated temperature studies exacerbate the situation since the materials may become reactive and any contact with the test specimen may then invalidate the measurement. Under these conditions, the optical measurement methodologies must be non-contacting.

In a previous project, a non contacting methodology for the optical measurement and analysis of the ultrasonic response along a fiber was developed. In this work, the technique was upgraded to accommodate elevated temperature capability.

The elastic modulus and Poisson's ratio of a random selection of SCS-6 CVD-SiC fibers were measured and analyzed by enhanced optical interferometry at room and elevated temperatures. The elevated temperature investigation was performed under oxidizing and non-oxidizing ambient conditions in order to assess the effect of oxidation on the empirically determined material properties of the fiber. A significant increase of the Poisson's ratio with temperature was observed under oxidizing conditions.

An independent investigation of the effect of a consolidating matrix on the fiber properties was performed. The data were analyzed in terms of the residual stress state at the fiber-matrix interface. An analysis of the frequency content of the propagating ultrasonic response provided an indication of the level of constraint due to residual stress at the interface.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 134, Laser Interferometric Analysis of Fiber and Composite Material Properties at Elevated Temperatures.

TASK: 176

TASK TITLE: Novel Processes for Fabrication of Metal Matrix Composites

TASK OBJECTIVE: To establish processing windows for novel, high rate fabrication of metal matrix composites.

SCIENTIST: Perikles D. Nicolaou, Ph.D.

DESCRIPTION OF WORK:

This project consisted of four parts describing different issues and processes concerned with the fabrication of continuous fiber, metal-matrix composites (MMCs).

The first part dealt with a new approach to achieve consolidation of foil/fiber/foil (f/f/f) layups. In an effort to reduce processing costs a non-isothermal forging technique, that enables a substantial reduction of the consolidation time, as well as the use of conventional metalworking equipment, was inherited. As part of this effort, it was shown that it is feasible to produce fully dense composites by forging, while issues such as can design, foil to foil and foil to fiber bonding, composite microstructure, fiber fracture, were also addressed in various degrees.

The second part covered design issues and processing parameter selection criteria of MMC consolidation practices. An approach to define suitable processing windows for MMC consolidation was developed. The results were summarized in terms of multi-attribute processing maps on which limitations related to the processing equipment or process economics can also be delineated.

The third part described a sensitivity analysis of process parameter variability on HIP consolidation of MMCs. It was shown that the variation of the consolidation time due to temperature, pressure, or fiber spacing variations increases as the magnitude of the strain rate sensitivity, that characterizes the foil deformation, decreases. Based upon this finding processing maps that account for increased reproducibility of the consolidation process were developed.

The fourth part covered the phenomenon of fiber fracture during MMC fabrication. Based on experimental observation a general model that describes fiber fracture was developed. Model results showed that the propensity for fracture is very sensitive to the distance between crossweave wires in adjacent fiber mats. Also, it was shown that fiber fracture is more likely in areas of the composite in which the fibers are arranged in a rectangular rather than triangular pattern. Finally, experimental and theoretical results were combined to develop guidelines for the design of f/f/f layups to avoid fiber fracture during processing.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 193, Fabrication of Continuous Fiber Metal-Matrix Composites from Foil/Fiber/Foil Layups.

TASK: 177

TASK TITLE: Experimental Photoconductivity Mechanism Determination

TASK OBJECTIVE: To determine the photoconductivity mechanism in rigid-rod and ladder polymers.

SCIENTIST: K.S. Narayan, Ph.D.

DESCRIPTION OF WORK:

The ladder polymer BBL is appreciably photoresponsive with a sizable, measurable photocurrent. Previous results have indicated that the photogenerated charge carriers have characteristic dynamics. The anisotropic nature of the polymer in thin films has been revealed by photocurrent measurements using surface cell and sandwich cell configuration. This research focused on a photoconductivity experiment in a sandwich cell arrangement.

This research was performed to investigate further into the type of photogenerated carriers. In the sandwich configuration, the voltage bias across the sample was changed and the magnitude of the photocurrent was monitored. The electrodes used were transparent indium tin oxide (ITO) and silver paint in contact with an Au/Pd sputtered coating on the sample, thereby forming dissimilar junctions at the two interfaces. Dark (dc) current Vs voltage (I-V) curves were recorded for the two polarities.

The experiment was also repeated as a function of chopping frequency and the difference in magnitude of the photocurrent remained practically constant throughout the range from 4 Hz to 400 Hz.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 132, Electronic Properties of the Ladder Polymer BBL.

TASK: 178

TASK TITLE: Robust Control Techniques for Hot Deformation Processes

TASK OBJECTIVE: To investigate modern control theory applied to the robust control of microstructure, material deformation, and temperature variations throughout workpiece during forging processes.

SCIENTIST: W. Garth Frazier, Ph.D.

DESCRIPTION OF WORK:

The fundamental objectives of this task were to develop techniques for applying modern control theory to hot deformation processes in order to control in-process microstructural evolution in a robust manner and to develop a mathematical model and computer simulation of the 1000 ton Erie forge press

located in Building 653 at Wright-Patterson AFB.

A systematic strategy was developed for determining process parameters such as temperature, strain-rate, and ram velocity for hot deformation processes such as forging and extrusion with the objective of achieving a particular microstructural state. The solution approach is based upon numerical techniques for solving open-loop optimal control problems where the control variable is either strain-rate (the microstructural evolution problem) or ram velocity (the processing problem). The code for determining strain-rate is written in the language of a popular numerical analysis software package. The code for ram velocity determination is written in the C programming language.

A mathematical model and simulation of the Erie forge press were developed. The computer simulation was developed using MATLAB™, a popular mathematical software package.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 228, Robust Control Techniques for Hot Deformation Processes.

TASK: 179

TASK TITLE: Fatigue in Titanium Aluminides and Composites

TASK OBJECTIVE: To evaluate the role of environment in damage evolution in titanium aluminide composites during fatigue.

SCIENTIST: Andrew H. Rosenberger, Ph.D.

DESCRIPTION OF WORK:

This research consisted of four separate experimental investigations, namely: 1) the effect of $P(O_2)$ on the embrittlement of Timetal®21S, 2) the isothermal and thermomechanical fatigue of SCS-6/Timetal ®21S$[0]_4$ composites in inert conditions, 3) the preliminary assessment of the environmental sensitivity of Ti-22Al-23Nb (a/o) neat laminates, and 4) the environmental effects on the mechanical properties of gamma TiAl alloys.

Effect of $P(O_2)$ on the Embrittlement of Timetal®21S

The effect of oxygen partial pressure on the yield strength, ultimate tensile strength, and ductility in Timetal®21S subjected to a stress free thermal exposure was investigated. Tests were conducted at 760°C in a variable total pressure vacuum environment and in a recirculated gettered helium atmosphere. The tests were performed in an environmental chamber attached to a servohydraulic test

system. This system was used, rather than a variable vacuum furnace to understand the influence of the testing apparatus on the oxygen absorption before using the system to perform more complex isothermal and thermal mechanical fatigue experiments.

The post exposure tensile ductility of the specimens was measured at room temperature in air on the same test frame using a displacement rate of 0.0021 mm/sec. Strain was measured using a 12 mm nominal gage length quartz rod extensometer. The fracture surfaces and polished cross sections were examined in a scanning electron microscope (SEM) using secondary electron and back scatter electron imaging. Qualitative compositional examination of the embrittled layer was performed using electron dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS). Hardness profiles from the exposed surface were measured using a Knoop tester. Qualitative measurements of oxygen diffusion depth were obtained through SEM fractography, Knoop hardness profiles, and ß to α phase transformation. These tests showed a distinct embrittlement under vacuum conditions as low as 8×10^{-4} torr. Results in a gettered helium environment compared well with that from high vacuum.

Isothermal and Thermomechanical Fatigue of SCS-6/Timetal®21S[0]$_4$ Composites in Inert Conditions

The influence of test environment on the isothermal and thermomechanical fatigue behavior of SCS-6/Timetal ®21S[0]$_4$ composites was examined. Tests were performed at a maximum temperature of 650°C in a novel, getter-recirculated helium environment which is ideally suited to thermal cycling. Post test fractographic and metallographic techniques were used to determine damage mechanisms. A series of interrupted out-of-phase TMF tests were initiated and preliminary results made concerning the relative damage accumulation in air and the inert environment.

The material used in this study consisted of continuous fiber SiC (SCS-6) fibers in a beta titanium matrix (Timetal®21S Ti-15Mo-3Nb-3Al-0.2Si-wt%). Composites were fabricated by the foil-fiber-foil method using rolled foils of Timetal®21S and fiber mats of SCS-6 fibers held together by metal ribbon and consolidated by hot isostatic pressing. Specimens were tested in an environmental chamber mounted on a computer controlled, servohydraulic load frame. Heating was realized by a four zone quartz lamp system with independent temperature zone control via thermocouples welded to the specimens. The specimens were loaded using water cooled, hydraulic friction grips. Tests were conducted using MATE software which controlled the symmetric triangular wave forms used for both load and temperature (TMF). The software automatically adjusted the four temperature setpoints to maintain proper temperature ramp rates and load/temperature phasing.

Four baseline inert TMF tests were performed and compared to results obtained in air on similar materials. This brief test matrix of inert thermomechanical fatigue indicated that in-phase TMF is mildly affected by environment. A 2x increase in fatigue life was found under inert conditions. In general, the damage mechanisms operative in TMF in air also appear to be active in an inert environment. The matrix fiber in OP-TMF appears to be predominantly a pure mechanical fatigue process and only mildly environmentally-assisted.

A series of interrupted thermomechanical fatigue (TMF) tests were completed in air and inert

environments on specimens manufactured from the same SCS-6/Timetal ®21S$[0]_4$ composite panel. The objective of this study was to determine the degradation of the composite strength during fatigue and relate this to the degradation of the fiber and matrix separately.

Prior to the destructive testing of the specimens, a number of non destructive examination techniques were performed to determine the level of matrix crack initiation and composite damage. These techniques included ultrasonic reflector and immersion surface wave scans, SEM examination, X-ray, and scanning acoustic microscopy (SAM). The ultrasonic reflector plate scans showed little difference in the composites tested in air or inert environment or fatigued to different levels of fatigue life.

Four baseline inert isothermal tests, two at 1 Hz and two at 0.01 Hz, were performed and compared to results obtained in air on similar material. The 1 Hz testing indicated that at high stress levels there is no effect of environment while lower stress tests show a 2 x increase in life under the inert conditions. The 0.01 Hz tests showed a decrease in fatigue life compared to the baseline air data.

Preliminary Assessment of the Environmental Stability of Ti-22Al-23Nb(a/o) Neat Laminates

The influence of high temperature exposure on the tensile strength and ductility of four ply neat composites was examined. The results indicated that a certain embrittlement does occur after high temperature exposure in air. A thin embrittled zone was measured using microhardness measurements. A lesser embrittlement was observed after an elevated temperature dynamic vacuum exposure which indicates a possible high sensitivity to oxygen and a relatively easy embrittling oxygen pickup. The material used in this study was obtained in the form of 4 ply neat laminates processed by the foil-foil-foil technique.

Specimens were exposed for 100 hours at 760°C in laboratory air and a dynamic high vacuum chamber, 2×10^{-6} torr, prior to tensile testing. One unexposed specimen was tensile tested following the identical case removal for use as a control.

After a vacuum exposure, a slight reduction in yield strength was realized and a more substantial reduction in ductility. This indicates that the strength is unaffected by the exposure but that some embrittlement occurred. After an exposure in air, the yield strength indicated that more embrittlement occurred and that there was an impact on the material strength.

Environmental Effects on the Mechanical Properties of Gamma TiAl Alloys

A study to systematically investigate environmental effects on fatigue crack growth in gamma titanium aluminides as a function of temperature and microstructure was initiated.

The objective of this study is to closely examine this environmentally-assisted crack growth

phenomenon as a function of temperature and microstructural condition. This study will baseline a understanding of this mechanism(s) on a comparison of the crack growth behavior and crack growth threshold levels in air and vacuum in order to separate the roles of temperature, and environment. Differences in the crack growth mechanisms will be determined by a careful examination of the fracture surfaces using SEM analysis. The relative roles of intrinsic and extrinsic fracture toughening mechanisms will also be examined in each case.

Vacuum tests will be performed in an ultra high vacuum chamber attached to a servo hydraulic test machine. This investigation will be completed under a follow-on project.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 187, Environmental Effects on the Fatigue and Crack Growth of High Temperature Titanium Alloys and Their Composites.

TASK: 180

TASK TITLE: Innovative Carbon-Carbon Research

TASK OBJECTIVE: To provide creative research for an in-house research team, whose purpose is to provide inventions and scientific breakthroughs, which will enable the synthesis and processing of lightweight, high temperature structural materials with dual-use applications in advanced air and space weapon systems and commercial products, particularly as enabling materials for primary thermal energy conversion processes.

SCIENTIST: Joseph W. Hager, Ph.D.

DESCRIPTION OF WORK:

This research addressed two fundamental problems with current carbon-carbon composites: 1) the complexity and associated cost of manufacture and 2) the inherent susceptibility of carbon-carbon to high temperature oxidation mass loss. Two innovative concepts were introduced and explored. To address complexity and cost of manufacture it was proposed to replace the *disconnected* carbon fiber reinforcement networks of current composites with reticulated graphitic foams. Such *interconnected* networks of graphitic reinforcing micro-struts, each possessing a morphology similar to that of commercial carbon fiber, were blown from anisotropic pitch and were subsequently stabilized, carbonized, and graphitized. To address oxidation mass loss, it was proposed to protect hot carbon surfaces from oxidation by bathing the surface with gases with which the carbon is in thermodynamic equilibrium. Having previously studied this protection concept analytically, construction of a flow reactor apparatus was undertaken to experimentally confirm the viability of the concept.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 214, Innovative Carbon-Carbon Research: Progress in Graphitic Carbon Foams.

TASK: 181

The government canceled this task.

TASK: 182

TASK TITLE: Polymeric Ceramer Precursors

TASK OBJECTIVE: The synthesis and preliminary characterization or organic polymers as ceramer precursors.

SCIENTIST: Jom Pin Chen, Ph.D.

DESCRIPTION OF WORK:

The organic-silica hybrid materials prepared via sol-gel processing can have desirable properties, such as hardness, optical clarity, scratch and abrasion resistance, and thermal stability from silica, or toughness, flexibility,and weight lightness from organic components. However, the incompatibility of organic polymers and metal alkoxides in water miscible solvents is a common problem in the preparation of organic-inorganic hybrid materials by the sol-gel process. Especially, it is not easy to find a high temperature, high molecular weight polymer which retains the solubility in the mixture of water miscible organic solvents and metal alkoxides. It is important to retain the solubility before the occurrence of gelation to avoid phase separation. In other words, organic polymers, metal alkoxides, and the hydrolysis-condensation oligomeric products of metal alkoxides must be compatible and able to stay as homogeneous solution before gelation and during aging of gels. The other difficult problem for producing xerogel hybrid materials is the large shrinkage and cracking during drying. A wet gel with weak interparticle bonding and uneven micropores is most likely to have cracking. The problem can be minimized to some extent by using extensive aging to increase the strength of the interparticle bonds, slow drying rate, and enlarging the pore size to reduce the capillary stresses.

In order to extend the scope of understanding the problems, two series of organic polymers were selected to incorporate with silica by the sol-gel method. Sulfopolybenzothiazoles, sulfopolyamide and polyamic acids which can be converted to rigid-rod or extended-rod polyimides were chosen due to the solubility of these polymers in alcohol with teritaryamine and their excellent thermal and mechanical properties.

The detailed project description, method, results, and discussion are reported in Contributive

Research and Development Final Report, Volume 194, Preparation of Organic-Silica Hybrid Sol-gel Processing.

TASK: 183

TASK TITLE: Discovery Systems, Associative Memories, and/or Genetic Algorithms for Concept Formation

TASK OBJECTIVE: Investigate applications of discovery systems utilizing episodal associative memories (EAM), genetic algorithms (GA), rough sets, neural nets, and scripting.

SCIENTIST: Allen G. Jackson, Ph.D.

DESCRIPTION OF WORK:

Design of new materials, processes, and applications were considered by exploring methods for systematically identifying patterns in real data sets. Identification of patterns present in experimental data sets, for example, electro-optical data from semiconducting compounds, must be considered from several viewpoints. If the data is well quantified, then analysis can be accomplished via statistical methods. When, however, the data contains both quantitative and qualitative data, recourse must be made to other methods. Also, the intent of the search must be included. Together these methods are part of a discovery process that any researcher or designer must accomplish to reach goals. The starting point in this work was consideration of how to discretize, or bin, the data. This is a general problem with wide applicability to tables of data.

Discretization of quantitative data, referred to as binning of data, can be accomplished simply, by using uniform intervals, or more complex approaches may be applied. Experiments on the effects of varying bin size showed that results of analysis of patterns present vary depending on the size of the bin in a rather nonlinear manner. Although intuitively varying interval size is expected to strongly influence the analysis, the highly nonlinear behavior observed was unexpected. Conceptually, the interval choice must be made either by a user to reflect a specific interest or by a machine to investigate all possible patterns in a data set. Once binned, the data was analyzed using pyramidal net of Gladun, rough sets, and concept memories of Pao-Hafez. The Gladun pyramidal net is a directed graph that allows relationships among objects and their attributes to be quickly found. Concept formation is also possible via the net. A comparison among objects and their attributes to memory and rough sets was made. Each approach has unique aspects it brings to an analysis. The concept memory is useful for resolving ambiguities in concepts, pyramidal nets for identifying relationships and forming concepts, and rough sets for identifying classes of objects. Nearest neighbor algorithms were briefly examined and were found to be not suited to discovery methods. The results of experiments using these methods motivated consideration of classification schemes in general, as well as cause, effect, and association definitions. A discovery architecture was formulated.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 189, Discovery Systems, Associative Memories, and/or Genetic Algorithms for Concept Formation.

TASK: 184

The government canceled this task.

TASK: 185

TASK TITLE: Computational Chemistry Evaluation of Halon and Halon Replacements

TASK OBJECTIVE: To develop a fundamental understanding of the chemical mechanisms of Halon fire suppressant action through computational chemistry. To use this understanding to evaluate alternative compounds presently being considered, and other completely different compounds, for fire suppressant capability.

SCIENTIST: Rajiv J. Berry, Ph.D.

DESCRIPTION OF WORK:

The overall goal of this project was to understand and predict the detailed mechanism of flame suppression by potential halocarbon suppression agents. The agents currently used for flame suppression for the protection of aircraft, computer centers, and communication systems are bromine-containing halocarbons grouped under the name halon. The production of halons is banned under the Montreal Protocol because they have been shown to be responsible for the depletion of ozone found in the stratosphere. The desirable characteristics of a suitable halon replacement agent are low global environmental impact (ODP-ozone depletion potential and GWP-global warming potential), acceptable toxicity, cleanliness, volatility, and effectiveness. The candidate replacement agents can be classified as hydrobromofluorocarbons (HBFC), chlorofluorocarbons (CFC), hydrochlorofluorocarbons (HCFC), perfluorocarbons (FC), and hydrofluorocarbons (HFC).

In order to investigate the mechanisms of flame propagation and suppression, one must accurately model all the reactions possible in a flame scenario. The kinetic modeling required for this purpose needs accurate thermochemical (enthalpies) and kinetic (rate constants) data for each reaction as well as the transport properties of all chemical species involves. Computational methods such as the ATOM EQUIVALENTS, BAC/MP4, G1, and G2 have been reported as an alternative source for accurate enthalpies.

Towards the elucidation of the thermochemistry of the elementary chemical reactions associated

with the suppression of hydrocarbon flames by perfluorocarbons (FC) and hydrofluorocarbons (HFC), the present work aimed to study the feasibility of computing accurate enthalpies of formation for stable C_1 and C_2 fluorocarbons.

The enthalpies of formation (ΔH_f^0) for C_1 and C_2 fluorocarbons were computed by the ATOM EQUIVALENT'S (AEQ) method as well as the *ab initio* G1 and G2 methods. The computed quantities were compared with experiment and with a method specifically parameterized to reproduce fluorocarbon ΔH_f^0's (viz. the BAC/MP4 method). For the selected test molecules (CH_3F, CH_2F_2, CHF_3, CH_3-CH_2F, CH_2F-CH_2F, CH_3-CHF_2, CH_3-CF_3, CHF_2-CHF_2, CH_2F-CF_3 and CHF_2-CF_3) the root mean square deviation (RMS) of the computed enthalpies from experiment is 24.3 11.9, 16.5 and 26.4 kJ/mol, respectively for the AEQ, BAC/MP4, G1 and G2 methods, whereas the RMS uncertainty in their experimental enthalpies is only 5.2 kJ/mol.

The ΔH_f^0's for the test molecules was also obtained from isodesmic reactions using the ΔH_f^0 for CH_4 CF_4 and CF_3-CF_3 and the computed enthalpies of reaction (ΔH_r^0). The RMS deviations in the resulting enthalpies are 13.8, 3.6, 4.4 and 5.0 kJ/mol, respectively for the AEQ(iso), BAC/MP4(iso), G1(iso) and G2(iso) methods. Thus, with the exception of the AEQ(iso) method, the RMS deviation in the computed ΔH_f^0's is within the experimental RMS uncertainty.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 220, Ab Initio Thermochemical Computations for Stable C_1 and C_2 Fluorocarbons.

TASK: 186

TASK TITLE: Discovery Systems

TASK OBJECTIVE: To investigate and develop an architecture for a self-adaptive base in a scripting environment.

SCIENTIST: David A. Ress, B.S.

DESCRIPTION OF WORK:

A discovery system for extracting rules and mathematical models from raw data was specified, designed, developed, and implemented. The discovery system features a knowledge base where the rules and mathematical models developed reside, two tools for discovery, and the rummaging module for self-directed control. The rummaging module's design is unique in that it incorporates a feedback loop for gaining new directions in searching through a data set.

This system features connectivity to multiple databases and a graphical user interface. The normal operating mode is directed by the user; however, a second mode, called rummaging, is self-directed in the search for knowledge through the database. The system features two tools for helping to discover rules and mathematical relationships in the data. The first tool is a statistical analysis package for discovering the mathematical relationships (if any) that exist in the data set. The second tool is a rule induction algorithm for developing logical "IF...THEN..." rules about the data set under examination.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 179, Development of a Discovery System for Materials Research.

TASK: 187

TASK TITLE: Stochastic Processes in Neural-Net Computing/Evolutionary Programming

TASK OBJECTIVE: To establish an architecture for memory-based design in support of Semiconductor Wafer Growth using Molecular Beam Epitaxy.

SCIENTIST: Yoh-Han Pao, Ph.D.

DESCRIPTION OF WORK:

This study investigated the use of neural-net computing as an enabling factor in a scheme for monitoring and controlling the growth of multi-layer thin film structures; the films are grown with Molecular Beam Epitaxy or with variations on the theme. Spectral Ellipsometry is used for in-situ real-time monitoring and adaptively tuned PID controllers are used for control. The study was conducted in four parts.

In the first part, the difference between the multiwavelength single reading mode and the single wavelength multireading mode was clarified. The study pointed to the advantages of combining the two modes and described how it might be possible to infer composition, temperature, and surface condition by observing profiles in the wavelength dependence of estimated *n*film, *k*film, something difficult to do with single (ψ, Δ) profiles.

Part 2 described how inversion of (ψ, Δ) three or four point trajectories has been successfully carried out with the use of high efficiency neural-nets of the Random Vector Functional-Link nets (RVFL) type. These nets and the type of performance attainable in that practice were briefly described.

In Part 3, it was described how the paradigm of neural-net model-based feedforward control can be combined with the practice of PID implemented feedback control. The result is accurate, optimal, adaptive control with stable performance. It was suggested that this methodology be the mechanistic

basis for control of the film growth procedure.

Finally in Part 4, the various matters described in the preceding parts were integrated to describe somewhat schematically a unified monitoring and control system for controlling the fabrication of multilayered thin films structures.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 150, Neural-Net Computing and Spectral Ellipsometry for In-Situ Real-Time Monitoring and Control of MBE Film Growth.

TASK: 188

TASK TITLE: Stochastic Methods in Computing

TASK OBJECTIVE: To investigate the mathematical basis for randomly selected basis functions for nonlinear regression.

SCIENTIST: Boris Igelnik, Ph.D.

DESCRIPTION OF WORK:

In this project, the random choice of parameters in neural-net computing, further advances which might be made in this direction, and current related studies in nonlinear regression, were investigated. It was shown that the stochastic approach is an efficient way for solving real-world multidimensional tasks of a very wide range, including function estimation and approximation, data compression, and optimization.

Review of recent related works in nonlinear regression resulted in the conclusion that methods of parametric nonlinear regression are impractical in applications which require fast control actions. The Functional-Link net is one of the methods of nonparametric nonlinear regression. This net was recommended as the basis for application in in-situ control schemes. Some useful ideas taken from other methods of nonparametric nonlinear regression can complement the Functional-Link net.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 175, Stochastic Methods in Computing.

TASK: 189

TASK TITLE: Process Design Using Tagged Memory

TASK OBJECTIVE: To establish an architecture for memory-based design in support of Semiconductor Wafer Growth using Molecular Beam Epitaxy.

SCIENTIST: Jeffrey J. Heyob, M.S.

DESCRIPTION OF WORK:

Process design utilizing tagged memory is an ongoing development to assist material scientists in refining their material processes and to enhance their ability to discover new material compounds and materials processing methods. This work built upon the enhancements of the Molecular Beam Epitaxy control system and extended the Inter-Application Communication protocol to facilitate an Intelligent Process Module environment where information from materials processing instrumentation is accumulated in an extensible architecture for expedient access by knowledge engineering tools.

This development of an extensible memory tag architecture supports the use of coarse-coding ideas underlying connectionist processing of linguistic symbolic expressions, e.g.,geometric, processing, and/or material property features associated with organizing semiconductor wafer growth and design knowledge. The common foundation to support the information requirements of all these materials processes is an extensible tagged-memory information retrieval architecture. This architecture is accessed through a common inter-application communication network able language. This enables any information source involved with a materials process to merge its data with all other concurrent information sources for a materials process including post-process material test data. The architecture addresses the coupling of clustering, functional mapping, associative mapping, and optimization in support of a memory-driven process design system accessible over a network as part of an Information Highway for Materials Processes.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 157, Process Design Using Tagged Memory.

TASK: 190

TASK TITLE: Self Improving Concurrent Engineering System for Integrated Design and Process Planning

TASK OBJECTIVE: To apply genetic algorithm to integrate the design parameters with the process plan specifications to assist in the optimization of the machining process plan by altering the design parameters.

SCIENTIST: Adel Chemaly, TechnoSoft, Inc.

DESCRIPTION OF WORK:

For complex parts, an experienced machinist can develop a suitable process design by relying on experience in machining similar parts. The machinist makes use of inductive methods to relate similar part material, and geometries together with interdependencies and their associated machining sequences which have produced quality parts in the past with minimum time expended. If no previous part geometries are similar, the machinist must use deductive methods to generate a sequence by relating feature attributes and relations to heuristics generated from previous design experience. Of interest is the interaction between the two methods because their coupling enables a self-improving design system to be realized.

The goal of this project was to produce an inductive-deductive system that is capable of self-improvement. The system is made up of a design environment, process planning system, and inductive-deductive system. The user enters a design. The system analyzes the geometry. The process plan is then generated and optimized using the deductive memory. The user is then allowed to review the process plan and make changes to it. If no changes are made to the process plan, it is then used to generated the NC (numeric control) code that drives the NC machine. Otherwise, the changes that are made are passed to the inductive memory (to see what factors caused the user to make the changes). The results of the analyses are then used to update the deductive memory. The deductive memory is developed in such a way that old rules (conclusions) are not deleted but instead are retained in the memory along with a log that indicates the number of times they were used. The deductive memory used is based on Genetic Algorithms (GA) and the inductive memory developed is based on the concept of rough sets.

An evolutionary program based on the concepts of a GA was developed to solve the problem of feature, and operation sequencing. The problem was to develop a system of algorithms to efficiently design a sequence that optimally removes material. The process design is complicated by the combinatorial explosion of alternative solutions and interactions among process resources. Of more specific consideration is the generation of a process design for removing material which finds an optimal or near-optimal machining sequence involving conflicting criteria. In designing the evaluation function a two-fold strategy was implemented. Feature sequencing requires an analysis of the design geometry. The results of the analysis are stored in a data structure called the Interaction Matrix. Each intersection causes dependencies between two or more features which must be satisfied by the resultant sequence. The complexity introduced by feature intersections is so significant that the number of generations of the Evolutionary Programs needed to find a 'good' but safe sequence are highly correlated with the number of feature intersections associated with a process design problem. The problem generates a number of possible feature sequences, each sequence is evaluated using the Fitness Function. A fitness function was developed to evaluate the "goodness" of each sequence.

The primary goal when performing feature sequencing is to provide the machinist with a high-level view of the way features are to be sequenced considering a number of different criteria. Depending on the complexity of the feature, tolerances, material, and desired finish, up to twenty machining operations may be required to machine a feature. The goal is to provide the machinist with a 'near' optimal operation sequence, taking into account the following criteria: maintaining tool dependency, minimizing tool changes, and minimizing tool travel. The problem, a set of operations required to machine the

setup, is read from an input file. Depending on the material and the feature type, certain operations have to be performed in order. The dependency list captures the order in which operations have to be machined in for a single feature. The goal is to perform operation sequencing across features. The Fitness Function has the same structure as the one used for feature sequencing.

More work, testing, and data collection are needed in order to produce a reliable production system. The same methodology can be used in competing materials and processes. Knowledge about different processes and materials can be collected and reasoned about using the inductive-deductive system.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 195, Self-Improving Concurrent Engineering System for Integrated Design and Process Planning.

TASK: 191

TASK TITLE: Application of Discovery Systems to Materials Research

TASK OBJECTIVE: Investigate applications of discovery systems qualitative process theory, pattern recognition techniques, and rough set analysis.

SCIENTIST: Jack Park, ThinkAlong Software, Inc.

DESCRIPTION OF WORK:

The focus of this research was to 1) develop enhancements to a Discovery System (TSC) for support of research in materials processing, 2) to assist in the application of the enhancements, and 3) to deliver source code for the enhancements including rough sets, and nearest neighbor pattern recognition techniques.

The task included the following activities:

- Transliterate TSC Lisp code to the C language for a Nearest Neighbor algorithm
- Transliterate TSC Lisp code to the C language for a Rough Sets algorithm.

The algorithm's are based on the ThinkAlong Software, Inc. TSC scheme implementation. The code was written to permit the algorithm to be ported to a parallel implementation of C for super computers.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 161, Nearest Neighbor in "C" Notes.

TASK: 192

TASK TITLE: Cold Forming of LCB Titanium Alloy

TASK OBJECTIVE: To establish feasibility of cold forming LCB titanium alloy for light weight vehicle applications.

SCIENTIST: Isaac Weiss, Ph.D.

DESCRIPTION OF WORK:

Titanium alloys have long been used in aerospace industry for structural and engine applications because of their low density, and high specific stiffness and specific strength, in comparison to steels. Recently a low cost beta titanium alloy (LCB-Titanium) containing iron and molybdenum has become available. This alloy is cold formable, and can potentially replace steel components in the automobile industry. The research was undertaken to evaluate the cold forming characteristics of LCB-Titanium for use in light weight vehicle applications. In addition, the cold forming behavior of 8720 steel was evaluated for comparison with that of LCB-Titanium.

Room temperature compression tests were carried out on cylindrical samples of LCB-Titanium at strain rates in the range of 0.01 to 20 per second and to strains of 0.7 and 1.4 (50% and 75% reduction in height). The length to diameter aspect ratio of samples was varied from 1.5 to 1, and two different heat treatment conditions were used: sub-transus (760°C, 1450°F) annealing (as-received) and super transus (816°C, 1500°F) annealing. Tests were also carried out at 300°, 400°, 500°, 700°, and 1000°F (149°, 204°, 288°, 371°, and 538°C) to estimate the effects of deformation heating on the behavior of the alloy.

Two significant factors that affected the deformation behavior were the annealing temperature and the aspect ratio of the specimens. Material annealed below the transus temperature of the alloy showed a morphological texture, which, after deformation, appeared as flow lines. Material with this microstructure was more prone to localized shearing and fracture along planes of high shear (45° to the loading axis). Localization of deformation was severe for aspect ratios greater than 1.15, resulting in cracking and fracture of the samples. This was specially true for the sub-transus annealed material. Significant deformation heating occurred at strain rates greater than 0.01 per second. The observable effect of deformation heating was a drop in flow stress with increasing deformation. The effect was similar for strain rates of 5, 10, and 20 per second. Flow curves were corrected for deformation heating assuming 95% of the work of deformation was converted to heat.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 184, Cold Forming of LCB Titanium Alloy.

TASK: 193

TASK TITLE: Analysis of a Titanium Forming Process

TASK OBJECTIVE: To investigate if a component manufactured with a titanium alloy can be substituted for a steel material.

SCIENTIST: Anil Chaudhary, Ph.D., UES, Inc.

DESCRIPTION OF WORK:

The constant velocity (CV) joint is currently produced at GM Saginaw Operations using the 8720 steel material. The currently utilized forming process involves four stages of forming. The process involves two intermediate annealing operations as well. This process is an attractive candidate for material substitution due to the feasibility of weight reduction as well as economy of scale offered by a high volume. As a result, the LCB-Ti material was considered as a candidate substitute material. The LCB-Ti material is observed to have a higher flow stress at low strains compared to the 8720 steel and have a lower flow stress at high strains. In other words, the LCB-Ti has substantially less work hardening as compared to the 8720 steel material. As a result, an important consideration in the possible manufacturing of a titanium CV joint arises in the adequacy of the tooling in the starting deformation stages.

This research dealt with the simulation of the titanium forming process using the existing tooling design and forming sequence. The first objective being the evaluation of the tool stresses in the early stages of forming. The second objective to evaluate the process feasibility.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 160, Analysis of a Titanium Forming Process.

TASK: 194

TASK TITLE: Qualitative Reasoning about Materials

TASK OBJECTIVE: Design, develop, and demonstrate a prototype system for automating the reasoning about materials knowledge and for providing dynamic ad-hoc access to distributed heterogeneous materials databases.

SCIENTIST: Jack Park, ThinkAlong Software, Inc.

DESCRIPTION OF WORK:

This task developed an overview of discovery cast in the roll of integrative manufacturing technology. Scientific and engineering discovery was discussed from a systems point of view, with emphasis on the communication of information by means of a Visual Programming Language. Application of visual programming was illustrated in a technical domain.

A view of the application of The Scholar's Companion™ (TSC) to the domains of science and engineering was outlined. TSC is a discovery system, designed for a variety of kinds of discovery projects. These range from database mining, to conducting experiments (or analyzing the results of those experiments), to pedagogical discovery projects. Discovery plays a role in the design, manufacturing, and application of products in any domain. All of the processes involved in this domain start with the database, and all of the elements of the domain contribute back to the database. TSC is implemented in a combination of environments: Think C, and Prograph CPX. These environments provide the necessary tools to build a large, complex artificial intelligence application, which TSC is.

The entire notion of a visual language, whether for TSC, or any other program environment, calls for the ability to extend the vocabulary. Indeed, the TSC vocabulary of concepts is extensible, and its visual vocabulary is deemed equally extensible. TSC will provide an icon-building window such that a new icon can be built by any user, and used immediately in a project. The icon identifier will then be associated with the concept for which it stands. For science and engineering, an entire vocabulary of icons is anticipated. These will cover issues of design, manufacturing, and application. Specific manufacturing processes will have process rules in the TSC ontology, and will have their own custom icon.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 185, A View of Discovery for Science and Engineering with TSC™.

TASK: 195

TASK TITLE: Vibronic Effects in Nonlinear Optical Responses

TASK OBJECTIVE: The programming, testing, and implementation of computer codes capable of performing vibronic effect calculations.

SCIENTIST: Guru P. Das, Ph.D.

DESCRIPTION OF WORK:

A study of the vibronic contributions in benzene and the system bis-(trimethoxy phenyl vinyl) benzobisthiazole (MPBT) was completed using approximate ab initio theory. The approximate ab initio approach, which until recently has been applied primarily to planar systems, essentially consists of making use of orbitals and integrals, resulting from the treatment of fragments that make up the total

system, to formulate an approximate Hamiltonian for the latter. The present scheme was aimed at generalizing this approach to include all electrons, sigma and pi.

A computer code was developed and tested for the computation of dynamic (hyper)polarizabilities and other properties.

The polarizabilities in this study were calculated using the coupled Hartree-Fock method. While the polarizabilities compare favorably with the corresponding AM1 values, the vibronic contributions are drastically different.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 149, Vibronic Contribution to Second Order Hyperpolarizabilities Based on Approximate Ab Initio Theory.

TASK: 196

TASK TITLE: Self-Directed Control of Pulsed Laser Deposition

TASK OBJECTIVE: To apply advanced computer technology to the control of pulsed laser deposition (PLD). Develop self-directed control algorithm to stabilize the PLD system and improve quality of the deposited film.

SCIENTIST: Samuel J.P. Laube, Ph.D.

DESCRIPTION OF WORK:

Improvements in material thin coatings for the year 2000 and beyond require a radical new approach to deposition processes. Pulsed Laser Deposition (PLD) is one such deposition process which offers deposition of complex materials currently not possible with other deposition methods. Unfortunately, it is not enough to control thin film material composition, but thin film stochiometry and thickness as well. It is also desirable to have a deposition process that is easy to use and is repeatable. In order to propel the current thin film deposition culture into accepting PLD as a manufacturing process, the automation of PLD is inevitable. The inception, development, and implementation of PLD automation methods was the objective of this project.

PLD is a process for depositing thin films (100-1000Å) of many different materials, ranging from superconductors to solid lubricants. A PLD system typically consists of a high energy excimer laser (248nm), beam handling optics, and an ultrahigh vacuum (UHV) chamber. The vacuum chamber contains the part to be coated, as well as a source of coating material called a target. Laser pulses are focused on the target surface. Target material is ablated and deposits in a thin film on the part surface.

Improvements were realized in stabilizing the excimer laser and substrate thermal control.

Additional improvements in spectroscopic sensor and ion probe design were also realized during this effort. Verification of IPM hierarchical control were realized, as well as new applications of PLD thin films.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 196, Pulsed Laser Deposition Improvements by Self-Directed Control.

TASK: 197

TASK TITLE: Electroluminescence of Rigid-Rod and Ladder Polymers

TASK OBJECTIVE: To demonstrate efficient electroluminescence in various polymers produced in the Polymer Branch.

SCIENTIST: Ashwini K. Agrawal, Ph.D.

DESCRIPTION OF WORK:

One of the potential candidates for making light emitting devices is a rigid-rod conjugated polymer poly(p-phenylenebenzobisthiazole-2,6-diyl) (PBZT). PBZT is a mechanically strong, thermally stable polymer with good optoelectronic properties. In this study, improved methods of making light emitting devices using PBZT were investigated.

Both single and bi-layered light emitting diode (LED) devices were fabricated using PBZT as an active electroluminescent layer. Indium tin oxide (ITO) coated glass and magnesium:silver (Mg/Ag) pads, respectively, were used as hole injecting and electron injecting contacts. In bi-layered devices, a electron transporting layer was spin coated over the PBZT layer using a dichloroethane solution of PMMA and oxadiazole compounds.

A broad band electroluminescence between the wavelengths of 400 nm and 800 nm was observed in both types of devices at an onset voltage of 2-3 volts. However, due to very short life-times (few seconds to couple of minutes) and instability of the devices, accurate spectral response could not be recorded on a scanning type spectrophotometer.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 141, Electroluminescence of Rigid-Rod and Ladder Polymers.

TASK: 198

TASK TITLE: Modeling of Molecular Beam Epitaxy of III-V Thin Films

TASK OBJECTIVE: Develop computer models for MBE growth of III-V thin films which predict the atomic level structure as a function of growth parameters.

SCIENTIST: Krishnamurthy Mahalingam, Ph.D.

DESCRIPTION OF WORK:

Cation desorption behavior during molecular beam epitaxy (MBE) of III-V semiconductors at high temperatures was investigated via Monte Carlo simulations. A model was developed for cation desorption kinetics in the homoepitaxy of (100)-InAs and (100)-GaAs. Growth simulations were performed for substrate temperatures in the range of 800K-875K for (100)-InAs, and 930-990K for (100)-GaAs. Results show that in both cases the conventional Monte Carlo technique including only deposition, surface diffusion, and evaporation events cannot explain experimental data. However, a new model including a temperature dependent physisorption mechanism for cations, can accurately describe the experimental findings. The activation energy for the physisorption mechanism is estimated to be 4.31eV for In and 3.68eV for Ga.

In another study, a Monte Carlo simulation model was developed for MBE of GaAs/AlGaAs heterostructures. In this model a configuration dependent exchange reaction was included as a kinetic mechanism in order to explain the observed Ga desorption behavior. Growth simulations were performed for growth temperature at 970K with group-V/III flux ratio in the range of 5 to 15. The desorption rates of the individual species and the Al/Ga concentration profiles were obtained as a function of growth time. The results from these simulations show that the experimentally observed differences in Ga desorption behavior at AlGaAs-on-GaAs heterointerfaces and during growth of bulk AlGaAs are well described in terms of the exchange reaction mechanism. The predicted Ga desorption behavior results in the formation of a novel AlGaAs alloy which is superlattice-like, with a period corresponding to a bilayer.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 225, A Monte Carlo Simulation Study of Cation Desorption Kinetics During Molecular Beam Epitaxy of III-V Semiconductors.

TASK: 199

TASK TITLE: Synthesis of Monomers Containing Totally Aromatic Second and Third-Order Nonlinear Optical Chromophores

TASK OBJECTIVE: The synthesis of novel monomers containing all aromatic heterocyclic structural units with high 2nd-order NLO activity for polymerization to high molecular weight polymers.

SCIENTIST: Ram Kannan, Ph.D.

DESCRIPTION OF WORK:

Previous work at the Wright Laboratory Materials Directorate Polymer Branch identified a new class of second order non-linear optical chromophores that are totally aromatic. A representative example of this class possessing good second order optical properties is pyridyl thienyl ethene.

In this research, four monomers incorporating pyridyl thienyl ethene chromophores were synthesized using Kroenke's pyridine synthesis and several functional group transformations.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 148, Synthesis of Monomers Containing Totally Aromatic Second Order NLO Chromophores.

TASK: 200

TASK TITLE: Synthesis of Aromatic and Aromatic Heterocyclic Model Compounds and Polymers for Evaluation as Second and Third-Order Nonlinear Optical Materials

TASK OBJECTIVE: The synthesis of novel aromatic and heterocyclic oligomers with structural components which have high second and third-order NLO activity.

SCIENTIST: Jay C. Bhatt, Ph.D.

DESCRIPTION OF WORK:

Third order nonlinear optical materials typically are compounds consisting of extended π-electron conjugation and multiple aromatic rings. It is known that two photon absorption makes a very significant enhancement to the measured γ^3 value. The excited state generated by the two photon absorption also leads to the appearance of dramatic effects, such as strong visible blue fluorescence, which have several potential applications.

Soluble all para-polyphenylene compounds which are chemically and thermally stable have previously been synthesized. The purpose of this research was to: scale-up and improve the synthesis of decyl-substituted heptaphenyl material, and design and synthesize new fluorene-containing para-polyphenylene model compounds and monomer materials.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 167, Design and Synthesis of Novel Polyphenylenes as 2-Photon Absorbing Material.

TASK: 201

TASK TITLE: Synthesis of Aromatic and Aromatic Heterocyclic Conducting Polymers

TASK OBJECTIVE: To prepare and characterize new aromatic and aromatic heterocyclic polymers for conductivity studies.

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

DESCRIPTION OF WORK:

The aim of this project was to prepare conducting polymers. To achieve this goal, the preparation of electroactive moieties such as di- and triphenylamines and triphenylmethanols was undertaken.

Novel diphenylamine based monomers and their benzazole model compounds were prepared. Polybenzazole (PBX) homopolymers with the diphenylamine group were obtained with low to moderate intrinsic viscosities and exhibited high thermal stabilities. Copolymers of polybenzothiazole containing N,N-dimethylamino based triphenylamine moiety were prepared as medium viscosity polymers and exhibited good thermal stabilities. In the preparation of triphenylamine-benzothiazole homopolymer containing a hydroxy group, a polymer containing the hydroxy and phosphonic pendant was obtained. The triphenylmethanol monomers preparation was also attempted and were obtained in low yields.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 169, Synthesis and Properties of Diphenylamines, Triphenylamines, and Triphenylmethanols.

TASK: 202

TASK TITLE: Applications for Nondestructive Evaluation (NDE)

TASK OBJECTIVE: Use ultrasonic and electromagnetic methodologies for NDE and characterization of advanced materials.

SCIENTIST: Peter B. Nagy, Ph.D.

DESCRIPTION OF WORK:

The axial Young's modulus of thin fibers can be readily determined from both static tensile strain and ultrasonic velocity measurements. In comparison, the radial modulus, which is of particular importance in many areas such as designing, manufacturing, and nondestructive characterization of fiber reinforced composites, is much more difficult to determine. Since the usually very small diameter renders any direct measurement in the radial direction unfeasible, indirect axial measurements based on the so-called Poisson effect have to be used. In this research, the feasibility of two versions of the axial guided wave technique was studied. The more conventional first method determines the Poisson ratio of the fiber from the low-frequency dispersion of the axial guided mode, which is proportional to the square of Poisson's ratio. The second technique is based on a novel approach exploiting the excess attenuation of the same mode due to leaky losses when the fiber is immersed in water. The leaky attenuation, which is caused solely by the normal component of the surface vibration, is also proportional to the square of Poisson's ratio in the specimen.

Preliminary experimental results indicate that both techniques can be used to determine the transverse modulus of thin ($\varnothing$0.3-1.5mm) metal wires in the 200 kHz - 2 MHz frequency range. The measured Poisson ratios were generally higher than the corresponding values in isotropic materials, which is indicative of the significant anisotropy routinely found in such specimens. The ultimate goal of this study was to develop ultrasonic methods to measure the axial Poisson ratio in thin fibers used for composite reinforcement. Typically, such fibers range between 10 to 250 μm in diameter and are expected to have relatively low Poisson's ratios around 0.2 Therefore, both dispersion and leaky attenuation measurements have to be done at much higher frequencies where adverse effects such as intrinsic attenuation in the fiber and viscous losses in the water present major technical problems for both methods. Although, the results well demonstrate the feasibility of both investigated ultrasonic materials characterization techniques, further analytical and experimental efforts are needed to adapt these methods to the assessment of Poisson's ratio in thin fibers below $\varnothing$300 μm.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 165, Ultrasonic Assessment of Poisson's Ratio in Thin Rods.

TASK: 203

TASK TITLE: Characterization of Ceramic Composites

TASK OBJECTIVE: To establish processing, microstructure, property relationships in ceramic matrix composites. Specifically, the candidate will examine novel oxidation resistant interface treatments for improved ceramic composites. The work will also seek to find economical methods of processing these composites.

SCIENTIST: Michael K. Cinibulk, Ph.D.

DESCRIPTION OF WORK:

One of the specific objectives of this task was to investigate the feasibility of using cleavable oxides as a fiber-matrix interphase in alumina-based composites, to achieve enhanced toughness and oxidation resistance. The processing of such an interphase was shown previously to produce a highly crystallographically oriented interphase. Work on this effort attempted to obtain relevant mechanical data of the interface and composite. YAG-fiber reinforced alumina composites were prepared for pushout testing to place the fiber under radial tensile stress and allow for fiber debonding. However, fiber fracture was found to occur prior to fiber pushout. Composites, having a laminate geometry, of alumina substrates bonded by hibonite were investigated to determine strain energy release rate of the interphase. Hibonite on single-crystal substrates resulted in complete texture of the basal planes parallel to the surface. Bonding experiments were initiated.

A second objective was to focus on the coating and microstructural characterization of coated fibers and fiber-reinforced composites. Cloths of Nextel 550 were coated with ZrO_2 by a batch process to investigate the viability of coating cloths in this manner. Preferential deposition and wicking of the sol to fiber-fiber contacts was observed. A new method of preparing specimens for electron optic characterization was developed and is superior to conventional polishing of specimens with diamond pastes on cloth for producing high quality surfaces with minimal surface relief and very thin ($<2\,\mu m$) sections.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 172, Cleavable Oxides as an Interphase in Alumina-Based Composites and Coating and Characterization of Ceramic Fibers.

TASK: 204

TASK TITLE: Alternative Design

TASK OBJECTIVE: To develop a prototype architecture for alternative shape, process, and material design.

SCIENTIST: Adel Chemaly, TechnoSoft, Inc.

DESCRIPTION OF WORK:

Traditionally, the product design and the manufacturing process planning have been done independently. In the short span of the last fifteen years CAD systems have been extensively used in the automation of the product design, while the process design or planning has remained a manual effort with little or no automation. There have been numerous efforts (e.g. group technology involving variant and generative techniques) and research in the area of product design and process planning integration. Most research has addressed only a part of the problem, either the product design or process planning.

Integration of product design and material characteristics, with the automatic generation of the machining process plan, is a goal which offers many challenges to overcome.

This project presented an approach for integrating the product and process design. This approach presents an architecture based on an object oriented modeling paradigm developed and marketed by TechnoSoft, Inc. as the Adaptive Modeling Language (AML). The success of the approach, for an automated process planner integrated with a design system, comes from its capability to reason about and automatically extract a manufacturing representation from the part design geometry. By analyzing the part geometry, and planning around the problems that could be encountered in machining, the automated planner can overcome the difficulties in automating the process plan.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 197, Concurrent Engineering System Architecture for Competing Shape, Process, and Material of Machined Parts.

TASK: 205

TASK TITLE: Materials Discovery

TASK OBJECTIVE: To develop a feature-based knowledge base for biologically-based materials.

SCIENTIST: Robert B. Trelease, Ph.D.

DESCRIPTION OF WORK:

The purpose of this project was the development of the structure and function of a feature-based knowledge base and model for biological materials systems and processes that operates in conjunction with the artificial intelligence software discovery system called The Scholar's Companion (TSC). The knowledge base, based on published scientific research findings, contains a hierarchical collection of fundamental biological concepts, substances, structures, organs, organisms, taxonomic relationships, process descriptions, predicates, and biological process rules. The knowledge base is constructed so as to allow representations of biological systems functions from the molecular to the organism/population levels of abstraction. In conjunction with the accompanying experimental paradigms and initial conditions process rules, the knowledge base produces a variety of experimental qualitative simulations (models) of biological processes characteristic of cellular compartments of the immune system. These simulations can be used to test assumptions about the interactions and behaviors of biological cells mediated by the production of biological substances in response to defined pathogenic agents. Due to the hierarchical structure of the knowledge base, it can be easily expanded to include processes related to new additional pathogenic agents and biological materials, including regulatory molecules and toxic agents. The knowledge base can readily be extended to handle molecular biosynthesis at the atomic level of detail.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 145, Development of a Feature-Based Knowledge Base for Biologically-Based Materials and Processes.

TASK: 206

TASK TITLE: In-situ Fiber Optic Raman-Rayleigh-Brillouin Spectroscopy (FORRBS) Sensor

TASK OBJECTIVE: To establish the feasibility of using FORRBS to sense polymer composite material properties during cure for use in effecting real-time control.

SCIENTIST: John F. Maguire, Ph.D., Southwest Research Institute

DESCRIPTION OF WORK:

This project consisted of an initial feasibility analysis into the usefulness, or otherwise, of Raman spectroscopy in the characterization of materials during materials and process operations. The objective was to characterize through the use of Raman spectra the vibrational spectra of ß aluminas for real-time control of chemical vapor deposition (CVD). A number of physico-chemical models were developed from which the vibrational Raman spectra were calculated. These models show clearly that the Raman technique has the potential to probe the atomic and crystal structure of CVD-coated material such as lanthanum stabilized ß-alumina.

In addition, the feasibility of making *in-situ* measurements on such coatings was evaluated using a number of Raman approaches. In this activity, spectral performance was evaluated using a selection of materials of interest and a number of coated fibers. While spectra of these materials were not obtained *in-situ* during processing, the material samples provide model data on what reasonably can be expected from *in-situ* measurements.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 226, Theoretical Characterization of Raman Spectra.

TASK: 207

TASK TITLE: Nonlinear Optical Characterization of Biopolymers

TASK OBJECTIVE: To characterize the chi(2) and chi(3) properties of biopolymers being developed in the materials laboratory in-house research programs.

SCIENTIST: Paul A. Fleitz, Ph.D./Jiaoshi Si, Ph.D.

DESCRIPTION OF WORK:

This project consisted of two parts: 1) the investigation of materials with potential as optical power limiters, and 2) synthesis and characterization of large conjugated porphyrin compounds.

Materials with potential as optical power limiters were investigated to understand their nonlinear optical properties and their behavior under intense laser irradiation. The nonlinear optical properties of diphenyl butadiene were studied using the Z-scan technique. The Z-scan technique is a simple, single beam technique to measure the nonlinear refraction and nonlinear absorption in materials. The technique has been modified to facilitate the investigation of materials with low solubility. In these measurements the material is heated above its melting point into the isotropic liquid state. Z-scan measurements are then made on the molten sample. Both nonlinear refraction and nonlinear absorption were observed. Under intense laser irradiation, many of the organic materials used as optical power limiters photodegrade. Several different analytical techniques were used to investigate the photodegradation products of these solutions.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 224, Characterizing Materials with Potential as Optical Power Limiters.

Molecules with very long π-system are of intense interest because these materials are expected to have nonlinear optical properties. Porphyrin is one of these compounds, because the porphyrin ring holds the coplannar π-system which provides maximum overlap. The synthesis of a large conjugated porphyrin ring involves more than six chemical steps and some more chemical steps on its derivatives. The first four steps, that is: the synthesis of pyrrole ring, oxidation to acetate, coupling to diporphyrin and Grignard reaction to make trimethylsilylpropynal were successfully finished. The products were identified by their melting points, infrared spectroscopy, and NMR spectroscopy.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 230, The Synthesis and Characterization of Large Conjugated Porphyrin Compounds.

TASK: 208

TASK TITLE: Characterization of Ceramic Composites

TASK OBJECTIVE: To characterize the mechanical properties of state-of-the-art ceramic matrix composites.

SCIENTIST: James M. Staehler, Ph.D.

DESCRIPTION OF WORK:

Four CMC's are being considered by the Air Force for use as divergent flaps and seals in the exhaust nozzle of an F110 engine. In addition to evaluating the feasibility of using the candidate materials for this specific task, a second objective was to improve the understanding of these materials, their strengths and weaknesses, and to make suggestions for improvement. To be successful at this, the materials were subjected to controlled tests and the microstructures thoroughly characterized. The work focused primarily on the characterization of the four CMC's. This included density, porosity, specific surface area, and volume fractions of constituents. It also included fiber-matrix interface characterization using fiber push-out and push-in techniques.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 232, Characterization of Ceramic Composites.

TASK: 209

TASK TITLE: Theoretical Modeling of the Photoconductivity of BBL

TASK OBJECTIVE: To evaluate numerically and analytically, a collection of recent photoconductivity, resistivity, and optical data on BBL, a polymer which is known to exhibit electronic-optical properties similar to those of a semiconductor.

SCIENTIST: K.S. Narayan, Ph.D.

DESCRIPTION OF WORK:

The ladder polymer BBL exhibits a substantial photocurrent. The electronic properties of BBL were investigated using steady state and transient photoconductivity techniques.

The photocurrent was studied as a function of temperature at selected photon energies above and below the bandgap (at 1.90 eV and 1.54 eV, respectively).

The photocurrent response of the polymer film in the surface cell and sandwich cell configurations were compared along with the absorption spectra, and the results correlated with the surface and bulk morphology. The steady state photocurrent showed a nonlinear response with respect to the electric field, accompanied by features in the infrared region. The photocurrent was also studied as a function of photon intensity, chopper frequency and temperature. A long lived transient photocurrent (>100 ms) was present on exposure to nanosecond laser pulses revealing the presence of deep traps.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 147, Photoconductivity of the Ladder Polymer BBL.

TASK: 210

TASK TITLE: Automated Inspection Planning

TASK OBJECTIVE: To develop a prototype architecture for automating scan plan generation.

SCIENTIST: Russell E. Duttweiler, B.S.

DESCRIPTION OF WORK:

An automated inspection planning system, AUTO-INSPECT, was developed which uses a 3-D solid modeler to perform geometric reasoning in a feature based CAD environment. This project applied this system to eddy current process planning which offers new degrees of flexibility to the inspection planning process. The purpose of this project was to bring about a significant reduction in process planning time for the F100-PW-229 engine components by replacing the presently used manual method of Eddy Current scan plan generation.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 173, Automated Inspection Planning for Eddy Current Systems.

TASK: 211

TASK TITLE: Alternative Design Deduction System

TASK OBJECTIVE: To develop a deduction system to enable the automated generation of alternative materials and process designs.

SCIENTIST: Frank M. Brown, Ph.D., University of Kansas

DESCRIPTION OF WORK:

A number of recent papers from Eastern Europe (Gladun) have introduced a new alternative derivational learning system called pyramidal nets. These nets have been applied to the problem of deriving and predicting the existence of chemical compounds and their properties. Unfortunately, pyramidal nets and the methods involved in producing them are not well understood in the English language literature for a number of reasons: In some instances the methods are vaguely defined whereas in other instances the methods are explained in pseudo codes rather than in standardized

computer languages which can be executed on computers. Another problem is that the English translations of many presumably technically meaningful words have no readily apparent precise technical meaning.

For these reasons this effort focused on developing a deeper understanding of pyramidal nets and Gladun's algorithm. In particular, the following five issues were addressed: What Gladun's algorithm does, the problem of describing and implementing Gladun's algorithm so that it may be easily understood and modified, the problem of determining whether Gladun's algorithm is sensitive to the order of data input and other orderings inherent in the algorithm, and the uses of Gladun's algorithm.

Pyramidal nets and Gladun's algorithm were described and investigated using the Logistica Language. It was shown that Gladun's algorithm produces taxonomic descriptions of data without always producing maximally inclusive descriptions and that this leads to sensitivity in the order of input of the data objects. Various non-sensitive approaches were explored along with a discussion of the uses that may be made of Gladun's algorithm.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 176, Alternative Design Deduction System.

TASK: 212

TASK TITLE: Algorithmic Learning for Neural Network

TASK OBJECTIVE: Develop an algorithm to automate training of neural network.

SCIENTIST: C.L. Philip Chen, Ph.D.

DESCRIPTION OF WORK:

Recently, much effort has been focused on design of network architectures for fast learning, adjustable weight matrices for learning, and fast learning algorithm. The existing back-propagation algorithm decides the weight matrices using gradient descent methods. Based on the back-propagation training algorithm, network converges to minimum error after repeated iterations. However, the network architecture must be given before the training commences.

In this study, a supervised single-hidden layer neural network architecture and an instant algorithm for finding the weights of the supervised learning problem were developed. The upper bound of the number of the hidden nodes to be able to solve the weight matrix exactly was provided. For an n dimensional, N-pattern training set, a maximum of N-r hidden nodes are required to learn all the patterns within a given precision (where r is the rank, usually the dimension, of the input patterns).

Several testing examples were used to show the generalization capability of the algorithm. The

weight matrix, *W*, depends on the linear independency of the input matrix and the weights of the hidden layer. Once *rank* ([A | $\underline{A}$])= *rank* ([A | $\underline{A}$]),a global minimum of the error space that corresponds to the weights of the single hidden-layer can be obtained.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 174, An Instant Supervised Learning Neural Network: A Rank-Expansion Algorithm.

TASK: 213

TASK TITLE: Self-Lubricating Metal-Matrix Composite Wear and Debris Analysis

TASK OBJECTIVE: (1) Determine the friction behavior of aluminum metal-matrix composites (MMCs) against ceramic surfaces and (2) identify the mechanisms of lubrication in self-lubricating MMCs.

SCIENTIST: Somuri V. Prasad, Ph.D.

DESCRIPTION OF WORK:

The objective this research was to establish the mechanisms of lubrication in self-lubricating aluminum metal-matrix composites reinforced with silicon carbide (SiC) and tungsten disulfide (WS_2) particles. This was accomplished in part by analyzing the third-bodies formed during a two-million-cycle wear test. Composites were prepared by a powder metallurgy route involving blending, compacting, and sintering. Friction and wear tests were run in air on polished surfaces of MMCs with a 440C steel counterface. The wear scar, transfer film on the steel counterface, and the wear debris were characterized by electron microprobe analysis.

Scanning electron microscopy examination confirmed that tungsten disulfide platelets were not present either in the wear debris or in the wear-induced transfer film on the steel counterface. The sulfur to tungsten (atomic) ratio in the WS_2 phase on the wear track was much lower than 2.0, indicating wear-induced oxidation of tungsten disulfide. Back scattered electron imaging and electron microprobe analysis revealed the formation of a new phase on the wear track. The debris was predominantly spheroidal in shape. The debris and the transfer film were different in chemical composition from any of the constituent phases of the MMC. Sliding of tungsten disulfide (hexagonal) platelets was not a probable mechanism of lubrication in the case. A new mechanism of lubrication based on tribochemistry was proposed to explain the self-lubricating behavior in Al-SiC-WS_2 metal-matrix composites.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 182, Characterization of Third-Bodies in Self-Lubricating Aluminum Metal-Matrix Composites by Electron Microprobe Analysis.

TASK: 214

TASK TITLE: NDE and Aging Systems Technology Transition Development

TASK OBJECTIVE: Identify, analyze, and/or develop enhanced methods for technology transition of sonic, electromagnetic, radiographic, and optical methodologies for use in nondestructive evaluation (NDE) and in aging systems.

SCIENTIST: Matthew J. Golis, Ph.D., Advanced Quality Concepts

DESCRIPTION OF WORK:

This project provided assistance in the development of enhanced methods for technology transition of Nondestructive Evaluation (NDE) technologies between the private sector and the Wright Laboratory Materials Directorate NDE Branch (MLPO). A special emphasis was placed on matters relating to the aging systems within the U.S. Air Force. Project activities centered around three distinctly different types of tasks: (1) promotion of liaison activities directed at obtaining prompt technical responses to the NDE needs of the Air Logistics Centers and program offices; (2) assistance in developing statements of work aimed at improving the performance of the aging Retirement for Cause systems at San Antonio and Oklahoma City ALCs and (3) assisting in creating links between the branch's technical staff and the private industrial sector as well as other governmental agencies.

Liaison activities centered around continuation of developing and reporting on an approach developed to inspect cracking weep holes in the lower wing planks of C-141 fuel tanks on behalf of the Warner Robins ALC (WR/ALC). Two new initiatives involved development of a means to inspect electron beam (EB) welds in Titanium blades and structural members. The first initiative was on behalf of the San Antonio ALC (SA/ALC) interested in repairs to Titanium TF39 2nd stage compressor blades. This work was done in cooperation with a private repair contractor involved in used-blade refurbishment. The second initiative was on behalf of the F-22 Program Office interested in the integrity of the EB welds found in structural members of the under-development F-22 aircraft. The suggested schemes are considered to be the prime approaches for inspecting these intricate geometries.

The status of the RFC systems in use at SA-ALC and Oklahoma ALC (OC/ALC) was determined through personal site visits, interviews with experts familiar with the RFC systems, and independent review and analysis of reports and recent performance data. Results indicated that the performance of these systems had met the expectations of the original reliability review team, but that on-going problems related to background noise, detection of cracking in tight corners, and the development of generalized scan plans remained as issues in need of future resolution. To this end, a statement of work for a new project start was prepared and advertised by MLPO as a pending PRDA for integrating improvements in the technologies found in the RFC system by contractors familiar with both the latest

technical advancements and the general operation of the RFC system.

Participation in several technology conferences took place in order to bring the activities of the NDE Branch to the attention of the private commercial sector. Sessions on NDE at the AeroMat Conference and the Spring and Fall conferences of ASNT were chaired with papers given related to contracting activities and technical initiatives taking place at the NDE Branch. Several other technical meetings were attended including the QNDE, ASIP and MFPT meetings in order to identify possible NDE technologies which have the potential for adaptation to areas of interest to the USAF.

Ways were recommended in which the Air Force NDE technologies can be transitioned to both the private sector and other agencies based on continued close interactions with key individuals active in the NDE field.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 244, NDE and Aging Systems Technology Transition Development.

TASK: 215

TASK TITLE: Investigation of Advanced Metallic Composites II

TASK OBJECTIVE: To develop an understanding of the relationships between the composition and microstructure of matrices, the bonding at fiber/matrix interfaces, and composite properties in advanced metallic composites.

SCIENTIST: Douglas B. Gundel, Ph.D.

DESCRIPTION OF WORK:

The off-axis properties of composites are dependent upon the ability of the interface to transfer load from the matrix to the fiber. The stress at which the fiber-matrix interface debonds, therefore, is a critical parameter which currently limits the application of continuously-reinforced composites. Interface debonding experiments have typically relied upon the measurements at the free surface, using techniques such as optical microscopy and surface replication. However, recent evidence suggests that there may be a debond at this location prior to the application of load due to residual thermal stresses. In addition, the discontinuity at the surface is thought to give rise to a concentration of residual thermal and applied loads. Tests that focus on the free surface or allow the interface at the surface to be loaded by the applied stresses may therefore underestimate the LCC of titanium-matrix composites.

In this project, a new specimen design was proposed to minimize the influence of the stress singularity at the free surface, providing a more realistic measurement of the transverse load-carrying capability of the fiber/matrix interface. This new technique for measuring deformation in a single-fiber

composite, in the absence of "free-edge" effects, was successfully used to measure the stress and strain of fiber-matrix debonding in various SiC-fiber/Ti-6Al-4V composites. The new sample geometry isolates the free surface from the region stressed by the applied load and therefore gives a more accurate estimate of the interface strength.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 233, The Intrinsic Interface Debond Stress in Fiber-Reinforced Composites Subjected to Transverse Tension.

TASK: 216

TASK TITLE: Shubnikov - de Haas Effect in Strained Layer Superlattices

TASK OBJECTIVE: Evaluate the quality of strained layer superlattices made of III-V semiconductors containing antimony and determine the effect of intrinsic defects both in the bulk of the semiconductor layers and at the interfaces of different semiconductors on the carrier concentration in the superlattices.

SCIENTIST: Ikai Lo, Ph.D.

DESCRIPTION OF WORK:

The primary objective of this program was to search for new materials for the applications of infrared photoelectronic detectors and high speed devices. The superlattice is the best choice of the structure for these devices due to its varied properties; for example, the tunable band gap, strain induced band deformation, and so on. Because of the difficulty in the growth of superlattice, the simple structures like quantum well or heterostructure are used to characterize the electronic properties of the new materials which were theoretically predicted for the applications. This project was focused on the GaInAs-based materials. The basic properties of the two-dimensional electron gas in this material, including the effective mass, the quantum lifetime, and carrier concentration, were determined. These properties are necessary to understand the materials for applications. The persistent photoconductivity effect in this material was investigated as well.

The electronic properties of GaInAs-based heterostructures were investigated by the Shubnikov-de Haas measurements for magnetic fields up to 4.5T and temperatures down to 1.2K. The quality of the δ-doped $Al_xIn_{1-x}As/Ga_xIn_{1-x}As$ samples was better than that of the modulation-doped $Ga_xIn_{1-x}As/InP$ samples. Two oscillations corresponding to two kinds of carriers were observed in the δ-doped $Al_xIn_{1-x}As/Ga_xIn_{1-x}As$ samples. From the Shubnikov-de Haas measurements with different tilted magnetic field, it was concluded that the lowest two subbands of the two-dimensional electron gas were occupied. After illuminating the samples at low temperature, the electron density increased from 17.3 to $18.2 \times 10^{11} cm^{-2}$ for the first subband and 3.6 to $4.1 \times 10^{11} cm^{-2}$ for the second subband. Electrons started populating the

second subband when the first subband was filled at a density of $10.3 \times 10^{11} cm^{-2}$. The effective mass of the second subband determined from the temperature dependent Shubnikov-de Haas measurements was equal to $(0.045 \pm 0.003)m_0$. It was shown that the band nonparabolicity is significant in this material.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 168, Shubnikov-De Haas Effect in Strained Layer Superlattices.

TASK: 217

TASK TITLE: Stochastic Modeling of III-V Thin Film Epitaxy

TASK OBJECTIVE: Develop computer models for MBE growth of III-V thin films using the stochastic technique.

SCIENTIST: Ramasubramanian Venkatasubramanian, Ph.D.

DESCRIPTION OF WORK:

As part of this project two growth problems in the molecular beam epitaxy (MBE) of III-V compounds, low temperature GaAs growth kinetics and doping kinetics, were theoretically studied. The use of column IV dopants in III-V compounds is of great interest because they are easy to handle and in the case of Si, readily available in most molecular beam epitaxy (MBE) chambers. It should be noted all column dopants are amphoteric in all III-V compounds. An element which is predominantly a donor in one material may act as an acceptor in another material depending on its size relative to the cation and anion, the substrate orientation during growth, and other growth conditions. In this work, rules were presented for predicting group IV dopant site selection in III-V compounds. These rules take into account the relative covalent radii of the atoms, types and relative numbers of surface dangling bonds available, and the anion to cation flux ratio. Preliminary predictions showed excellent agreement with available experimental data. Predictions for the donor and acceptor atoms were made for GaN, AlN and related compounds.

Reflection high energy electron diffraction (RHEED) intensity oscillations were observed during the MBE growth of GaAs even at growth temperatures as low as 60°C. It was found experimentally that the amplitude of the oscillation depends on the anion to cation flux ratio and temperature. The stochastic model of growth was employed with modifications to include time evolving As physisorbed state with a surface life time. Preliminary results indicate that the RHEED oscillations at low temperatures are a consequence of layer by layer growth mechanism and that the scattering from the physisorbed state plays a major role in influencing the oscillation amplitude. The results of this work agreed semi-quantitatively with experiments.

The detailed project description, method, results, and discussion are reported in Contributive

Research and Development Final Report, Volume 163, Stochastic Modeling of Molecular Beam Epitaxy of III-V Compounds.

TASK: 218

TASK TITLE: Modeling of NLO Materials Using Parallel Computers

TASK OBJECTIVE: To calculate the structure and properties of biologically derived nonlinear optical materials using massively parallel computers.

SCIENTIST: James A. Lupo, Ph.D.

DESCRIPTION OF WORK:

Three efforts were undertaken on this project. The first involved additional porting work on the Pfortran and UHGROMOS programs, completing a sequence of ports which cover a majority of massively parallel systems available at the Department of Defense (DoD) High Performance Computing (HPC) Shared Resource Centers. The second effort was devoted to developing a UHGROMOS model of bacteriorhodopsin (**bR**) with a retinal chromophore attached. The final effort concentrated on the establishment of a virtual reality based molecular docking simulator facility.

The benchmark comparisons of UHGROMOS were completed with the final part of Pfortran to the IBM SP2. Results show that the IBM SP2 machine is significantly faster than any other of the massively parallel processors currently in the Department of Defense High Performance Computing program. The choice of machine can now be made on the basis of performance and or production turn-around time. A model of bacteriorhodopsin (**bR**), with a retinal chromophore attached has been developed for simulation with UHGROMOS. The **bR** model design and initial testing is presented. Finally, a molecular docking simulator facility, DOCKER, has been installed and is operational. This facility allows researchers to examine the interaction of two molecules using virtual reality involving stereo vision and real-time force feedback.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 229, Modeling of NLO Materials Using Parallel Computers.

TASK: 219

TASK TITLE: Project Management/Administration

TASK OBJECTIVE: To provide support activities necessary to establish project task orders and overall contract management administration.

SCIENTIST: Milton E. Zellmer

DESCRIPTION OF WORK:

The contributive research and development project required extensive management and administration activities that were not readily charged to a specific task. These activities fell into three general categories:

1. Those contract management administrative requirements to establish planning and control procedures that applied to the project as a whole. Examples are status reporting, project management meetings, and other general overall project reporting.

2. Those management activities required to establish each of the task assignments. These activities could not be charged to the task since the task was not yet approved during this phase.

3. Recording and reporting the performance and cost for the overall management and administrative activities.

This task provided project management/administration from 26 June 1994 - 14 July 1995.

TASK: 220

TASK TITLE: Quantum Dynamics of Charge Carrying Quasi-particles in Conducting Polymers

TASK OBJECTIVE: Study the dynamic behavior of charged solitons and polarons in conducting polymers while in their conductive state. Various polymer chains, with and without defects, will be studied in an attempt to understand the basic principles of conductivity in known conducting polymers. This understanding may be used to design more efficient polymers.

SCIENTIST: Guru P. Das, Ph.D.

DESCRIPTION OF WORK:

An ab initio study of the transport of charged solitons as carriers of electricity in doped polyacetylene was performed. The prototype, the charged oligomer $C_9H_{11}+$, was dealt with in treating the polymer. Two different procedures were considered. In the first a set of dynamical equations based on the time-dependent Schroedinger equation was solved leading to a time evolution of the system. In the other the same solution was attempted based on the assumption that the global wavefunction consists of two solitons (a left and a right one) spanning seven carbon atoms. While the former study used a Hartree-Fock electronic wavefunction, the latter used a more accurate correlated wavefunction.

Although both the studies are preliminary, the results are quite different pointing to some important conclusions. The Hartree-Fock based time evolution indicates a virtually stationary soliton, while the second method predicts a highly mobile soliton capable of generating the high conductivity found in doped polyacetylene.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 227, Ab Initio Study of Transport of Solitons in Trans-Polyacetylene.

TASK: 221

TASK TITLE: Computational Modeling of Liquid Crystal Siloxanes

TASK OBJECTIVE: To explore the interactions and possible interferences between chromophores and liquid crystal mesogens.

SCIENTIST: Barry L. Farmer, Ph.D.

DESCRIPTION OF WORK:

Semiempirical molecular orbital calculations were undertaken to model the conversion of 1'-isopropyl-3',3'-dimethyl-indoline-spiro-6-nitro-8-methoxy benzopyran and to the corresponding merocyanine. One possible mechanism for this conversion, simulated by progressively stretching the carbon-oxygen bond which is known (experimentally) to rupture, was studied in detail.

This conversion from the non-absorbing (in the visible) and therefore uncolored spiropyran form to the highly absorbing merocyanine form which has a blue color, is of interest for applications such as optical devices which may take advantage of such photochromism. The photochromism is sensitive to the substituents on the molecule as well as the environment in which the conversion takes place. This work was part of an ongoing study of the fundamental nature of this photochromism undertaken to provide a scientific basis which may ultimately lead to the ability to tailor the properties of the material - color, temporal stability, etc. - to a specific application.

To begin to explore the process by which the spiropyran-merocyanine interconversion takes place, semiempirical molecular orbital calculations were used to progressively stretch the carbon-oxygen bond. Of particular interest was whether one of the four stable forms for the merocyanine might be preferred by virtue of occurring naturally along the reaction pathway traced out by this bond lengthening. Semiempirical molecular orbital calculations were carried out using the AM1 hamiltonian in MOPAC 5.0. Default convergence criteria were used. Calculations began with the fully minimized, lowest energy structure for spiropyran.

To achieve a stable isomeric structure, it was necessary to perturb the structures from those along the bond-breaking pathway identified by the molecular orbital calculations. This was accomplished by minimizing the energy of the molecule using the Tripos molecular mechanics force field and SYBYL. To make this step as consistent as possible with the MO calculations, the geometry of the carbon atom and the bond orders of the three central bonds in merocyanine were modified. The carbon was changed from tetrahedral sp^3 to planar sp^2 and the three central bonds were defined as double, single, and double, respectively. Minimization was carried out to convergence, and then the resultant structure was again minimized using MOPAC.

The results show that none of the four possible isomeric forms of merocyanine occurs simply along this reaction path. Instead, the molecule maintains the orthogonality of its ring systems. Relaxation processes allow the formation of either the trans-cis or the cis-trans isomer, depending on the initial distance between the spiro carbon and the pyran oxygen atom. Both kinetic and thermodynamic factors seem to favor formation of the trans-cis isomer.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 188, Computational Modeling of a Spiropyran Chromophore.

TASK: 222

TASK TITLE: Alternative Materials Design Via Multi-Physics Analysis

TASK OBJECTIVE: Demonstrate the capability to evaluate a multi-material design via multi-physics analysis.

SCIENTIST: Bruce Webster, Ph.D., Webster Associates

DESCRIPTION OF WORK:

A study of alternative materials (composites) for automobile axle shafts and the development of a differential gear sizing using AML™ were performed under this effort. AML™ provides a dynamic object oriented modeling environment which provides the means to develop a customized user interface that incorporates graphics, sophisticated geometric modeling, parametric/feature-based modeling, and knowledge-based engineering. Such an environment is ideally suited to automate upstream design applications through sophisticated finite element analysis including automated mesh generation and scientific visualization.

Multiphysics analysis of different alternative axle shaft designs using composite materials was performed using finite element analyses as well as standard strength of materials considerations. The development of a differential gear sizing program using AML™ was performed to demonstrate how

actual torque levels needed in sizing andalternate material axle shaft are calculated in the design process of automobile differentials. Both the axle analysis and the differential design efforts were successful and illustrates that AML™ can provide the architecture framework to develop customized engineering applications easily.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 177, Multiphysics Composite Axle Shaft and Differential Gear Sizing Design and Analysis.

TASK: 223

TASK TITLE: Gallium Arsenide - Indium Arsenide Superlattices

TASK OBJECTIVE: Evaluate quality of strained layer quantum wells and superlattices grown by molecular beam epitaxy composed of GaSb and InAs. Determine the effect of growth conditions on the electrical and optical properties.

SCIENTIST: Mohamed Ahoujja, University of Cincinnati

DESCRIPTION OF WORK:

Conventional Hall effect measurements are typically used to determine the electrical transport properties of semiconductors. These properties are the temperature dependence of the carrier concentration, resistivity, and carrier mobility. In addition to Hall effect measurements, the so-called Shubnikov-de Haas (SdH) and quantum Hall effect measurements are also used. These effects occur in very high magnetic fields, where the motion of electrons is such as to form full orbits around the magnetic field. The quantization of these orbits and the conductivity in this magnetic field regime provide valuable techniques to study various properties of the semiconductors.

In this research, electronic transport properties of three different categories of semiconductor samples were investigated using conventional Hall and Shubnikov-de Hass effects. These are: (1) heterostructures, (2) single and double quantum wells, and (3) bulk materials. The samples examined were InGaP/GaAs single quantum well and double quantum wells, δ-doped AlInAs/GaInAs heterostructures, and OMK GaSb, JK GaSb, OMK InAs, and OMK InSb bulk materials.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 178, A Study of Electronic Transport Properties of Semiconductor Heterostructures and Quantum Wells using Conventional Hall Effect and Shubnikov-de Haas Measurements.

TASK: 224

TASK TITLE: Synthesis of Monomers and Polymers Containing Aromatic Heterocyclic Functional Groups for NLO Evaluation

TASK OBJECTIVE: The synthesis of highly pure, second-order NLO active monomers for incorporation into thermoplastic aromatic heterocyclic polymers.

SCIENTIST: Ram Kannan, Ph.D.

DESCRIPTION OF WORK:

A dicarboxylic acid monomer, 2,6-(3-carboxy phenyl)-4-(2-thienyl)-ethenyl pyridine, incorporating an all aromatic heterocyclic second order NLO chromophore, was synthesized in a multistep process from thiophene carboxaldehyde and bromo acetophenone, and then successfully converted to a bis-benzoxazole derivative, a model compound for polybenzoxazoles.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 156, Synthesis of 2,6-(Bis-3'-Carboxy)-Phenyl-4-(2-Thienyl)-Ethenyl Pyridine - A Monomer Incorporation a Second Order NLO Chromophore.

TASK: 225

TASK TITLE: Investigation of Advanced Metallic Composites

TASK OBJECTIVE: To develop an understanding of the relationships between the composition and microstructure of matrices, the bonding at fiber/matrix interfaces, and composite properties in advanced composites.

SCIENTIST: Lingang Xiao (Leon L. Shaw), Ph.D.

DESCRIPTION OF WORK:

An interfacial region (i.e., an interface coating or a reaction product) between the fiber and matrix is known to exist in most metal-matrix composites. Since the load transfer between the fiber and matrix depends on the properties and conditions of this interfacial region, the mechanical behavior of the composite is strongly affected by its characteristics.

In this study, finite element analysis was used to investigate the effects of the interfacial region on the distribution of residual thermal stresses, characteristics of interfacial crack initiation and propagation, and mechanical response of the composites under transverse tensile loading. The matrix material was taken to be Ti-6Al-4V and behaves elasto-plastically, while the SiC-fiber was assumed to be elastic. The

interface was treated as a thin layer with a finite thickness between the fiber and matrix. The effects of the interfacial region with independent thermal and mechanical properties for Ti-6Al-4V/SiC composites with a graded carbon coating, with a Y_2O_3 coating, and without a coating were evaluated. For comparison, an infinitely strong bond at the interface was also assessed.

The results indicated that the properties of the interfacial region affect the stress distribution, the interfacial crack initiation and propagation, and the mechanical response of the composites. Based on results, the thermal and mechanical properties of the coating for improved performance of the composites under transverse loading conditions were proposed.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 186, Effects of Interfacial Region on the Transverse Behavior of Metal-Matrix Composites.

TASK: 226

TASK TITLE: Axiomatic Design of Aluminum Extrusion Processes

TASK OBJECTIVE: To evaluate the feasibility of Suh's axiomatic approach to design aluminum extrusion processes.

SCIENTIST: William M. Mullins, D.Sc.

DESCRIPTION OF WORK:

The application of axiomatic and other model-based design methods to the design of aluminum extrusion processes is limited by the availability and applicability of microstructural evolution models for materials. This study investigated the current understanding of most of the microstructural evolution models being currently considered and critically assessed model applicability and limitations. In addition, numerical models were constructed to demonstrate some of the more obscure details of the analytical models that are of considerable importance to the design of processing operations.

The study was initiated by examining the Yada models for grain growth, static, and dynamic recrystallization in austenite. It also examined and reanalyzed the models of Guillard for dynamic spheroidization. The models were dissected with the standard physical models for the processes involved and semi-epirical relationships for the different parameters in the models were derived. Weaknesses and/or discrepancies in the models were pointed out and alternative methods were suggested. A simple numerical model was proposed for the processes, and some numerical results were shown for austenite and a γ-Ti alloy.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 181, Microstructural Evolution for Axiomatic Design.

TASK: 227

TASK TITLE: Signal Pattern Analyses of Metal Forming Processes

TASK OBJECTIVE: To establish an analysis technique for real-time identification of material defect formations, metal flow instabilities, and forming equipment malfunctions.

SCIENTIST: John Erdei, Ph.D.

DESCRIPTION OF WORK:

Acoustic emission (AE) is a common NDE technique. A transducer (or microphone), attached to the sample, detects the elastic (acoustic) energy emitted by the sample. The transducer typically has a center frequency of 80-200kHz and is relatively insensitive in the audible range. This makes the test fairly insensitive to ambient mechanical noise such as motors and hydraulic systems. The usual test procedure records the number of detected, high-frequency acoustic "events"vs. time. Correlation of the AE data and the test conditions is done *post mortum*.

In this project, physical models for acoustic emission (AE) were introduced and expressions were derived to predict AE activity from such parameters as stress, strain, and strain-rate. These models were then incorporated into a visco-plastic finite-element simulation program. Simulation results were presented for upsetting operations on a typical C-Mn type steel for various friction and die geometry conditions. The results compared well to literature results and demonstrated that AE may be useful as a quantitative tool in verifying a metal forming process design.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 198, Simulation of Acoustic Emission for Forging of C-Mn Steel and Volume 199, Signal Pattern Analysis of Metal Forming Processes.

TASK: 228

TASK TITLE: Particle Size Effects on Continuum Yield Functions

TASK OBJECTIVE: To establish the effect of particle size and size distribution on the yield function of intermetallic alloy powders.

SCIENTIST: Shivaramaiah Shamasundar, Ph.D.

DESCRIPTION OF WORK:

In this analysis, a hybrid continuum-microstructural yield function formulation was developed. The yield function uses a 'stress intensification factor' (a scalar variable) to scale the yield stress of a fully dense material to that of the partially dense compact of a given relative density. A simple experimental technique based on microhardness measurements of partially dense compacts was demonstrated to be adequate to derive the stress intensification factor. The yield function was applied to model a variety of consolidation processes such as sintering, sinter forging, die-pressing, and hot isostatic pressing.

In the first part of the task, a numerical exercise of microhardness test was conducted to give further credence to the 'relatve microhardness ' based stress intensification factor and the hybrid model. Good correlations were observed with the simulation of room temperature microhardness indentation tests for various conditions of speed, load, and strain rate sensitivity factor.

In the second part, the model was applied to the compression of porous rings to generate interface friction calibration curves. Using the simulation results, an approximate semi-empirical model was proposed to relate the effect of interface friction to the porosity of the material.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 181, Modeling the Powder Consolidation Processing.

TASK: 229

TASK TITLE: Analysis and Characterization of Liquid Crystalline Materials

TASK OBJECTIVE: To develop thermotropic liquid crystalline materials based on steroidal architectures. To analyze X-ray diffraction data taken from rotating anode generators and real-time information obtained from a synchrotron source.

SCIENTIST: Colin M. McHugh, B.S.

DESCRIPTION OF WORK:

A base-catalyzed and acid chloride reaction scheme were employed to make three liquid crystalline mesogens. The experimental conditions, product identification, purification, and thermal transitions were described in detail. Three liquid crystalline mesogens were attached to a penta- or tetramethylhydrosiloxane core via hydrosilation chemistry. Representative FT-IR, NMR, DSC, and POM pictures showing mesophase textures were provided. Preliminary wave guiding experiments, on thin films consisting of a commercially available liquid crystal system (Wacker Blue), were performed in order to determine the "mode" of wave guiding through the medium. Film thickness, determined by a stylus probe, was related to sample preparation.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 166, Analysis and Characterization of Liquid Crystalline Materials.

TASK: 230

TASK TITLE: Application of Rapid Foundry Tooling System

TASK OBJECTIVE: Demonstrate the capability of an integrated product-process design system for sand casting patterns.

SCIENTIST: Ron Cass, AI WARE

DESCRIPTION OF WORK:

The purpose of this project was to examine the use of the Rapid Foundry Tooling System (RFTS) for the design of a stereolithography part to be used as the pattern for a commercial sand casting. RFTS is a software system developed by AI WARE, supported by the Materials Directorate at Wright-Patterson AFB, which enables the rapid design of patterns for sand-castings which are to be fabricated via stereolithography. The goal of the effort was to evaluate the effectiveness of RFTS in a commercial foundry setting, and to accomplish technology transfer from AI WARE, Inc. and the Air Force to the commercial sector.

The participants in this effort were AI WARE Incorporated of Cleveland, Ohio, who operated RFTS, Columbiana Foundry, a commercial foundry located in Youngstown, Ohio, who provided the design to be created in RFTS and evaluation of the fabricated pattern, and the Technology Development Center (TDC) at Youngstown State University, who provided support services and facilitated the technology transfer between the parties. Columbiana Foundry presented AI WARE with the casting print for a typical part manufactured by them. AI WARE quickly created a design of the part in RFTS and generated a stereolithography model of the part. This model was then forwarded to stereolithography shops at both Wright-Patterson AFB and Kelly AFB, where the pattern was fabricated. Columbiana Foundry then evaluated the effectiveness of these parts as casting patterns.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 200, Application of Rapid Foundry Tooling System.

TASK: 231

TASK TITLE: Technology Transfer of Rapid Foundry Tooling System

TASK OBJECTIVE: Generate and consult on design problems to exemplify the capability of an

integrated product-process design system for sand casting patterns.

SCIENTIST: Wilbur C. Dyer, YSU-Technology Development Corporation (TDC)

DESCRIPTION OF WORK:

The purpose of this project was to collaborate with an automated design system developer to generate one or more example designs of a structural casting. Consult with developer to enable automatic generation of patterns, involving parting line, rigging, cores and match plate, which can be fabricated using stereolithography. The sand casting pattern design effort was to be documented for comparison of design time, pattern generation time and stereolithography file generation time with conventional practice.

Two patterns were received at Columbiana Foundry that were produced by stereolithography using the computer program from the A.I. Ware Company. Although neither pattern was in useable condition the process showed merit and should be further investigated. With improved techniques in the stereolithography process this could be an advantageous tool in reducing lead time required to produce pattern equipment.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 201, Technology Transfer of Rapid Foundry Tooling System.

TASK: 232

TASK TITLE: MBE Growth Model

TASK OBJECTIVE: Continuation of development of predictive capability and verification for MBE growth parameters.

SCIENTIST: Donald R. Thomas, M.S.

DESCRIPTION OF WORK:

The molecular beam epitaxy (MBE) growth chambers used in Wright Laboratory's MLBM work group are controlled and monitored by a computer control process system developed by Wright Laboratory's Materials Process Design Group (MLIM). This control process system, called the Intelligent Process Module (IPM), generates huge files containing the data collected while controlling and monitoring the MBE growth chambers. Reducing this data to a manageable size and modeling the MBE growth process were the two main objectives of this research project.

In order to develop a predictive MBE growth model, data collected during the MBE film growth

must be extracted from its original data files and transformed into a usable format. A commercial neural network computer application is being used to develop the growth models, so the MBE growth data must be converted to a format readable by the neural network application. Computer software was developed to reduce the original data files to a manageable size, and then to interactively search the reduced files for data matching user-defined criteria. Additionally, this software allows the user to add data to the data files which describes *ex-situ* measurements made on the MBE grown films.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 183, Development of Molecular Beam Epitaxy Growth Modeling Software.

TASK: 233

TASK TITLE: Aromatic-Heterocyclic Oligomers for Electronic Conductivity

TASK OBJECTIVE: The synthesis and characterization of novel aromatic-heterocyclic oligomers for evaluation as electronic conductors.

SCIENTIST: Girish S. Patil, Ph.D.

DESCRIPTION OF WORK:

The making of highly conducting polymers was investigated using a novel approach - Symmetric Ground State Systems (SGSS). This project was aimed at synthesizing novel structures that would satisfy the requirements of SGSS. The project involved the choice of target molecules, synthetic strategy employed for making them and identifying and resolving problems encountered in the process.

A major objective of the research was the improvement of compressive strength and other mechanical properties of rigid-rod polymers. In this regard, three-dimensional rigid-rod polymers which have rigid PBO chains attached to an adamantyl core were investigated. It is expected that the three-dimensional rigid-rod polymers will significantly enhance the mechanical properties in directions other than the main chain axis.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 234,High Performance Polymers, Part I: Conducting Polymers: Symmetric Ground State Systems Approach Part II: Multi-Dimensional Rigid Rod Polymers.

TASK: 234

TASK TITLE: Synthesis of Heterocyclic Monomers, Model Compounds, and Polymers with Increased 2-Photon Absorption Cross Sections

TASK OBJECTIVE: The synthesis of highly pure, heterocyclic model compounds and polymers with increased 2-photon resonant nonlinear optical response.

SCIENTIST: Ram Kannan, Ph.D.

DESCRIPTION OF WORK:

Organic materials for non-linear optics are characterized by the presence of extended conjugation; while the third order materials are symmetrical, the second order ones have non-symmetrical electron densities at the various centers. Oligomeric poly- phenylenes are emerging as an important sub-class of third order materials, and there is a need to look at the NLO properties of polyphenylenes terminating in a heterocycle.

In this research, propargylamine, which is needed to make quinoxaline terminated polyphenylenes, and bithiophene, which is designed as a material for optical switching purposes, were synthesized. The synthesis and chemical characterization of a second-order NLO monomer and a naphthalene bridged second order chromophore were also accomplished.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 180,Second and Third Order NLO Materials Derived from Heterocycles.

TASK: 235

TASK TITLE: Polymer-Based Process Design of Shafts

TASK OBJECTIVE: To investigate the issues surrounding the alternative design of a component manufactured with a polymer-based composite in lieu of a steel material.

SCIENTIST: Russell E. Duttweiler, B.S.

DESCRIPTION OF WORK:

The primary focus of this task was to investigate the issues surrounding the alternative design of a component manufactured with a polymer-based composite in lieu of a steel material. The purpose was to facilitate a reduction in the weight of the object shaft without any loss in strength. An assessment was made of the current manufacturing process which involves steel components to evaluate if the same or similar tooling and preform shapes could be utilized for a polymer-based composite material. An alternative processing route with fewer stages and reduced processing costs was also explored.

Two prototype composite shafts were constructed. These shafts were of a three-piece design which incorporated two steel spline end pieces bonded to an epoxy-matrix-graphite-filament-wound torque tube. Two shafts of this design were constructed and one was torque tested and failed at 75% below the desired value. An improved two-piece shaft design was then made. Technical promise for success of this shaft design is quite high.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 202, Polymer-Based Process Design of Shafts.

TASK: 236

TASK TITLE: Modeling Electronic and Optical Materials Systems

TASK OBJECTIVE: To develop mathematical models that describe the response of electronic and optical materials to external stimuli.

SCIENTIST: John Hurley, Ph.D.

DESCRIPTION OF WORK:

Recent AFM images clearly represent the high temperature superconductor grains as "oblong-like", almost cylindrical structures. Many of the present models characterize the grains as spherical bodies. In this study, we looked at the magnetic fields and currents of the superconducting spherical and cylindrical grains to evaluate the accuracy of the models. This project focused exclusively on YBa_2 Cu_3 O_7 thin film materials grown on $LaAlO_3$ structures. In addition, it has been proposed that the current conduction paths for these materials resides primarily below the interfaces that support the grains and outgrowths. We also looked at the presence of other paths, particularly above the interfaces to determine possible current contributions. It was found that under certain conditions, the "ideal" superconducting sphere magnetic fields and currents approximate reasonably well the current and field values for the "ideal" superconducting cylinder. In addition, it was determined that the azimuthal component of the current for the superconducting cylinder produces a linear current of magnitude, M_0 on the side wall of the cylinder that must be considered in determining overall contributions to current conduction.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 245, Modeling Electronic and Optical Materials Part II: Modeling the Conduction Paths of Grains and the Effect of Geometry on the Magnitude of the Current and Magnetic Fields of Thin Film High Temperature Superconducting Structures.

TASK: 237

TASK TITLE: Material Behavior Modeling of TiAl

TASK OBJECTIVE: To study and model hot deformation behavior of a TiAl alloy.

SCIENTIST: Isaac Weiss, Ph.D.

DESCRIPTION OF WORK:

The deformation of the processing window for gamma titanium aluminide requires an in-depth understanding of the mechanisms controlling the hot deformation of these alloys. In particular the effect of deformation temperature and strain rates, on flow stress and the critical strain needed for microstructure refinement associated with the occurrence of dynamic recrystallization are important.

Material with an equiaxed microstructure was deformed at temperatures of 1125°C, 1150°C, and 1175°C and at strain rates of 10^{-3}, 3 x 10^{-3}, and $10^{-2}s^{-1}$ to a total strain of 1.0. These tests were carried out in order to evaluate the effect of deformation temperature and strain rate on microstructure refinement. Samples with a lamellar microstructure were deformed at temperature of 1100°C and at a strain rate of $10^{-3}s^{-1}$ to final strains of 0.5, 0.7, and 1.2 to evaluate the effect of plastic strain on dynamic recrystallization and the resulting microstructure. Strain rate modulation (strain rate change) tests were carried out on samples with lamellar microstructure to assess dynamic effects of strain rate change on microstructure evolution. Tests were conducted at temperature of 1100°C while increasing the strain rate from $10^{-2}s^{-1}$ to $10^{-3}s^{-1}$ and then to $10^{-4}s^{-1}$ at strain increments of 0.3, and while decreasing the strain rate from $10^{-2}s^{-1}$ to $10^{-3}s^{-1}$ to $10^{-4}s^{-1}$ at the same strain increment of 0.3.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 236, High Temperature Deformation and Recrystallization of Gamma Titanium Aluminide.

TASK: 238

TASK TITLE: Acoustical Analysis of Metal Forming Processes

TASK OBJECTIVE: To conduct acoustical analysis of metal forging process.

SCIENTIST: Bayard S. Holmes, Ph.D., Centric Engineering Systems, Inc.

DESCRIPTION OF WORK:

The objective of this project was to demonstrate how acoustic emissions (AE) from a metal forming process might be used to monitor and eventually control that process. The approach used was to evaluate a previously postulated phenomenological model of AE using the results from a nonlinear

stress analysis of the forming process. The postulated relationship links the acoustic emission to the distribution and rate of plastic strain to predict the energy of the AE "signature" characteristic of the process. This AE model was evaluated for a punch stretching process and showed good agreement with the experimentally recorded signal.

This effort represents a qualitative and quantitative improvement upon earlier efforts to evaluate this AE model in closed form using simplifying assumptions to describe the mechanical behavior. This study illustrates that finite element simulation can successfully replicate, and provide insight into, the AE signal measured for a simple, but nontrivial metal forming operation.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 203, Acoustical Analysis of Metal Forming Processes.

TASK: 239

TASK TITLE: Processing/Structure/Property Relationships in Foams Derived from Mesogenic Carbon Precursors

TASK OBJECTIVE: To examine the properties of graphitic microcellular foams produced from liquid carbon precursors.

SCIENTIST: Debashis Dutta, Wright Materials Research

DESCRIPTION OF WORK:

This project continued the research on graphitic microcellular foams. It has been predicted that foams with interconnected strut networks of aligned graphite crystallites will have attractive mechanical properties. It was previously demonstrated that graphitic foams with the desired morphology can be processed with homogeneous nucleation techniques. This effort studied the effect of processing parameters like cooling rate, sample thickness and mold surface characteristics on foam morphology. These studies are expected to improve the foaming process. The work included efforts to process foams from hydrogenated coal tar pitch, which can be foamed at a lower temperature, and to melt mix the pitch and polymers with carbon fibers. The main research activity was directed towards designing/fabricating a larger foaming device. This will enable the processing of samples for mechanical tests. This device was nearly ready for operation by task end.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 235, Processing and Characterization of Graphitic Microcellular Foams from Anistropic Pitch.

TASK: 240

TASK TITLE: Design of New Materials

TASK OBJECTIVE: Optimization for Polymers, Surfaces, and Biomolecules: The evaluation of the global energy minimum or most stable conformation of large molecular structures, particularly biopolymers being developed in the materials laboratory in-house research programs.

SCIENTIST: Zhiqiang Wang, Ph.D.

DESCRIPTION OF WORK:

As C_{60} and its derivatives exhibit increasingly interesting materials properties, such as superconductivity and non-linear optical response, a great deal of attention has also been received on the smallest carbon cluster which can form the closed fullerene structure, C_{20}. This interest in C_{20} is due to not only its relevance to the understanding of C_{60}, but also its possibility as an intermediate in the formation of C_{60} and larger fullerene. As to the most stable structure of C_{20}, experiments show evidence for it to be a monocyclic ring. Theoretical study has focused on four forms: linear chain, monocyclic ring, corannulene-like bowl, and fullerene-like cage.

The gradient-corrected LDA (BLYP) and CCSD(T) are considered to be the most accurate approaches among others in the *ab initio* study of C_{20} structures. Conflict between them suggests the need for more accurate studies. One shortcoming of these applications is that they are both single point calculations.

In this study, full geometry optimizations were performed for three isomers of C_{20}, ring, bowl(corannulene-like), and cage(fullerene-like), using both local density functional approximation (LDA) and gradient-corrected density functional theory (BLYP). The gradient-corrected DFT results were qualitatively consistent with previous single point calculations based on Hartree-Fock geometries, which is in favor of ring geometry, while local density functional predicts a reverse order of energy, favoring cage geometry.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 204, Full Geometry Optimization of C_{20} Isomers Using Density Functional Theory.

TASK: 241

TASK TITLE: Design of New Materials

TASK OBJECTIVE: Optimization for Polymers, Surfaces, and Biomolecules: The evaluation of the global energy minimum or most stable conformation of large molecular structures, particularly biopolymers being developed in the materials

laboratory in-house research programs. This effort will enable the design of polypeptides and liquid crystalline materials for the development of new ordered 3-D networks of chromophore-substituted bio/macromolecules with controlled properties.

SCIENTIST: Paul N. Day, Ph.D.

DESCRIPTION OF WORK:

Solvation effects are considered to be important in the properties of a number of materials of interest for use in optical limiting devices. Since the material will be in some kind of condensed medium, either a solution or possibly a thin film, when it is operating as an optical limiting device, the effects of neighboring molecules on the molecule of interest must be considered in order to produce a realistic simulation of a molecule's properties. The effective fragment method is a novel approach to including solvent effects in ab initio calculations. Effective fragment calculations can effectively reproduce full ab initio calculations on aqueous microsolvated pyran and nitrochromene molecules. The effective fragment method has been used to simulate up to three water molecules interacting with nitrochromene and its open ring isomer, and can be used to simulate the entire first solvation shell. In order to simulate solvation effects on fullerenes in nonpolar solvents, the self-consistent reaction field method is recommended.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 205, The Modeling of Solvation Effects on Nonlinear Optical Materials by the Effective Fragment Potential Method: Quantum Chemistry Calculations in the Gas-Phase and in Solution.

TASK: 242

TASK TITLE: Damage Evolution in Ceramic Matrix Composites

TASK OBJECTIVE: To evaluate the development and propagation of damage in composite materials under thermal and mechanical cycling.

SCIENTIST: Shin S. Lee, Ph.D.

DESCRIPTION OF WORK:

The degradation of high temperature mechanical performance in several CMC systems was studied. It was found that mechanical performance of CMCs was greatly influenced by the high temperature embrittlement which caused catastrophic crack propagation in structures. It was concluded that the loss of toughening mechanisms due to high temperature environments was a common phenomenon that related to the reduction of high temperature mechanical performance and durability in CMC systems.

Thus, in order to improve the high temperature performance of CMCs, it is necessary to maintain both the thermal stability of materials integrates and toughening mechanisms in CMCs. Following the above concept different protective methods were developed to protect the load carrying fibers from aggressive environments and maintain a functional fiber/matrix interface which is an essential element for toughening in CMCs. Three of the four systems investigated in this effort (Nicalon/SiNC, Nicalon/C, Nicalon/Al_2O_3) were designed and fabricated following this concept. However, as observed and reported, the high temperature embrittlement which caused the degradation of mechanical performance of the CMC systems was still a common problem in these systems. Similar life limiting issues of high temperature performance existed in the Nicalon fiber reinforced CMCs with different surface, matrix fillers, and fabrication techniques.

A newly developed material system, oxide/oxide (Nextel 610/AS), without any engineered interface and coating showed very promising potential for high temperature engineering applications and the highest 1000°C fatigue limit in CMCs so far; however, a relatively low creep resistance was observed in this oxide/oxide system at temperatures above 1000°C.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 237, Degradation of High Temperature Mechanical Performance of 2-D[W] Fiber Reinforced Ceramic Matrix Composites.

TASK: 243

TASK TITLE: Research on Oxide Fiber Preform Coatings

TASK OBJECTIVE: The objective of this work is to devise viable approaches to the application of a variety of solution based fiber coatings to entire preforms after weaving, rather than to fiber tows before weaving.

SCIENTIST: Michael K. Cinibulk, Ph.D.

DESCRIPTION OF WORK:

The objective of this research was to investigate the feasibility of using cleavable oxides as a fiber-matrix interphase in alumina-based composites, to achieve enhanced toughness and oxidation resistance. The processing of such an interphase was shown previously to produce a highly crystallographically oriented interphase.

Work during this project involved the examination of stresses developing during debonding and sliding of sapphire-reinforced alumina composites and coating of sapphire substrates, testing them in flexure to determine steady-state strain energy release rates (G_{ss}), and characterizing the interphase microstructure and fracture surfaces. A hibonite interphase with near perfect texture, with basal planes parallel to the interface, was obtained between single-crystal alumina substrates. Steady-state strain

energy release rates (G_{ss}) of $2.2\,J/m^2$ were measured. Interphases containing a reaction of misoriented grains had a higher G_{ss} of $2.8\,J/m^2$. Crack propagation occurred by cleavage of hibonite basal planes. Delamination of hibonite from sapphire did not occur, rather, the hibonite interphase failed by cleavage of hibonite basal planes (transgranular and intragranular fracture).

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 190, Continuing Study on the Determination of Mechanical Behavior of a Cleavable Oxide Interphase.

TASK: 244

TASK TITLE: Analysis of Metal and Ceramic Matrix Composites

TASK OBJECTIVE: To develop and apply analytical tools to predict the response of high temperature metal and ceramic matrix composites.

SCIENTIST: Efthymios S. Folias, Ph.D.

DESCRIPTION OF WORK:

Residual stresses due to curing and thermal stresses due to differences between the thermal expansion coefficients of the matrix and fiber may have a major effect on the micro-stresses within a composite material system and must be added to the stresses induced by the external mechanical loads. Such micro-stresses are often sufficient to produce micro-cracking even in the absence of external loads, example during the cooling process. Furthermore, if the material system is thermally fatigued, these residual stresses may cause some of the existing micro-cracks to grow and coalesce and thus form the presence of larger cracks.

Thus, if rational designs in the use of fiber-reinforced metal matrix composites are to be made, their performance under static, dynamic, and thermally fatigued loads need to be predictable. The first step towards this goal is the realization that the ultimate failure, as well as many other aspects of the composite behavior, are the result of growth and accumulation of microdamage to the fibers, matrix and their interfaces. Thus, it appears that any generally successful model of performance and failure must incorporate the effects of this damage in some way. This research addressed the form of such damage due to the residual stresses developed as a result of the thermal expansion mismatch between the fibers and the matrix.

A systematic, 3D, micromechanics approach was used in which the fibers of a composite material system were modeled as cylindrical inclusions that are embedded into a matrix plate. The analytical model was then used to predict the residual stresses due to a thermal expansion mismatch, e.g. during a cooling process. The model provides better understanding of how the residual stresses are developed and how they can be controlled particularly in relation to ceramics where there is no ductility to

accommodate any plastic deformation.

The analysis reveals the dependence of the residual stress field on the fiber volume fraction ratio, identifies the critical locations where a crack is most likely to initiate and subsequently propagate, recovers the interface shear stress profile and provides important information and guidance to material designers for the pre-selection of fiber and matrix materials in order to alleviate some of the residual stresses. The theoretical model is applicable to ceramic and metal/matrix composite systems.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 215, Predicting Crack Initiation in Composite Material Systems Due to a Thermal Expansion Mismatch.

TASK: 245

TASK TITLE: Can Shielding in HIP Consolidation of Porous Media

TASK OBJECTIVE: To establish the effects of can shielding on densification of porous metals.

SCIENTIST: Shivaramaiah Shamasundar, Ph.D.

DESCRIPTION OF WORK:

Hot Isostatic Pressing operation was modeled using a yield function and associated flow rule. The effect of aspect ratio, encapsulating material property, encapsulation thickness, interface friction on the densification was analyzed using a finite element simulation procedure. Alpha-two titanium aluminide was used as a model material for experimental modeling. The results were discussed in terms of product integrity, retention of net shape and optimization of process parameters.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 206, A Study of the Effect of Encapsulation Shielding in Hot Isostatic Pressing Operation.

TASK: 246

TASK TITLE: Morphology of Hybrid NLO Materials

TASK OBJECTIVE: To advance knowledge of morphology of structured, hybrid organic nonlinear optical materials being examined in the Materials Directorate in-house research programs.

SCIENTIST: Hongqin Shi, M.S.

DESCRIPTION OF WORK:

The morphological and rheological properties of cyclohexane-based liquid crystals were investigated by x-ray diffraction and dynamic moduli measurement. Like cyclosiloxane-based liquid crystals, mesogens in cyclohexane-based liquid crystals align themselves along the fiber drawing direction. However, in contrast to cyclosiloxane-based liquid crystals, there is no significant one-dimensional lattice structure existing in cyclohexane-based liquid crystals. The stereochemical features (*cis* vs *trans*) of cyclohexane ring were found to have no noticeable effect on mesophase structure. All three viscoelastic relaxation regions typical of a monodispersed flexible linear polymer chain were observed for a cyclohexane-based liquid crystal sample, 3CT4PTP. However, the time-temperature principle was not followed by 3CT4PTP. The drastic decrease of zero-shear viscosity with increasing temperature in 3CT4PTP is expected to facilitate device fabrication processes for practical applications.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 207, Cyclohexane-based vs Cyclosiloxane-based Liquid Crystals: X-ray Diffraction Results and Rheological Behavior.

TASK: 247

TASK TITLE: MBE Growth Model

TASK OBJECTIVE: Continuation of development of predictive capability and verification for MBE growth parameters.

SCIENTIST: Donald R. Thomas, Ph.D.

DESCRIPTION OF WORK:

The molecular beam epitaxy (MBE) growth chambers used in Wright Laboratory's MLBM work group are controlled and monitored by a computer control process system developed by Wright Laboratory's Materials Process Design Group (MLIM). This control process system, called InfoScribe®, generates huge files containing the data collected while controlling and monitoring the MBE growth chambers.

In order to develop a predictive Molecular Beam Epitaxy (MBE) growth model, data collected during the MBE film growth must be extracted from its original data files and transformed into a useable format. Computer software was developed to reduce the original data files to a manageable size, and then to interactively search the reduced files for data matching user-defined criteria. The matching data can then be written to a character-delimited ASCII text file. Additionally, this software allows the user to add data to the data files which describes *ex-situ* measurements made on the MBE grown films.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 208, Development of Molecular Beam Epitaxy Growth Modeling Software.

TASK: 248

TASK TITLE: Evaluation of Fatigue Damage in Titanium Aluminides and Composites

TASK OBJECTIVE: To evaluate the role of environment on damage modes in titanium aluminides and titanium aluminide composites during fatigue.

SCIENTIST: Andrew H. Rosenberger, Ph.D.

DESCRIPTION OF WORK:

This project examined the post creep ductility in the Ti-22Al-23Nb (a/o), orthorhombic titanium aluminide alloy. Dogboned specimens of 4 ply neat material were crept at 650°C/ 172 MPa and 760°C / 69 MPa to creep strains of 0.2 and 0.4 % in both air and vacuum (10^{-6} torr) environments. Following these creep exposures, the residual, room temperature tensile strength and ductility were measured. Stress-free isothermal exposures were also performed in air at times and temperatures identical to the air creep exposures to determine the influence of the prior creep strain on ductility. The ductility reduction found after creep in air was determined to be solely an environmental phenomena - based on the results of stress-free exposures and fractographic examinations of the specimens.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 209, Effect of Environment on the Post-Creep Ductility of an Orthorhombic Titanium Aluminide.

TASK: 249

TASK TITLE: Innovative Composites Research

TASK OBJECTIVE: To provide innovative concepts, which will enable the synthesis and processing of lightweight, composite structural and thermal management materials for dual-use applications in air and space weapon systems and commercial products, particularly as enabling materials for thermal energy conversion processes.

SCIENTIST: Joseph W. Hager, Ph.D.

DESCRIPTION OF WORK:

This task was performed as a part of the in-house composites research program within WUD 45 of the Wright Laboratory Materials Directorate. This part of the WUD 45 research program is directed at the design and synthesis of novel composite microstructures, composite environmental durability in severe environments, and low cost composite processing. Specific tasks address the synthesis and characterization of novel forms of carbon, such as graphitic foam; vapor-grown carbon fiber and composites derived therefrom; and the protection of carbon in hot oxidizing environments with gas layer protection. To address complexity and cost of manufacture it is proposed to replace the *disconnected* carbon fiber reinforcement networks of current composites with reticulated graphitic foams. Such *interconnected* networks of graphitic reinforcing micro-struts, each possessing a morphology similar to that of commercial carbon fiber, have been blown from anisotropic pitch and have been subsequently stabilized, carbonized, and graphitized.

A previous report, designated as Volume 214 of this series, described progress in graphitic carbon foam research made during the period November 1993 through October 1994. To protect hot carbon surfaces from oxidation mass loss, it is proposed to bathe the surface with gases with which the carbon is in thermodynamic equilibrium. Having previously studied this protection concept analytically, construction of a flow reactor apparatus was undertaken to experimentally confirm the viability of the concept.

This task continued the investigation of gas layer protection. Gas layer protection is based on the concept of artificially maintaining an equilibrium gaseous environment adjacent to the surface of a hot C-C structural component otherwise exposed to oxidizing conditions. Based on analysis of thermochemical equilibrium compositions in the presence of hydrocarbon combustion, it was hypothesized that protection could be achieved by generating an environment rich in CO and hydrogen, and then blowing the gas either over the surface or from the inside to the outside of a porous C-C component. Two such protection concepts invoking the notion of gas layer protection were outlined. In these concepts, the oxidizing species are envisaged to react with the protective species away from the hot carbon surface.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 216, Innovative Composites Research: Design and Fabrication of a Flow Reactor to Study Gas Layer Protection of Hot Carbon in Oxidizing Environments.

TASK: 250

TASK TITLE: Wear Debris Analysis

TASK OBJECTIVE: Perform electron microscopy analysis of wear debris generated from self-lubricating aluminum metal-matrix composites (MMCs).

SCIENTIST: Somuri V. Prasad, Ph.D.

DESCRIPTION OF WORK:

Wear debris analysis is crucial to the understanding of lubrication mechanisms in self-lubricating materials. This research described the transmission electron microscopy (TEM) analysis of wear debris generated from a self-lubricating aluminum metal-matrix composite. The composite was comprised of 5 percent by volume of tungsten disulfide (WS_2) and 10 percent by volume of silicon carbide (SiC) dispersed in an aluminum alloy (Al-0.40Si-0.75Mg) matrix. Wear test on the MMC surface was performed in laboratory air with a 440C steel counterface. The debris was collected after two million cycles of sliding. Wear debris specimens for transmission electron microscopy (TEM) examination were prepared by microtoning. TEM analysis confirmed that the debris was comprised of both crystalline and amorphous phases. In the two cases that were analyzed by selected area diffraction (SAD), polycrystalline phases of alumina (Al_2O_3) and aluminum hydroxide (AlO(OH)), and a single crystal grain with a large 'd' spacing of 0.87 nm (8.7 Å) were detected.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 210, TEM Analysis of Wear Debris from Self-Lubricating Aluminum Metal-Matrix Composites (MMCs).

TASK: 251

TASK TITLE: Investigation of Advanced Metallic Composites

TASK OBJECTIVE: To develop an understanding of the relationships between the composition and microstructure of matrices, the bonding at fiber/matrix interfaces, and composite properties in advanced composites.

SCIENTIST: Lingang Xiao, Ph.D.

DESCRIPTION OF WORK:

On this project, the feasibility of utilizing an ultrasonic imaging technique to in-situ monitor and study the failure of the fiber/matrix interfaces in Ti-based metal matrix composites (MMCs) under transverse loading conditions was investigated. The technique, Ultrasonic Shear Wave Back Reflectivity (SBR), is based on the imaging of the interface using a pulse-echo mode with an ultrasonic shear wave.

SBR has been demonstrated to be much more sensitive to the interfacial conditions than ultrasonic imaging techniques using longitudinal waves and successfully used to evaluate the fiber/matrix interfacial "stiffness coefficient", matrix texture, consolidation quality and high temperature degradation of MMCs, and fiber fracture in matrices.

The current study extended this technique to investigate the interfacial fracture and deformation of titanium-based MMCs under transverse loading conditions. The samples used in this study were Ti-

6Al-4V matrix containing a single SiC (SCS-6) fiber. The purpose of using the single-fiber composites was to avoid the fiber interactions in high-volume-fiber composites. The composites were fabricated by hot pressing two Ti-6Al-4V sheets with a single SiC fiber at 930°C with 17 MPa for 2 hours. The consolidated samples were cut into dog-bone shape with the fiber axis perpendicular to the loading axis of the samples. Transverse tensile tests were carried out using a micro-straining stage. The loading was applied stepwise so that the ultrasonic scanning could be carried out under the loaded condition at different stress levels. For each ultrasonic scanning, both in-situ optical microscopic images and edge replicas of the composites were taken to keep track of the microscopic damage of the fiber/matrix interface during loading.

The change in the amplitude of the ultrasonic signals with transverse loading indicates the sensitivity of this technique to the fracture and deformation of the interfaces in the Ti-based MMCs and has been explained in terms of multiple reflection theory of ultrasonic wave. Based on the multiple reflection theory, the interfacial separation between the fiber and matrix as a function of the loading can be estimated from this technique. In conjunction with finite element modeling, this technique also has potentials to quantify the interfacial strength in-situ. Because of these characteristics, this technique can be an effective method to study the dependency of the transverse properties of MMCs on the fiber/matrix interfaces.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 211, A Novel Method of In-Situ Assessment of Fracture and Deformation of the Fiber/Matrix Interface in Metal-Matrix Composites.

TASK: 252

TASK TITLE: Experimental Nondestructive Evaluation (NDE)

TASK OBJECTIVE: Analyze material response to ultrasonic excitation, develop theoretical models, and characterize advanced materials.

SCIENTIST: Peter Nagy, Ph.D.

DESCRIPTION OF WORK:

The propagation of longitudinal guided waves in free and fluid-loaded transversely isotropic rods was investigated. The ongoing experimental efforts lead by Dr. Renee Kent to characterize fiber properties and their stress-dependence necessitated the development of a new analytical technique capable of estimating the velocity and attenuation of guided modes in free and immersed fibers. It is expected that this continuing effort will lead to the development of sophisticated analytical tools needed to study interface properties between embedded fibers and the surrounding solid matrix. An analytical solution was derived for transversely isotropic rods based on the superposition of partial waves. These results are exact, albeit numerical, solutions of the wave equation in homogeneous transversely isotropic

rods of circular cross section. The calculated results exhibit the right asymptotic behavior both at low and high frequencies as well as at the cut-off frequencies of individual modes. Numerical results indicate that there is a mode switching between the two lowest order modes when the rod is loaded by a relatively high density fluid. The attenuation and, to a lesser degree, the velocity of the axial guided wave in a thin fiber was shown to be strongly affected by leakage into the surrounding medium. For an embedded fiber these results indicate that the leakage is also strongly affected by the interface stiffness which therefore can be assessed from the propagation parameters of the leaky guided wave along the fiber.

A special experimental technique was developed to measure Poisson's ratio in SCS fibers from the dispersive phase velocity of the lowest order axisymmetric guided mode in an immersed fiber. The preliminary experiments clearly demonstrated the feasibility of the suggested technique, however the measured Poisson ratio was around 0.25,substantially higher than expected. Further experimental and analytical efforts are needed to resolve this discrepancy between the ultrasonic data and the calculated micromechanical value.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 212, Longitudinal Guided Wave Propagation in a Transversely Isotropic Fiber.

TASK: 253

TASK TITLE: Modeling of Liquid Crystal Siloxanes

TASK OBJECTIVE: To explore the interactions and possible interferences between chromophores and liquid crystal mesogens.

SCIENTIST: Barry L. Farmer, Ph.D.

DESCRIPTION OF WORK:

Semiempirical molecular orbital calculations were undertaken to model the conversion of 1′-isopropyl-3′,3′-dimethyl-indoline-spiro-6-nitro-8-methoxy benzopyran and to the corresponding merocyanine. The mechanism for reforming the spiropyran was also modeled. One possible mechanism for the spiropyran-to-merocyanine conversion was simulated by progressively stretching the carbon-oxygen bond which is known (experimentally) to rupture. The results show that none of the four possible isomeric forms of merocyanine occurs simply along this reaction path. Instead, the molecule maintains the orthogonality of its ring systems. Relaxation processes allow the formation of either the trans-trans isomer or the cis-cis isomer, depending on the distance between the spiro carbon and the pyran oxygen atom at the start of the relaxation. The trans-trans form would seem to be preferred since it forms from intermediates having a less elongated carbon-oxygen bond.

The mechanism for the reconversion from merocyanine to spiropyran was studied (in analogous fashion) by progressively reducing the carbon-oxygen distance. Each of the four merocyanine isomers was used as a starting configuration. The trans-trans and cis-trans isomer were able to revert directly to spiropyran, while the cis-cis and trans-cis isomers seemed to require an intermediate conversion to a modified cis-trans isomer. The barrier to ring opening was about 40 kcal/mol. Closing the ring had a barrier of about 35 kcal/mol.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 217, Computational Modeling of a Spiropyran Chromophore.

TASK: 254

TASK TITLE: Deformation Mechanisms in Gamma Titanium Aluminides

TASK OBJECTIVE: The objective of the task is to analyze, characterize, and understand the fundamental deformation behavior in gamma titanium aluminides.

SCIENTIST: Sriram Seshagiri, Ph.D.

DESCRIPTION OF WORK:

Binary Ti-50Al and 52Al alloy buttons were prepared by vacuum arc-melting high purity electrolytic Ti sponge and 99.999% pure Al ingots. The cast buttons were given a homogenization heat treatment. In both the alloys interstitial oxygen was ~250wt.ppm. The average grains sizes following homogenization were 300mm and 500mm in the 50Al and 52 Al alloys, respectively. Parallelepiped samples measuring 5 x 5 x 12.5 (mm) were electro-discharge machined from the homogenized alloys and deformed in compression (in air) at a constant strain rate of $1.7 \times 10^{-4} s^{-1}$ up to ~ 1-3% strain, over a wide temperature range between 77°K-1173°K.

The stress at 0.2% offset strain, defined here as the flow stress, was plotted as a function of deformation temperature. The 0.2% temperature profiles comprised three distinct regimes: Regime I (between 77-~600°K), regime II (between ~600-1073°K), and regime III (above 1073°K). Deformation temperature influences the types of dislocations present, the nature of superdislocation dissociations, and morphological characteristics of both the ordinary and superdislocations. It is argued that the flow properties at low temperatures (regime I) are controlled by lattice friction, whereas at higher temperatures flow properties are dislocation obstacle controlled. Apparent activation energies were determined from the flow stress-temperature plots. Thin foils made by standard twin-jet thinning from the deformed samples (sliced at an angle of 45° to the compression axis), were observed in a Philips CM20 transmission electron microscope operated at 200 kV, utilizing bright field (BF), weak beam dark field (WBDF) and selected area diffraction (SAD) techniques.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 218, Deformation Behavior and Dislocation Mechanisms in TiAl Alloys.

TASK: 255

TASK TITLE: Statistical aspects of neural-net computing in control of semiconducting wafer growth and in prediction of material structural failure.

TASK OBJECTIVE: To define and increase accuracy of neural net computing estimates in the presence of process noise and material property deviations.

SCIENTIST: Boris Igelnik, Ph.D.

DESCRIPTION OF WORK:

This project investigated statistical aspects of neural-net computing in control of semiconducting wafer growth. A new technique, different from the neural-net and standard nonlinear regression methods, was also developed for interpretation of optical parameters and thickness of the film. This technique is based on a new optimization algorithm and is likely to increase accuracy in the interpretation of process parameters in the presence of noise.

An explicit and full description of the neural-net parameter interpretation procedure was proposed including estimates of temperature T and composition χ. It was shown that, combining neural-net approach for simultaneous determination of optical constants and film depth d, and polynomial parameterization of measured variables by temperature and composition, estimates of these underlying parameters (T and χ) can be achieved substantially more efficiently than by the nonlinear regression approach. It was also shown that using the model ambient-medium 1-medium 2...medium$m$ - substrate, the results can be extended to apply to nonuniform layered structures, containing layers of roughnesses, voids and so on. This neural-net based methodology (NNBM) enables the estimation of temperature and composition given a rather modest amount of training data in terms of temperature and composition, all at a single wavelength.

In addition, a new technique for interpretation of optical parameters (SOPT) was developed in the case if the training phase of the neural-net based procedure is judged to be too severe in time and memory requirements. This new technique, based on a new stochastic optimization algorithm, provides for accuracy in the presence of noise, using ellipsometry measurements for different values of depths but at a single wavelength. The numerical simulations showed that SOPT can at least be recommended as a supplement to NNBM, because it can be used in the learning phase with neural nets of lesser resolution, thus reducing requirements in time and memory. Accuracy can be enhanced by SOPT in the generalization phase. Final decision either in favor of NNBM or for a combination of NNBM and SOPT (NNBM+SOPT), or only SOPT can be made only after completing experiments on industrial

scale with real data.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 219, Statistical Aspects of Neural Net Computing in Control of Semiconducting Wafer Growth.

TASK: 256

TASK TITLE: Functionally Gradient Design of Shafts

TASK OBJECTIVE: To investigate the issues surrounding the alternative design of a component manufactured with polymer-based composites together with a metal alloy material.

SCIENTIST: Russell E. Duttweiler, B.S.; Allen Jackson, Ph.D.; and Jack Park, ThinkAlong Software, Inc.

DESCRIPTION OF WORK:

This task consisted of three separate efforts. The first effort was the study of the functionally gradient design of shafts.

Reduction of weight in aircraft and in vehicles is of considerable interest because of the potential for reduction in energy consumption. Issues relating to wear and durability of components is also a major concern, because of the potential for high replacement costs. Performance goals have increased substantially and are continuing to do so, requiring consideration of new materials that can satisfy these specifications. These issues are being considered in terms of alternative and new materials. Of particular interest in this investigation are functionally gradient materials. The objective of this research was to investigate the issues surrounding the alternative design of a component manufactured with a polymer-based composite together with a metal alloy material.

In this brief survey of issues, a list of parameters and effects was generated that can be used as a guide for further explorations. Hybrid structures consisting of carbon composites and metals appear to be viable. Ti alloys are attractive because of their low density relative to steels and their rather high strengths. Carbon composites offer similar advantages. Hence, the combination of these two materials is attractive where weight and wear are controlling parameters. For shafts, this combination offers interesting technical challenges, particularly with respect to torque strength. Design of the interface to achieve sound linkage and an acceptable margin of safety against failure must be addressed early.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 221, Functionally Gradient Design of Shafts.

The second effort established the development of an Ontology for Materials Science. The beginnings of the ontology was developed and tested using a qualitative inference engine called The Scholar's Companion™ (TSC). This ontology is aimed at support of all phases of the materials domain, from discovery of new materials to product design, manufacturing, and marketing.

An ontology gives us a way to divide up the world. How we recognize things, how we describe them; these and other elements of an ontology let us converse on uniform grounds. The ontology developed provides two important devices: a *lexicon* (vocabulary) with which to discuss materials, and a *taxonomy* (structure) for that lexicon.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 222, Towards an Ontology for Materials.

The third and primary focus of this task was to investigate the issues surrounding the design of a component combining the manufacture of a hybrid shaft with a polymer-based composite overwrap. A carbon fiber wound composite shaft capable of 2300 newton-meters (20,300 in-lbs) of torque requires a central high strength torque tube incorporating metal end-fittings to properly interface with the mating drive surfaces. This task investigated various shaft design alternatives to enable the development of maximum torque capability from a combined polymer-metal component. An assessment was made of the current metal shaft dimensional and physical process limitations to define the best possible design and manufacturing process for the new shaft design.

Two prototype 3-piece steel shafts of a truly novel design were constructed and filament wound using graphite epoxy. These shafts incorporated two steel sleeves adapted to the spline end pieces and shrunk-fit to the premachined torque tubes. Two shafts of this design were constructed and both were torque tested. One failed at 90% of the goal torque value of 20,300 in-lbs. The other at 80%. Design of a third novel 3-piece shaft design with further improvements based on these results was initiated.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 223, Polymer-Based Process Design of Shafts.

TASK: 257

TASK TITLE: Mathematical Basis for Functional-Link Net

TASK OBJECTIVE: A comparative investigation of neural networks and nonlinear regression methods for modeling transcendental functions involved in optical ellipsometry.

SCIENTIST: Boris Igelnik, Ph.D.

DESCRIPTION OF WORK:

In this project stochastic methods were investigated for interpretation of optical parameters and depths of thin films in the presence of noise. A number of algorithms based on those methods under conditions where measured values were corrupted by simulated noise were suggested and tested.

Two types of algorithms were considered. First algorithms which take as initial data known intervals of parameters to be interpreted, with relatively moderate sizes, and reduce them to acceptable values. The lengths of the initial intervals may be of order of $\pm 10\%$ of unknown values, while the lengths of final intervals may be less than 1%. The algorithms of the second type take as initial data known intervals, the lengths of which may be of the order of $\pm 100\%$ of unknown parameters, and reduce them to the order of 10%. The algorithms of the first type can work satisfactorily when the amplitude of noise is within 2% of measured values, while the algorithms of second type work satisfactorily when the amplitude of noise is within 1% of measured values.

Algorithms of the first type cope with noise by making use of redundancy in measurements. But the number of redundant measurements were still quite small, 2 or 3 in simulations. This good result can be explained by the fact that unknown parameters are supposed to lie in relatively small intervals. Algorithms of the second type apparently need many more additional measurements (on the order of 100) which may not be feasible. A new algorithm was suggested and tested, based on the Pincus formula, interpolation and simulation of noise. Preliminary results were satisfactory but additional checking is needed.

The possibilities of enhancing random version of the Functional-link net by different techniques including stochastic optimization were also considered in this analysis.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 238, Stochastic Methods for Interpretation of Optical Parameters and Film Depths in the Presence of Noise.

TASK: 258

TASK TITLE: Fatigue and Environmental Effects in Titanium Intermetallics and Composites

TASK OBJECTIVE: To examine the role of environment on fatigue damage accumulation in gamma titanium aluminides and titanium matrix composites.

SCIENTIST: Andrew H. Rosenberger, Ph.D.

DESCRIPTION OF WORK:

The objective of this study was to: 1) determine the environmental effect on the isothermal and thermomechanical fatigue of SCS-6/Timetal ®21S, and 2) determine the mechanisms of the fatigue damage accumulation in these composites.

The material used in this study consisted of continuous SiC (SCS-6) fibers in a beta titanium matrix (Timetal ®21S Ti-15Mo-3Nb-3Al-0.2Si- wt%) and sheet Timetal ®21S (0.5 mm thick) from heat G-1664. Composites were fabricated by the foil-fiber-foil method using rolled foils of Timetal ®21S and fiber mats of SCS-6 fibers held together by metal ribbon and consolidated by hot isostatic pressing. Samples were wrapped in tantalum foil and heat treated at 621°C for 8 hours in a vacuum furnace to prevent any oxidation damage. Unidirectional $[0]_4$ straight sided specimens were used with a width of 10 mm, length of 110 mm and nominal thickness of 0.9 mm. The axial strain was monitored during the tests by a nominal 12 mm gage length quartz rod extensometer. Specimens were tested in an environmental chamber mounted on a computer controlled, servohydraulic load frame. Heating was realized by a four zone quartz lamp system with independent temperature zone control via thermocouples welded to the specimen. The specimens were loaded using water cooled, precisely-aligned hydraulic friction grips. Tests were conducted using MATE software which controlled the symmetric triangular wave forms used for both load and temperature (TMF). The software automatically adjusted the four temperature setpoints to maintain proper temperature ramp rates and load/temperature phasing.

The effect of environment on the fatigue behavior of SCS-6/Timetal ®21S $[0]_4$ composites was examined through a comparison of fatigue lives and damage progression for tests performed in air and high purity helium. Isothermal and thermomechanical tests were conducted at 650°C and 150°- 650°C, respectively. Out-of-phase thermomechanical fatigue (TMF) lives of specimens tested in the inert environment show a 2x increase in life. The main difference in damage between inert and air environments is a decrease in matrix cracking due to the deleterious embrittlement that is seen in Timetal ®21S after high temperature air exposure. In-phase TMF lives in inert and air environments are comparable.

Isothermal fatigue tests in the inert environment performed at 1.0 Hz show that at high stresses, the life is not affected by the environment but at lower stresses, where the time to failure is substantially longer, a 3.5x increase in life was observed. Reducing the fatigue frequency to 0.01 Hz caused a reduction in life at both high and low stresses in the inert condition as compared to the low frequency air condition. The effects of variables such as fiber volume fraction were considered in the analyses and help explain some of the observed behavior.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 239, Environmental Effects on the Isothermal and Thermomechanical Fatigue of SCS-6/Timetal ®21S Unidirectional Composites.

TASK: 259

TASK TITLE: Metallurgical Phenomena in MMC Processing

TASK OBJECTIVE: To establish the importance of various metallurgical mechanisms in controlling consolidation and bonding during the fabrication of foil-fiber-foil, metal matrix composites (MMCs).

SCIENTIST: Perikles D. Nicolaou, Ph.D.

DESCRIPTION OF WORK:

This project contained two parts studying different issues and processes concerned with the fabrication of continuous fiber, metal-matrix composites (MMCs).

The first part was a continuation of a previous task and addressed two issues:

(i) fiber fracture during composite forge-consolidation
(ii) quality of the forge consolidated MMCs, compared to composites fabricated by different routes and techniques.

Experimental results showed that fiber fracture occurs due to tensile tangential stresses in the SiC of the SCS-6 fiber in the vicinity of the carbon/SiC interface. FEA simulations provided predictions of the magnitude of these stresses and allowed the selection of the processing parameters so as fiber fracture is avoided or at least minimized. Room temperature tensile testing was performed to examine the quality of the forge consolidated MMCs. The mechanical test results obtained were similar to those earlier reported in the literature for conventionally processed MMCs, indicating the ability of this approach to fabricate good quality MMCs.

The second part presented a sensitivity analysis of the required consolidation time of continuously reinforced composites due to lot-to-lot variations of the matrix material flow behavior. The analysis was applied to two different matrix materials: (a) alpha-2 Ti-14Al-21Nb, and (b) Ti-6Al-4V. It was shown that lot-to-lot variations in the flow stress-strain rate behavior for the alpha-two titanium aluminide alloy Ti-14Al-21Nb may give rise to required consolidation times which vary approximately by a factor of six. On the other hand much smaller variations in material behavior and hence consolidation time are predicted for the conventional titanium alloy Ti-6Al-4V.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 240, Processing and Properties of Continuously Reinforced MMCs.

TASK: 260

TASK TITLE: Innovative Composites Research

TASK OBJECTIVE: To provide advanced innovative concepts, which will enable the synthesis and processing of lightweight, composite structural and thermal management materials for dual-use applications in air and space weapon systems and commercial products, particularly as enabling materials for thermal energy conversion processes.

SCIENTIST: Joseph W. Hager, Ph.D

DESCRIPTION OF WORK:

This task was performed as part of the in-house composites research program within WUD 45 of the Wright Laboratory Materials Directorate. This part of the WUD 45 research program is directed at the design and synthesis of novel composite microstructures, composite environmental durability in severe environments, and low cost composite processing. Specific tasks address the synthesis and characterization of novel forms of carbon, such as graphitic foam; vapor-grown carbon fiber and composites derived therefrom; and the protection of carbon in hot oxidizing environments with gas layer protection. To address complexity and cost of manufacture it is proposed to replace the *disconnected* carbon fiber reinforcement networks of current composites with reticulated graphitic foams. Such *interconnected* networks of graphitic reinforcing micro-struts, each possessing a morphology similar to that of commercial carbon fiber, have been blown from anisotropic pitch and have been subsequently stabilized, carbonized, and graphitized. A previous report, designated as Volume 214 of this series, describes progress in graphitic carbon foam research made during the period November 1993 through October 1994.

To protect hot carbon surfaces from oxidation mass loss, it is proposed to bathe the surface with gases with which the carbon is in thermodynamic equilibrium. Having previously studied this protection concept analytically, construction of a flow reactor apparatus has been undertaken to experimentally confirm the viability of the concept. A report, designated as Volume 216 of this series, covering the period November - December 1994, discusses the progress in gas layer protection.

Vapor grown carbon fiber (VGCF) is a class of highly graphitic discontinuous carbon fiber which can be synthesized directly and cheaply from hydrocarbon gas. VGCF is of interest to the Air Force, because it represents a new form of carbon fiber reinforcement for polymer-, metal-, ceramic-, and carbon-matrix composites. This project examined the characteristics of this novel material, research issues, and potential applications of these composites.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 241, Innovative Composites Research: Characteristics of Vapor Grown Fiber and Potential Composite Applications.

TASK: 261

TASK TITLE: Computational Chemistry Evaluation of Halon and Halon Replacements

TASK OBJECTIVE: To develop a fundamental understanding of the chemical mechanisms of Halon fire suppressant action through computational chemistry. To use this understanding to evaluate alternative compounds presently being considered, and other completely different compounds, for fire suppressant capability.

SCIENTIST: Rajiv J. Berry, Ph.D.

DESCRIPTION OF WORK:

The overall goal of this project was to understand and predict the detailed mechanisms of flame suppression by potential halocarbon suppression agents. The agents currently used for flame suppression for the protection of aircraft, computer centers, and communication systems are bromic-containing halocarbons grouped under the name halon. The production of halons is banned under the Montreal Protocol because they have been shown to be responsible for the depletion of ozone found in the stratosphere.

The desirable characteristics of a suitable halon replacement agent are low global environmental impact (ODP-ozone depletion potential and GWP-global warming potential), acceptable toxicity, cleanliness, volatility, and effectiveness. Among the large number of chemicals that have been tested as candidates for halon replacement so far none has been found as effective as presently used halons but with a low ODP/GWP. The candidate replacement agents can be classified as hydrobromofluorocarbons (HBFC), chlorofluorocarbons (CFC), hydrochlorofluorocarbons (HCFC), perfluorocarbons (FC), and hydrofluorocarbons (HFC).

In order to investigate the mechanism of flame propagation and suppression, one must accurately model all the reactions possible in a flame scenario. The kinetic modeling required for this purpose needs accurate thermochemical (enthalpies) and kinetic (rate constants) data for each reaction as well as the transport properties of all the chemical species involved. Accurate experimental enthalpies and rate constants are available for very few of the reactions needed for the modeling. On the other hand, computational methods such as the ATOM EQUIVALENTS, BAC/MP4, G1 and G2 have been reported as an alternative source for accurate enthalpies. Furthermore, since these calculations are not subject to the uncertainty associated with experiments, they can provide a benchmark for selecting/rejecting data obtained from different experiments.

A preceding investigation focused on the feasibility of computing accurate enthalpies of formation for stable C_1 and C_2 molecules. This study aimed to extend the calculations to select C_1 and C_2 fluorocarbon radicals.

The enthalpies of formation (ΔH_f^0) for C_1 and C_2 fluorocarbon radicals were computed by the ATOM EQUIVALENT'S (AEQ) method as well as the *ab initio* G1 and G2 methods. The computed quantities were compared with experiment and with a method specifically parameterized to reproduce fluorocarbon ΔH_f^0's (*viz.* the BAC/MP4 method). For the selected C_1 radicals ($\bullet CH_3$, $\bullet CH_2F$, $\bullet CHF_2$, and $\bullet CF_3$) the root mean square deviations (RMS) of the computed enthalpies from experiment are 4.9, 5.4, 7.1, and 8.8 kJ/mol, respectively for the AEQ, BAC/MP4, G1 and G2 methods. The RMS uncertainty in the experimental enthalpies for these molecules is 6.0 kJ/mol.

The ΔH_f^0's for the selected radicals were also obtained from isodesmic reactions using the ΔH_f^0(exp) for CH_4, $\bullet CF_3$, and $\bullet CF_3$-CF_2 and the computed enthalpies of reaction (ΔH_r^0). The computed RMS enthalpy deviations for the C_1 radicals ($\bullet CH_3$, $\bullet CH_2F$, and $\bullet CHF_2$) are within the quoted RMS experimental uncertainty (RMS = 5.5 kJ/mol) with the exception of the computed AEQ(iso) deviations (RMS = 25.9 kJ/mol).

For the C_2 radicals (CH_3-$CH_2\bullet$, CH_3-$CF_2\bullet$, and CF_3-$CH_2\bullet$) the computed enthalpies deviate from experiment by RMS values of 11.3, 5.6, 13.0, and 13.7, respectively for the AEQ, BAC/MP4, G1 and G2 methods, while the RMS experimental uncertainty in the measurements is 6.6 kJ/mol. Isodesmic G2 (as well as G1) calculations for the C_2 radicals await the completion of the G2 calculations for the CF_3-$CF_2\bullet$ and CF_3-$CHF\bullet$ radicals.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 242, Ab Initio Thermochemical Computations for C_1 and C_2 Fluorocarbon Radicals.

TASK: 262

TASK TITLE: TEM Studies on WS_2

TASK OBJECTIVE: Develop transmission electron microscopic (TEM) representations of WS_2 powder and wear debris.

SCIENTIST: Somuri V. Prasad, Ph.D.

DESCRIPTION OF WORK:

Determination of the chemistry and crystal structure of wear surface films is crucial to the understanding of lubrication mechanisms in self-lubricating materials. This research describes the transmission electron microscopy (TEM) analyses of wear transfer films from a self-lubricating aluminum metal-matrix composite. The composite is comprised of 5 percent by volume of tungsten disulfide (WS_2) and 10 percent by volume of silicon carbide (SiC) dispersed in an aluminum alloy (Al-0.40Si-0.75Mg)matrix. Wear test on the MMC surface was performed in laboratory air with a 440C steel ball. After a two-million-cycle friction and wear test, the steel ball was dismounted from the

apparatus and cleaned with isopropanol to remove the loose wear debris from the wear scar. The wear transfer film on the steel ball was then extracted with an acetate film, coated with carbon and placed on a TEM grid. When the acetate film was dissolved in acetone, the wear transfer film was left behind in the carbon matrix. Selected area diffraction (SAD) studies confirmed that the wear transfer film was comprised of both crystalline and amorphous phases. However, no crystalline WS_2 platelets were detected in sufficient quantity to confirm the improvement in tribological behavior of self-lubricating Al MMCs due to slippage of WS_2 platelets. One single crystal phase with an extremely large d-spacing (8.7 Å) was detected at several places, and there were also several new phases formed as a result of tribochemical reactions.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 243, Tribology of Self-Lubricating Aluminum Metal-Matrix Composites (MMCs): TEM Analysis of Wear Surface Films.