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NEW WORLD VISTAS
AIR AND SPACE POWER FOR THE
21ST CENTURY

MATERIALS VOLUME

NEW WORLD VISTAS

**AIR AND SPACE POWER FOR THE
21ST CENTURY**

MATERIALS VOLUME

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This report is a forecast of a potential future for the Air Force. This forecast does not necessarily imply future officially sanctioned programs, planning or policy.

Abstract

In this publication, important materials issues identified by the *New World Vistas* (NWV) Materials Panel are reported. The charter of this panel is provided in Appendix A. During this study, one or more members of the panel visited the organizations shown in Appendix C. From detailed discussions with technical leaders in these organizations, panel members attained an in-depth understanding of technology needs and potential technology developments relevant to the U.S. Air Force. In addition, several policy issues concerning how technology development is carried out within the Air Force (and within U.S. industry) were discussed and considered in detail by the panel.

The findings and recommendations of the NWV Materials Panel are provided in this report. Major recommendations, in both policy and technology opportunities (near-term and far-term), are compiled at the beginning of the Executive Summary. The next two sections of the Executive Summary describe the importance of materials and suggest policy and infrastructure changes to foster materials development. The remainder of the Executive Summary consists of short sections covering the most important materials applications in the Air Force. The full report consists of chapters corresponding to each section of the Executive Summary; these chapters are intended to provide more comprehensive detail on key issues of interest to technical experts and managers of research and technology development.

Advanced materials are crucial to the Air Force mission. This was a common theme borne out in discussions with each of the organizations visited by the panel. It is essential that this be recognized by Air Force policy makers, and indeed, by those who control the allocation of resources.

Panel Chairman

Professor Digby Macdonald

Panel Members

Mr. Tobey Cordell
Professor R. Judd Diefendorf
Dr. Douglas Dudis
Professor Hamish Fraser
Dr. Robert Hughes
Dr. Robert Schmitt
Professor Samuel Stupp

Staff

Major Robert Frigo Executive Officer
Major Mark Husband Executive Officer
2Lt Douglas VanderKooi Technical Editor

Acknowledgments

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Executive Summary

Overview

There is little question that the Air Force faces an exciting future in advanced materials. This is because materials can provide the technological edge that will maintain the U. S. Air Force (USAF) as the world's preeminent aerospace fighting force. One only has to examine the impact of materials in the past on Air Force systems (e.g., stealth materials in the F-117A and B-2) coupled with the fact that we are just entering the designed materials age, to appreciate the quantum leaps in performance and mission effectiveness that may be realized by the judicious use of advanced materials. We see this trend continuing and probably accelerating into the future. While it is difficult and perhaps even dangerous to predict technological developments many decades into the future, we outline below six scenarios as examples of materials development that would have a major impact on the USAF in the first half of the twenty-first century.

- Imagine an aircraft that is tailored made from materials that were computationally designed at the atomic/molecular level to allow the platform to accomplish a specific mission. The materials would be designed to be multifunctional via the specification of specific properties. In one case, these properties might include low observability and high strength/stiffness to render the aircraft technologically superior in a ground attack mode. In another case, the materials might be chosen to yield a low IR signature and yet be capable of sustained, high Mach number flight. Both aircraft would be designed by computer from "dialed-up" materials to accomplish specific missions. Indeed, it may be possible to change the properties of materials on a single airframe, as the mission demands, thereby yielding a vehicle of incredible multi-role capability.
- Imagine a precision weapon system in which the yield of the conventional warhead could be selected in flight so as to destroy a target and yet minimize collateral damage. Indeed, the yield might be selected automatically via sensors in the missile that would interrogate the target prior to impact to determine the minimum yield that is required to accomplish the mission.
- Imagine an aircraft that has been fabricated from self-healing materials and structures, such that battle damage is healed or the effects are minimized before the airplane returns to base. In the converse, imagine an aircraft that might consume, as fuel, unneeded appendages and systems after delivery of its weapons on target. Both ideas would greatly enhance survivability and mission effectiveness, and their gains would be achieved through the development of advanced materials.
- Fire has always been the Achilles' heel of high-performance aircraft from the earliest days of aviation. This is because the fuel is flammable and the higher the energy density (and hence potential for destruction of the airframe) the better the fuel. But does it have to be that way? Imagine then a fuel that is synthesized on board, as needed, from nonflammable components, thereby maintaining the inventory of flammable materials within the airframe to an absolute minimum. The impact on survivability would be enormous.

- Imagine a technology that would allow a maintenance depot to predict the development of damage due to fatigue, corrosion, or corrosion fatigue on a tail-number basis with sufficient temporal and spatial accuracy that maintenance could be scheduled on the basis of condition and condition alone. The savings would be enormous.
- Finally, imagine a technology whereby parts could be manufactured on an as-needed basis by using lasers to polymerize monomers in three dimensions, i.e., free-form manufacturing. Parts of many different shapes could be “dialed-up” from a single monomer system, thereby eliminating tooling time and expenses and greatly simplifying the manufacturing process. The need to maintain large inventories would be eliminated and changes in design would be as simple as reprogramming the computer.

The above are but a few of the opportunities that await the Air Force in advanced materials over the next fifty years. While these materials-based technologies are not with us today, except in very rudimentary form in some cases, they are not “pie in the sky.” They all stem from the incredible advances that are now being made in materials science and technology at the fundamental level. These advances, in turn, are the payoff for past investments in the future, in terms of basic research and education. Such payoffs are long-term, frequently requiring more than three decades to come to fruition. For the large part, they cannot be predicted, nor can one rely upon them happening, particularly in the absence of the appropriate prior investment. That some (perhaps even many) will become realities in the future is ordained by the nature of scientific discovery. It goes without saying that if we are to maintain the technological edge over potential adversaries, it must be we who harvest the crops.

We envision a future Air Force that is materially innovative and astute, one that has a robust R&D capability that proactively influences the development of advanced materials and advanced materials technologies. We see an Air Force that is not averse to reasonable risk in introducing new materials into aerospace systems and one whose metrics are enhanced performance and greater efficiency at a reasonable cost. Finally, we envision new materials as key enabling factors in allowing the Air Force to accomplish its mission of global reach and global power.

Policy Recommendations

During the next fifty years, the Air Force’s battlefield superiority will be threatened by today’s drastic and continuing reduction in U.S. long term industrial R&D in materials. To counter these effects, the Air Force needs to develop new mechanisms to ensure that the U.S. industrial base for advanced materials capabilities and infrastructure does not erode beyond the point of being responsive to Air Force materials needs. Thus, we recommend the Air Force commit to:

- Maintaining robust R&D programs and capabilities in innovation and development of materials for long range critical Air Force needs and not relying solely on commercial sources. Our national policy with regards to advanced materials should ensure technological advantage. Because the Air Force is a small customer for

advanced materials, commercial entities will not become reliable sources for R&D in materials unless large commercial markets exist for those same materials.

- Ensuring new funding and programs which integrate advanced materials into current and future systems, in order to help counter the downturn in military aerospace R&D.
- Demonstrating and incorporating new materials, which offer significant payoffs, in flight systems and rocket technology.
- Ensuring continued performance of aging aircraft and missiles. In order to reduce costs, the Air Force should move from programmed depot maintenance to condition based maintenance. This fundamental change in maintenance will require support for the development of new technologies in nondestructive evaluation/inspection (NDE/I), situational sensors, and life prediction techniques.
- Increasing resources for materials and processes R&D to alleviate the increasing cost of operating and maintaining the aging fleet.
- Aggressively pursuing new technologies for affordability that lessen the impact of advanced materials and Air Force operations on the environment. Environmental issues must be supported at the highest levels in the Air Force command structure.
- Adopting life cycle costing (LCC), which recognizes that early investments in materials and processes can dramatically lower life cycle costs of both new and upgraded systems. In addition, the Air Force must consider the potential cost of disposal of materials and systems and make the appropriate investments that can minimize those costs.

Opportunities in Materials and Process Technology

Some key factors driving future developments in materials and processes include: the need to lower costs and improve affordability of both new and upgraded military systems, providing the best performance systems to ensure military superiority by assuring longer life and reliability of systems and components, and addressing strategically important issues such as better stealth materials and non-polluting fluids and propellants. Finally, the Air Force needs to be the leader in novel materials R&D, such as computationally synthesized functional materials and computational materials processing, that will dramatically reduce the time and cost of development through elimination of extensive testing and current practices of creating expensive data bases for design and manufacture. Among the many opportunities in these and other areas, the paragraphs below list some premier candidates for both near term and far term applications.

Near Term Opportunities (Less than 20 years)

- Structures: Continued focus on implementation of enhanced fiber-reinforced composites with emphasis on combined multifunctional structural and electromagnetic characteristics. Explore opportunities for unexplored structural applications like hypersonic weapon systems. Continue evolution of revolutionary new process methods that guarantee reliability and durability while reducing component costs.

- **Aircraft Engine Materials:** Successful development of the advanced materials for the Integrated High Performance Turbine Engine Technology (IHPTET) initiative will enable turbine engines with improvements such as a 100 percent increase in the thrust-to-weight ratio and up to a 50 percent decrease in fuel consumption. These engine improvements will result in dramatic operational capabilities, such as fighters with a 45 percent increase in take off gross weight and increased range. Key materials and processes for IHPTET are in the classes of intermetallics, metal matrix composites, and ceramic matrix composites. Other classes of unique new engine materials will be developed for emerging non-manned hypersonic systems.
- **Fuels and Lubricants:** Endothermic fuels are the enabling technology for turbines in the future. An endothermic fuel uses the engine's waste heat to create a more energy-dense fuel. Advances in lubricants and seals are absolutely critical to meet mission requirements of aircraft and space vehicles of the future.
- **Optical and Electronic Materials:** The commercial technology in silicon electronics is on an evolutionary path without historical equal. While the Air Force has a significant challenge to apply this technology, it must also recognize that many of its force multiplying technologies are derivatives from niche (non-silicon) materials: IR sensors, radars, lasers, and high-temperature, adverse-environment electronics. Investment in these areas remains a critical need for the Air Force in order to maintain technology superiority.
- **Aging Systems:** Develop new methods for reducing the cost of maintaining the aging fleet. Promising approaches include: 1) Inspection without coating removal. Advanced, high resolution automated inspection methods will enable structural crack and corrosion inspection directly through paint. This will obviate the need to remove paint for inspection. 2) Direct fabrication of replacement components. New materials and processes will enable direct fabrication of finished components, allowing a dramatic reduction of inventories. This will be crucial to the required reduction in the infrastructure needed to maintain the fleet. These technologies will also enable life-cycle engineering modification of functional replacements for components that are causing problems. 3) Remote inspection of aging systems. Combined active optical inspection methods, such as laser-generated ultrasound with flexible fiber optics and MEMS, will enable assessment of internal structures without requiring disassembly.
- **Pollution Prevention:** Remediation is a very large expenditure for the Air Force. To prevent recurrence in the future, investments are required today for alternative green processes to replace existing hazardous material processes, many of which are unique for military systems.
- **Space:** Develop advanced high performance composites, both carbon-carbon and organics for thermally managed, lightweight, multifunctional structures and components. These can provide a highly desired order of magnitude improvement in thermoradiators for space applications via the use of ultrahigh conductivity

carbon fibers and conducting resins. Other significant opportunities include materials for sensors and new materials for systems to ensure access to space.

- **Transitioning Advanced Materials into Flight Systems:** The Air Force needs a program for the rapid introduction of advanced materials into flight test systems. We recommend the establishment of an Advance Materials Plane program (using existing vehicles as test beds) at the Air Force Flight Test Center.
- **Rocket Propellants:** 1) Implement major improvements in solid fuel motors by incorporating advances in binders and oxidizers (5-20 percent improvement in mass-to-orbit or a 5-15 percent increase in specific impulse). Similar improvements in liquid systems are possible. 2) Develop advanced hybrid systems with improved performance (goal of 350 sec for a strap-on) by using new oxidizers, TPE binders, gel binders, and new fuels like aluminum hydride 3) Use cryogenic high energy density materials and materials like metallic hydrogen (specific impulse greater than 1500 sec) to revolutionize access to space (performance several times greater than LOX/H₂).
- **Energy Generation and Storage:** Develop advanced secondary batteries and supercapacitors having energy densities and power densities in excess of 500 W·hr/kg and 10 kW/kg respectively, for use in advanced spacecraft. Advanced fuel cells that directly use (i.e. without reforming) liquid fuels or that employ biofuels need to be developed as LO, ground-based power sources.
- **Pyrotechnics:** Develop advanced flares for aircraft protection to defeat state-of-the-art missile seeker heads. Develop metastable interstitial composites to create extremely high temperatures for destroying chemical biological warfare agents.
- **Explosives:** 1) Exploit an opportunity for the Air Force to bring to the field advanced explosives and directed energy charges based on recently invented energetic materials. Emerging materials and technologies could result in a doubling of the explosive power of warheads. 2) Develop technologies to allow tuning of explosive charges (to fill the gap between conventional and nuclear weapons), implement advanced thermites, and exploit nanoformulated explosives to improve yield and control.

Far Term Opportunities (Greater than 20 years)

- Prediction-based computational methods that can be used to design and synthesize of high temperature materials that will be tailored for specific applications/components. These materials will tend to have microstructures on the nano-scale and be synthesized atom by atom, obviating all of the current methods of fabrication, such as casting and metal working, with the result that these materials will be defect-free and manufactured "right the first time". Performance, weight savings, and cost reductions will each be optimized.
- Nanophased organic materials and nanostructured composite materials, which integrate sensing, energy conversion, and structural functions. Develop new mechanisms for the systematic creation of new material structures and properties.

- Micro electromechanical systems to exploit revolutionary multifunctionality for systems at small scale approaching molecular dimensions.
- Aircraft Engine Materials: 1) Devise solutions to problems limiting the application of existing attractive materials (e.g. refractory alloys that will provide a 200°C increase in use temperature for high-pressure turbine (HPT) airfoils). 2) Synthesize new materials making use of innovative schemes for materials processing, such as laminating nano-scale composites (e.g., thermal barrier coatings that may lead to an increase of 260°C for HPT airfoils). 3) Evolve new systems applications such as hypersonic vehicles where improved or alternative materials will be used, possibly in conjunction with changes in design. These will lead to marked improvements in performance, including thrust/weight (e.g. single fluids for fuel and lubrication), resulting in savings in operational costs.
- Dynamic Stealth Materials: These materials would allow the pilot/system to change the signature characteristics of multifunctional materials at will to meet real time requirements, thereby providing the Air Force with a significant tactical advantage in the projected battle space.
- Field a family of new generation, environmentally friendly launch vehicles that are capable of inserting payloads ranging from 1000 to 100,000 pounds into LEO to meet increased demand for space access. The propulsion system should consist of entirely recyclable materials and components. Single-stage-to-orbit could become routine.
- Self-monitoring and self-healing materials to permit in-flight battle damage repair.
- Sprayable structural composite materials to cover surfaces with coatings that have one or several of the following functions: switchable antennas, tunable transmittance (e.g. for radomes), energy storage (e.g. batteries), energy production (e.g. solar cells), and sensing.
- Recyclable airframe materials that can be reversibly sintered. Organic and composite nanoparticles are particularly promising and are unexplored.
- Materials to enable enhanced optoelectronic and all-optical information gathering, transmission, processing, and storage. Processability, switching speed, and tunability give molecular and polymeric materials the greatest potential, and these materials should be further explored.
- Computer development of new materials and processes with experimental validation (e.g. complex compositional scanning for new materials and atomic-to-structural level understanding). This must also include the ability to model and assess flaws and damage in materials under realistic service conditions, especially in regions of high stress gradients, such as joints and interfaces.
- Functionally designed and fabricated material structures using localized placement of material, similar to methods employed in the semiconductor chip industry.

This could also lead to highly-unitized structures exploiting composite anisotropy with fully modeled and optimized three-dimensional (3-D) architectures.

- Path-dependent prediction of structure lifetime using real time sensor input of environmental parameters (temperature, stress, corrosion) coupled with deterministic damage models.
- Hybrid propellant systems having ultrahigh energy densities to replace liquid propellant systems.
- Novel component/materials design philosophy that provides for refurbishment of fatigue damaged areas of structural components with new materials to restore original functionality. This technology will be enabled through new computational predictive technology, coupled to materials processing, assembly, and manufacture.

Why Materials are Important to the Air Force

Air Force systems are an extremely complex integration of numerous materials and materials systems from high temperature turbine engine blades to airframe structural composites. Thus, the selection of key design materials impacts the life-cycle cost of a weapon system, including acquisition (materials and fabrication), operation, assurance, maintenance, and disposal costs. New materials offer improved performance and capabilities, such as stealth, non-chlorine-containing propellants, super-emitters, and composites that allow missions to be performed with minimum detection and loss of aircraft and personnel. In aeropropulsion systems, higher operating temperatures translate to lower specific fuel consumption and higher thrust to weight ratios.

Affordability is also a key criterion for assessing the value of new technology and its potential incorporation into military applications. Although enhanced performance continues to be a high priority, improvements must be achieved with affordable technologies. However, affordability must be considered in terms of the life cycle cost of the system. This means that revolutionary materials and processes, which in some cases are more expensive than those currently in use, may have a favorable overall impact on a system's life cycle cost (and may also provide performance advantages).

New Materials Policy and Infrastructure

The 20th century has seen the emergence of many materials that have enabled new technologies and have impacted directly our defense systems. The large scale refining of aluminum and synthesis of other airframe materials, (e.g. synthetic rubber for tires and silicon single crystals for computers), have all been key discoveries over the past century. The latent technology-enabling power of new materials is obvious if one considers a hypothetical 1995 world in which these three materials, or the processes for their large scale synthesis were not known, but remained to be discovered over the next 50 years. Our capabilities in chemical synthesis, materials characterization, and computation of properties are rising exponentially at the present time. Thus, statistically we have an excellent chance of discovering over the next 50 years comparable success stories in the realm of new materials that will enable new and important Air Force technologies. U.S. human resources alone in synthesis, characterization, and computation will

not lead easily to these critical discoveries. The key in raising the probability of success is for the interested parties, the Air Force being one, to develop a well thought-out new materials policy.

On the experimental side, the future mechanisms of materials discovery will have to include rapid property screening methodologies with very small laboratory scale quantities (milligrams to grams), and these efforts will have to be coupled closely to scale up processes when a promising new material is identified. On the theoretical side, there is no question that the search for new materials using computers will aid the exploration, thus raising the probability of critical discoveries. With regard to rapid screening, the use of the combinatorial libraries approach, as used in drug development, should be explored for new materials development, coupled with computational efforts that predict properties of new materials. Experimentally, the approach will require major hardware development for the rapid screening of micro-samples of new materials.

The full potential of a new material for technological implementation cannot be assessed without scale up of mass by at least three orders of magnitude relative to the amounts typically produced by the original discoverers. The infrastructure to pursue scale up of what appears to be a promising material as defined by the original target is, in most cases, nonexistent. This particular situation is very common in both academic and government laboratories, and presently even in industrial laboratories. Currently, the U.S. faces a major problem with regard to the exploration of new materials, since R&D efforts in this area are being rapidly downsized. The general U.S. picture for discovery of new materials that would impact directly on the Air Force over the next 50 years does not appear to be encouraging as of 1995. A new materials policy by the scientific establishment of the Air Force is therefore of critical importance. The model proposed is to fund new materials research at Air Force laboratories, and at industrial and academic institutions as well, searching carefully for in-house or external network capabilities to close the "new materials exploration loop". The new elements in the policy should include requirements for synthetic projects that demonstrate real, budget-committed connections to a structure-property screening capability and, most importantly, a second connection to a scaleup capability. The scaleup effort should probably be funded with 6.2 funds, but the basic premise in the proposed loop is to establish an early coupling of 6.1 and 6.2 funding, which seems to be critical for the successful development and implementation of new materials. This aspect of the new materials policy should also be facilitated through the creation of scaleup stations for new materials at either Air Force or academic laboratories. A final requirement before the 6.1 investment is made should be a vision by the investigators of what industrial establishments in the U.S. could implement the large scale production of proposed concepts.

The next 50 years might be totally infertile worldwide with respect to technological implementation of new materials or might give rise to dramatic developments that are beyond our current comprehension. This is the nature of discovery in the field of advanced materials; is frequently revolutionary in concept but slow in implementation. However, the real *policy* question to address is whether or not U.S. government institutions, the Air Force in particular, can afford to take the risk of not investing in the exploration for new materials. The risk is to be assessed in the context that other important countries are investing in new materials exploration, especially Japan, Germany, France, Korea, and China, as well as several emerging countries in the Third World. The lack of an aggressive U.S. government-supported campaign in new

materials in the future could cause us to lose the technological lead, since U.S. industry is only weakly involved in this exploration at the present time and most likely will remain so in the foreseeable future. Furthermore, government involvement in the area of new materials discovery has great potential for commercial payoff, since materials often have multiple applications. Examples that demonstrate this principle are the use of aerospace metals in orthopedic surgery and advanced composites in sporting and consumer goods. Therefore we have the following recommendations:

- Special funding of a 6.1/6.2 hybrid nature should be offered to establish “scaleup stations” to support development of new materials concepts at academic, commercial research, and Air Force laboratories.
- Establishment of a strong program of hybrid 6.1/6.2 funding for the exploration of relevant new materials. This program should be established under the guidelines of a new materials exploration loop with the objective of inducing some regeneration of the U.S. materials infrastructure.

An Air Force of Aging Systems

Reduced procurement of new aircraft is forcing the AF to extend the operational life of its current weapons systems. For the foreseeable future, this process will continue. This unanticipated extension is placing ever greater emphasis on the ability to find, characterize, and ameliorate the deleterious effects of age and use. Changes in mission requirements, to account for the lack of new aircraft for specific missions, are also accelerating the rate at which modifications must be made to existing aircraft in the fleet. In addition, many aircraft are now expected to operate with expanded mission requirements that were not envisioned originally. The health of the aging fleet is dependent on the ability to identify and characterize changes in materials and structures throughout their lifetimes. To meet these challenges, we need to:

- Develop life prediction methodologies: Integration of sensor outputs with deterministic materials behavior models will allow path-dependent lifetime predictions at the subsystem and component level, thereby leading to more cost effective maintenance decision-making.
- Validate corrosion prediction: Advanced, quantitative corrosion assessment methods will lead to validation of both corrosion and corrosion fatigue prediction methodologies, allowing much more effective control and reduction of fleet airframe and engine operation and maintenance costs. The assessment methods would include advanced sensors and multifunctional materials that would accurately track both environmental conditions and quantitative materials response.
- Refurbish materials and processes: As a corollary to condition-based maintenance (CBM) and turbine engine disk retirement for cause (RFC), a new materials/structures design philosophy will design key components to allow removal of corroded and fatigued areas with ready replacement via novel deposition/insertion/formation of new materials in place, thus eliminating 90 percent of the cost of current component replacement.

On a total system basis, retrofits, replacements, and upgrades are critical elements in all efforts to extend the life of the aging fleet. This is a particularly effective strategy for onboard electrical, electronic, and electro-optical systems, since these tend to be replaceable on a unit or modular basis; electronic, optical, and magnetic materials technologies are the enablers for this concept of life extension. As an example, the F-15 is expected to have two complete avionics suite upgrades before the airframe is finally retired.

Environment and Life Cycle Considerations

There is clearly a relationship between the environment and national security. Environmental considerations can affect national security in three fundamental ways—they pose a direct threat to the health or well-being of the public, they contribute to regional instability, or they threaten social stability.

We have probably entered the first phase of a major shift in national security thinking, involving planning to operate in a “green” future. Sherri Wasserman Goodman, Undersecretary for Environmental Security, supports this contention as revealed in her testimony to Congress in 1994—“At first the notion of a ‘green’ weapon system may seem absurd, but in reality it is not. These systems spend most of their lives in a peacetime role and often remain in the inventory for thirty years or more. During that time maintenance and refurbishment performed by contract and at our industrial depots use large quantities of hazardous materials and generate large quantities of waste.”

The Department of Defense (DoD) and the Air Force have been at the forefront of developing remediation technologies and pollution prevention processes that can contribute significantly to U.S. competitiveness. The Air Force can play a role in enhancing U.S. international competitiveness, while developing methods to control emissions, prevent pollution, and remediate past problems. At the same time, we must ensure that technologies vital to air and space supremacy can be utilized by requiring that the Air Force itself addresses the associated environmental concerns. One method to achieve this objective is to establish within the Air Force laboratories a group focused on developing the database and methodologies for performing life cycle analysis (LCA) for all current and future materials and systems.

Computationally-Driven Materials Development

Since materials are pervasive, significant changes in how materials are developed impact the AF acquisition of materials technologies. A revolution is on the horizon—a change to computationally-driven materials development. Though computers have reinvented other fields, applications in materials development have been more limited. A wholesale change in materials development practice has not yet occurred because of the complexities involved.

Computational development of new materials and processes with experimental validation is the wave of the future. Complex multicomponent systems can be studied systematically, which could not effectively be done by a purely experimental approach because of the large number of variables. The mechanical behavior of materials will be understood from atomic to structural levels. From this understanding, new materials will be developed which may have, for example, enhanced toughness. Significantly higher strength materials and higher temperature materials are also likely to result.

Recently, several examples of true materials design from atomistic simulations have emerged. To illustrate, the Air Force needs new, solid state materials such as IR detectors. Traditionally, such materials were developed by synthesizing candidate materials, growing suitable crystalline specimens, and evaluating their properties. A large number of iterations were necessary to generate enough candidate materials to explore all variables, and only a few of these materials were selected for further development. The first-principle techniques have now been used to design a series of new small band-gap compounds. Based on the calculated electronic properties, it was possible to down-select candidates for synthesis. Clearly, adoption of similar techniques to guide selection of materials for development, and to avoid unproductive research avenues, will dramatically shorten development times and enhance success rates.

Materials modeling is complex. Indeed, the task spans much of physics, chemistry, polymer science, materials science, chemical engineering, mechanical engineering, and electrical engineering. Integration of modeling with experiments will change the way the fields are practiced. The Air Force should support development of new materials modeling methods to increase the number and type of materials problems which can be economically and reliably modeled.

Structural Materials

Structural materials have been largely responsible for the major performance improvements in current Air Force systems, and will be enabling for any significant performance gains in current and future systems.

A second emerging development is multifunctional structural materials. In addition to supporting mechanical loads, the material may incorporate sensors to detect and evaluate loads or failure, and to interact with the surrounding electromagnetic environment. Intrinsically multifunctional materials have the potential of doing this without incorporating parasitic sensors. Multifunctionality may be homogeneously distributed throughout the material, as in a heat sink, but is more likely to be locally applied, such as a graded coating for oxidation resistance or as a thermal barrier. This approach is similar to semiconductor chip fabrication with localized placement of desired materials. The development of processes that can transport large quantities of material, such as plasma spray coating to build up a wing skin, are desirable. This is a continuation of the development of building up a material rather than machining it away. Direct spraying of parts will lead to significant cost reduction, compared to production and consolidation of a powder.

Limited production runs makes freeform manufacturing attractive, as well as providing the capability for easily building-in multifunctionality. Replacement of failed parts could be easily accomplished by using x-ray computed tomography to scan the part, adjusting for wear, and then freeform manufacturing from developed CAD/CAM data.

Longer range goals are the development of self-healing materials, recovery to the undeformed shape, and smart repair of cracks. These goals all try to restore a material to its original capabilities. There are approaches to each of these areas.

We recommend that the AF initiate the equivalent of an in-house X-plane program to enhance technology transition of new materials (composition or processing) to aircraft. New

systems are being built with old materials technology. Currently, the transition cycle for new materials is inordinately long, and hence the opportunities for introducing new materials in Air Force systems are severely limited. This engineering development effort would allow the accumulation of flight hours on new materials to provide the necessary systems application confidence.

Engine Materials

Research and development of materials suitable for use in turbine jet engines and other types of advanced propulsion systems may be considered over two time frames, one of 10-15 years and the other beyond 20 years. The importance of new engine materials to the Air Force can be translated into increased thrust-to-weight ratio, improved reliability and reduced maintenance, lower engine emissions, lower noise, and lower signatures. Goals include reducing engine weight by 50 percent and increasing thrust-to-weight by 100 percent. New materials and designs play a vital role in meeting these objectives.

In the shorter term, new materials for the following components are being developed as part of the IHPTET Materials Program: light weight fan blades—organic matrix composites and Ti alloys; T₃ compressor disks—Ti matrix composites; compressor blades— γ -TiAl; 816°C (1500°F) HPT disks—dual alloy superalloys; HPT airfoils—NiAl compounds and new superalloy processes; static components (cases, ducts, etc.)— γ -TiAl; and combustor and exhaust nozzles—ceramic matrix composites. Successful implementation of these developments will increase thrust/weight between 60 to 100 percent, and decrease fuel consumption by 30 to 40 percent.

In the longer term, progress in these areas will be curtailed by the markedly reduced long-range research investment by the engine producing companies. It is essential that new schemes be developed involving cooperative research between industrial technologists and others from universities and government laboratories to ensure that the long-range research on materials, which are clearly of interest to engine builders, is done. The responsibility for this lies fairly and squarely on the Air Force laboratories.

New research concepts for materials in engines to be developed beyond a 20 year period must consider not only advanced turbine engines but also hypersonic systor scramjets. It is possible to consider recommendations regarding these systems in three different categories. These are:

- Research on existing materials which have remarkable properties in one sense, but have undesirable properties in another sense, have limited their application. Research should be aimed at applying innovative concepts, including processing, and compositional and microstructural modifications, to overcome these limitations.

Example—oxidation resistant refractory alloys: high strength, good ductility and toughness leading to a 200°C increase for blades, while using innovative techniques to provide oxidation resistance.

- Developing and synthesizing new materials, making use of innovative schemes for materials processing. This represents a very exciting possibility for advances in engine technology business, with the possibility of truly revolutionary advances in performance factors.

Example—nanoscale laminated materials: enhanced thermal barrier coatings (260°C increase for HPT blades); erosion and wear resistant coatings; tunable coatings for signature control; metallic multilayers with improved properties in the areas of fatigue, fracture, and creep (similar temperature advantage over Ni superalloys), and multilayer processing of entire components from new alloys.

- Development of new systems applications, where improved or alternative materials will be used, possibly in conjunction with changes in design, which will lead to marked improvements in performance (e.g. thrust to weight).

Example—magnetic bearings: high temperature capabilities of new magnetic materials give rise to radical changes in design of disk systems. It will be possible to dynamically position disks during operation, eliminating contact of components in high-g turns. Ultimately, some classes of engines may be able to run with no liquid lubricant, dramatically reducing cost and maintenance.

Nonlinear Optical And Electronic Materials

Electronic and optical materials are key contributors to the present and future technology superiority enjoyed by the Air Force. They are all required for information gathering, transmission, processing, storage, and display, for the control of weapons systems, and for energy generation and directed energy concepts. Force multipliers, such as IR sensors, RADAR, GPS navigation, smart seekers, and lasers for rangefinders, and target designators are all part of this technology superiority. Certainly, the weapons systems central computer and its silicon microprocessors and circuits are also key. Currently, the electronics and photonics industries are built on only a handful of materials, principally semiconductors, such as silicon and gallium arsenide, and a few other solid state inorganic compounds. Silicon technology will be advanced by the commercial marketplace and the Air Force and DoD will struggle to keep systems up-to-date. The other technologies are all dependent on non-silicon materials—GaAs in digital radar, HgCdTe of IR sensors, unique laser materials, and custom sensor windows for both IR and microwave. These are often referred to as niche materials. The AF has had, and must continue to have, an aggressive R&D program to support emerging materials to maintain superiority of electronic and optical sensor systems.

We expect these materials to continue to play a major role in industry. However, for even higher performance systems, these materials are intrinsically limited, and new materials must be found and developed. In the future, a much wider array of materials, from novel multilayered semiconductors to new polymeric materials, will be available for advanced optical and electronic applications. These new materials will be designed and processed at the atomic scale to provide optimized electrical and optical properties to meet specific Air Force requirements. As our capability to custom design and grow new materials expands, electronics foundries will change to a flexible manufacturing format, where the same growth and processing equipment will be used to create a wide variety of optical and electronic devices on demand.

These improved materials will make possible sensors with high sensitivity across the entire electromagnetic spectrum, data transmission links with greater than 200 gigabits/second, parallel processing of data at breathtaking speeds, three-dimensional data storage with almost instantaneous access, and holographic cockpit displays. They will make possible the next generations of control systems, such as the mounting of sensors and processors directly on aircraft engines. These materials will lead to new weapon concepts, such as directed energy weapons, as well as to the systems which counter them.

Electrically conductive polymers have been evaluated for some time. Polyaniline is well on its way to being the first widely commercially available, processable conductive polymer. Yet more conductive polymers will be needed since polyaniline will not meet all requirements for conducting polymers. New conductive materials, still laboratory curiosities, need to be developed into viable materials, and still others need to be synthesized.

The applications of conductive polymers are myriad. Light emitting diodes, photovoltaics, and corrosion inhibitors based on conductive polymers have all been demonstrated. The AF has interest in these and should support their research and development, as engineering polymers. The Air Force needs these materials as gap sealants, conductive matrix resins, and conductive wires. For example, the F-15 contains approximately 500 pounds of thin-gage signal wire. This could be reduced to less than 100 pounds by conductive polymers. These are niche applications not likely to be addressed by non-DoD efforts.

Weapon systems present difficult materials challenges not often encountered in the civilian sector. The Air Force needs high temperature inorganic semiconductors, especially for applications in engines and other hot environments. While several candidate materials have been identified (e.g. doped diamond), development work should continue in order to bring these materials into the Air Force inventory.

Energetic Materials - Propulsion

Our platforms are vulnerable to longer range, higher performance weapons that are available from the former Soviet Union. Our current propellant systems utilize old technology and cost more and more as incremental patches are applied to bring out-of-date systems into compliance with current operational requirements. The current inventory of propellants and other energetic materials were identified 20 to 40 years ago as having the optimum fit to the cost and performance trade-offs of the time. We are currently flying or using systems that use storable propellants selected in the 1950s and 1960s to meet prevailing cold war performance, cost, availability, toxicity, and environmental needs. Our society, industrial base, and particularly environmental and health laws continue to evolve and redefine our operability restraints without evoking a concomitant change in the energetic materials we employ. Yet ingredients have been discovered and are available that are capable of providing revolutionary payoffs for the armed forces. Other new materials are under investigation. Thus, we can correct the situation by employing our best technology in a cost and time effective manner.

The Air Force needs an aggressive program of research and development to create a new generation of boosters, air-to-air interceptors, air-to-ground missiles, and spacecraft rocket motors based on new technologies. We have fallen behind our adversaries in important areas. High payoff items identified in rocket propulsion are as follows:

- *Near term:* Major improvements for solid fuel motors due to incorporation of advanced binders and oxidizer (5 to 20 percent improvement in mass to orbit or 5 to 15 percent improvement in specific impulse) with a concomitant improvement in liquid systems. Thermoplastic elastomers and gel binders will give environmental and processing advantages.
- *Middle term:* Development of advanced hybrid systems with improved performance (goal of 350 seconds for a strap-on), investigate the use of hybrid concepts, new oxidizers, and new fuels like aluminum hydride.
- *Long term:* Development of cryogenic high energy density materials and propellants like metallic hydrogen (specific impulse greater than 1500 sec, i.e. 4 times greater than LOX/H₂) to revolutionize access to space.

Energetic Materials - Explosives

New higher energy explosives are available, but only minimal usage has been made of these materials. These energetic materials all have the ability to dramatically increase the explosive potential of warheads and bombs. These new materials can be especially effective in directed energy explosive warheads, such as those proposed for use in the next generation of air-to-air missiles. We foresee, in the long term, explosive concepts being developed to allow for "tunability" of explosive charges, as a way to vary the energy output to match the mission requirements. We also need to rethink the design requirements for explosives to match the new needs of moving metal and momentum transfer in smaller warheads. Advanced thermites are available that provide the ability to attack chemical and biological warfare sites with improved probability of destroying the target without release of the agents. High payoff items in this area are:

- *Near term:* Major improvements in the capability and/or size reductions of specialized warheads due to implementation of new materials, such as CL-20, trinitroazetidine (TNAZ), and energetic binders. New explosives are valuable for reducing the size of precision weapons.
- *Middle term:* Enabling technologies to allow tuning of explosive charges, implementation of advanced thermites, nano-formulated explosives to improve yield and control.
- *Long term:* More esoteric concepts include using theoretically possible molecules, such as polymeric nitrogen (3 times the energy density of HMX), fuels such as metal hydrides, and cryogenic explosives.

Fuels

Fuels have two basic functions; as a dense energy source and as a coolant. The energy density of hydrocarbon fuels combusted with air is unsurpassed. As a cooling fluid, state-of-the-art fuels (JP-8) have only limited capacity. Current and next generation turbine engines are exceeding the capacity of the fuel to handle the heat load. This results in coking of the fuel and subsequent clogging of fuel passages and ignitors.

Endothermic fuels are the enabling technology for turbines in the future. An endothermic fuel uses the engine's waste heat to create a more energy dense fuel. Endothermic fuels are

simply fuels that decompose under a thermal stress to absorb heat (thereby providing a heat sink) and give hydrogen and an olefin. The engine is cooled by heat absorption caused by a chemical process, and more energy is available for the combustion process. Over the much longer term, it may be possible to synthesize fuels on-board from, for example, low flammability components in order to reduce the risk of battle damage. The synthetic route may be endothermic, thereby allowing the fuel to also act as an efficient coolant. High payoff items are:

- *Near term:* Implement improved thermal stability fuels and improved cleaning agents.
- *Middle term:* Endothermic fuels.
- *Long term:* Chemically reacting and in situ synthesized fuels.

Lubricants

Advancements in lubricants and seals, as well as sealants and other nonstructural materials, are absolutely critical for the Air Force to meet mission requirements of aircraft and space vehicles of the future. Increasing the thrust-to-weight ratios of future turbine engines will require the development of efficient lubricants that can withstand these higher temperatures. New lubricants must be developed to reduce the propensity for coking of current engines and when new, more efficient engines are fitted to aging aircraft. Turbine engine temperature requirements are exceeding the capacity of state-of-the-art lubricants. Current synthetic polyol esters have an upper temperature limit of 400°F, while perfluoropolyalkylethers, which are under development for future advanced turbine engines, will have upper temperature maximums of 630°F to 700°F. Compatible sealing technology must also be developed hand-in-hand with advanced lubricants. Both liquid and solid lubricant technology developments, including technology for hard coats and wear resistant coatings, will be necessary to meet the requirements of both expendable and man-rated engines of the future. Greatly improved liquid and solid lubricants must be developed to increase the lifetimes of spacecraft moving mechanical assemblies, such as control moment gyros and reaction wheels.

Thermal breakdown of lubricants is not currently a major maintenance problem for the Air Force. However, future systems may be severely compromised due to lack of adequate lubricants or adequate development of new concepts. High payoff items are:

- *Near term:* Increase the thermal stability of polyol ester lubricants to 450°F and increase the stability and capabilities of the perfluoropolyalkylethers and sealing systems to 700°F.
- *Middle term:* Investigate solid lubricant technology to provide lubrication to 1500°F-1800°F. Eliminate lubricant completely by use of single fluid concept (100 pound weight savings per engine), couple with endothermic fuel for additional gains or use vapor phase lubricant (Note: Single fluid concept is a very high risk approach).
- *Long term:* Magnetic levitation of motor parts and bearings. (Note: Solid or liquid lubricant may still be required for startup and shutdown).

Materials For Low Observability

Low observability (LO) is the application of technology to reduce aircraft signatures in selected regions of the electromagnetic spectrum in order to evade detection. LO is required in the radio-frequency (RF) and infrared (IR) regions, and it is highly desirable in the visible. These requirements are based on current sensing technologies: operating in the RF and IR ranges and on the ready availability of optical sensors.

The major gains in survivability achieved to date have come from the combination of improved designs and advanced materials. Future improvements in this area are not likely to be realized without advanced materials.

Materials interact with RF radiation in many ways, from bulk conductivity to molecular rotation modes and nuclear magnetic resonances, so there is a wide variety of possibilities in addressing LO. Many present and future trends in materials research can be expected to have LO/RF applicability. RF-absorbent materials and structures employing either conductivity or energy-coupling properties of the materials are bound to be the primary means of providing LO. Adding LO to fielded aircraft will continue to be a need. Additionally, to the extent that LO/RF is addressed with geometric solutions, materials that can change shape could enhance LO. Other "smart" materials may also be relevant, such as those with tunable dielectric and electronic properties. The scope of LO research should not be limited to IR and RF due to the possibility of future improvements in sensor technology.

Interactions with IR and visible radiation are more limited, with surface reflectivity and the photochemical realm carrying the current technologies. Innovative LO techniques in these regions will therefore require basic research, and the necessity for matches to background IR characteristics make solutions to this problem expensive.

A more extensive discussion of LO technologies is beyond the classification level of this document.

Materials for Missile, Space, and Launch Systems

Affordable, reliable, maneuverable, and smaller space systems are the key to the future of space systems. Of the many materials and materials processing technologies being pursued, two areas stand out as offering significant payoffs for missile and space systems: molecular self-assembly/nanotechnology and miniaturization/microelectronic machines (MEMS). Both fields have developed rapidly, and both offer potential for lowering the cost and improving the performance of space and missile systems.

Nanostructured materials have significant promise for a number of applications, both military and commercial. For aerospace uses, nanometer-based processing could provide advanced electro-optic materials, sensors, and specialized structural materials. Nanoassembly offers the possibility for creating multilayer structures specifically designed on a molecular level. For example, work is being conducted on multispectral windows, which consist of nanostructured silicon with specially designed dielectric properties imbedded in diamond or other high-temperature substrates.

Because of the high cost of inserting payloads into space, (\$10,000 - \$20,000/16) miniaturization of space components is a high-payoff investment. For missiles, cost impacts are less certain, but miniaturization clearly offers the advantage of improved performance. The reduced size will increase the need for effective thermal management. Continuing advances in miniaturization of electronics and sensors will reduce both the weight and volume of satellite and missile components. Micromachines enable extensive miniaturization of components and can provide devices with unique capabilities. Such devices include ultrasensitive acceleration sensors, microactuators, pumps, reflectors, and even gearboxes. High power density advanced IR sensor materials and nonlinear optical materials for high speed on board data processing and transmission will make major contributions to both weight and volume reduction and increased mission capability. Recent developments, such as microtubes, offer possibilities for micromachine applications as well as potential uses in processing unique components, such as self-cooled nozzles or self-monitoring "smart" devices and structures.

The achievement of micrometer precision in fabricating new devices revolutionized the electronics industry during the 1960s and 1970s, which in turn enabled development of a new generation of advanced weapons systems. Similar revolutionary advancements may be realized over the next few decades through nanometer processing. A consistent long-term investment in the fields of nanotechnology and miniaturization is strongly recommended. These fields offer great potential for enabling the development of new components and devices for aerospace systems and also have potentially broad commercial significance.

In addition to light weight, high temperature materials for launch systems, another key area in which improvements to rocket propulsion are needed are bearings in turbopump engines. Traditionally, vibrations experienced when the pump is cooled for liquid oxygen operation cause heat generation, leading to thermal runaway (LOX to GOX). In an attempt to solve this problem, these motor bearings are made of silicon nitride machined to a very fine finish with a low coefficient of friction to assist in maintaining low temperatures during operation. There are two problems with this approach. First, these bearings require high quality silicon nitride produced only in Japan. Second, the precision production and machining required for the necessary surface finish are done in Germany due to the absence of U.S. capability. Thus, there is no domestic source for these materials or components. Clearly, it is essential that our ceramics capabilities be markedly improved, not only for the production of high performance materials but also in the high level machining required to render these materials suitable for component application.

Another important area is developing approaches to combine high thermal conductivity, high modulus, and low coefficient of expansion with improved strength in carbon fiber composites. Thermal management and dimensionally stable structures are often limitations in space. Simultaneously achieving the thermal, electrical, and optical properties as well as the structural loads and displacement requirements will lead to decreased weight.

Function-Integrated Materials

The technological selection of materials commonly targets a given collection of properties, which define the material's primary function in a system. For example, in an Air Force context, carbon-epoxy composites of an aircraft serve a structural function and are selected

because they offer a good compromise on low density, high stiffness, and high strength. Piezoelectric materials, on the other hand, are not usually selected for a structural function but for their ability to perform mechanical-electrical energy transduction with high efficiency. The materials of optical fibers are selected, of course, because of their light transmission properties, but they do not have, in fact, ideal mechanical flexibility and repair processability. Materials as we know them and use them at the present time are largely "monofunctional." Many materials-enabled technologies can be envisioned through synthesis of structures in which multiple functions are integrated by molecular design in one material. The best examples of function-integrated materials by design are, in fact, found in biology and remain generally an unachieved goal in technology.

The vision for function-integrated materials would be materials in which sensing functions using photons, mechanical forces, and/or magnetic or electric fields are built into the molecular structure within the boundary conditions of a secondary or even tertiary function related to structure, or the ability to interconvert energy. Such binary and ternary combinations of functions by structural design has not really occurred technologically. An example of the application of such materials in Air Force systems would be sprayable and adhesive batteries or solar cells for the wings of aircraft to convert solar energy at high altitudes to electrical power. These sprayable batteries would be ideally composite structures that have the processability of currently known materials and even have load bearing capacity. Another relevant technology would be sprayable, structural composites that have a switchable antenna function to receive and process information or be stealthy on demand. The concept can be extended to sprayable materials for tunable radomes and special sensors. To close the loop on function integration, the new materials that should be explored must have potential to be recyclable. This is important not only for environmental purposes but also because function integration in materials will enable technologies at a cost.

An extremely promising and unexplored group of materials for function integration are nanophased organic materials and nanophased composites. The materials concepts proposed include the following:

- Nanoparticle polymers, that are polymeric materials made up of single molecule, nanosized particles with defined shape.
- Nanostructured composites containing organic materials and semiconductors.
- Self-assembling superlattices of discrete inorganic, organic, and/or composite nanostructures.

Energy Generation and Storage

As more advanced spacecraft are fielded in the next century, a need will develop for ultrahigh energy density and high power density secondary batteries and/or supercapacitors to act as electrical buffers and power sources. These power sources should be capable of delivering in excess of 100 kW for periods of minutes (a demand that would be met by supercapacitors) and 30 kW more-or-less continuously (to be met by secondary batteries). Current battery and supercapacitor technology cannot cost-effectively meet these needs. A concerted effort is required to develop advanced power sources. Promising approaches include solid polymer electrolyte batteries based on lithium, which are now being developed, and advanced "all polymer" batteries,

still to be developed, that involve the movement of protons through the lattice on charge and discharge. We need secondary batteries with specific energies of greater than 500 W-hr/kg, and supercapacitors with power densities greater than 10 kW/kg. Based on previous battery development cycle times, the required technology is unlikely to be available before 2020.

Significant gains in solar cell technology can still be accomplished. One approach is more extensive use of compound semiconductors with high conversion efficiencies. Another is to enhance the performance of solar cells by tuning the semiconductor band gap to match the solar spectrum. Record breaking conversion efficiency of 27 percent has been demonstrated using these strategies. Another exciting possibility for higher efficiency is the "discovery" of semiconductor materials that generate more than one electron per photon, through hot electron or Auger generation processes. These types of materials are predicted to have conversion efficiencies approaching 50 percent.

The Air Force should also consider developing advanced "ambient temperature" fuel cells as LO alternatives to diesel generators for ground support functions. The most promising systems are advanced proton exchange membrane fuel cells like those that flew on Apollo and Gemini, but fueled by methanol without reforming. The technical challenge is to develop electrocatalysts that will permit the direct oxidation of methanol at the anode. Even more advanced systems might use jet fuel as the fuel, but this will require enormous advances in electrocatalysis. Other more far reaching fuel cells include those that burn biofuels using enzymes as electrocatalysts.

There are opportunities for impressive advances in airborne power generation based on advances in magnetic materials. These include the development of superior soft magnetic materials, possessing simultaneously high strength, high temperature, high magnetic strength, and low electrical loss, for advanced motor/generators directly integrated with small and large turbine engines for airborne power and self-starting aircraft. Advanced hard magnetic materials are also required for bearing applications on these same systems.

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1.0 Why Materials are Important

Air Force systems are extremely complex integrations of numerous materials and materials systems from high-temperature turbine engine blades to airframe structural composites. Thus, the selection of key design materials impacts critical issues of cost, strategic performance, and reliability. While these issues are somewhat interdependent, and their impact on Air Force systems is sometimes difficult to separate into individual roles, there are a number of common themes that will drive future developments. Key driving factors include the need to lower costs and improve affordability of both new and upgraded military systems, continued high-performance systems that assure military superiority, longer life and more reliable systems and components, and strategically important issues, such as better stealth materials and nonpolluting fluids and propellants. Finally, we believe that the Air Force needs to be the leader in novel materials R&D, such as computationally synthesized functional materials and computational materials processing. Research and development in these areas could lead to dramatically reduced time and cost of development through elimination of extensive testing and current practices of creating expensive data bases for design and manufacture. In summary, we envision research and development of new materials in the above areas will revolutionize the warfighting capabilities of the USAF.

1.1 Costs and Affordability

Affordability is a key criterion for assessing the value of new technology to determine the feasibility of incorporating it into military applications. We define affordability in terms of the life-cycle cost of a weapon system, including acquisition, materials and fabrication, operating/maintenance/assurance, and disposal costs. Although enhanced performance continues to be a high priority, improvements must be achieved with affordable technologies. This means that revolutionary materials and processes, which in some cases are more expensive than those currently in use, may have a favorable impact on a system's life-cycle cost and may also provide performance advantages.

1.2 Performance Issues

New materials offer improved performance by being lighter and by possessing specific functional (i.e., mechanical, electrical, and optical) properties. Of course, for a given thrust, decreased weight leads immediately to increased thrust-to-weight. However, when considering life-cycle costs, (i.e., costs of manufacture as well as engine flight hour maintenance and operational costs), one pound of engine weight saved can lead to a savings of 9 million gallons of fuel per engine over the life of the unit. The savings are immediately realized when considering jet fuel costs \$0.55/gallon. Lighter materials play a significant role in reducing engine weight and therefore contribute directly to remarkable reductions in life-cycle costs. For example, the estimated weight of a compressor bladed ring made from existing materials is about 55 pounds, whereas the same component fabricated from Ti-based metal matrix composites would weigh 10 pounds, resulting in a significant savings.

In general, in gas turbine engines, thermodynamics are optimized by increasing the pressure of the air and the temperature of the combustion process. Hence, allowing higher operating temperatures will lead to increased efficiencies, which can be translated into either reduced

specific fuel consumption or increased power. For example, if materials and innovative designs were available for compressors, for combustors, and for high-pressure turbines, increased compressor discharge, higher combustion temperatures, and high-pressure turbine inlet temperatures would markedly increase the efficiency of the engine. Materials improvement, in this context, should emphasize not only better mechanical properties but also improved resistance to corrosion and oxidation for extended times.

1.3 Reliability Issues

Repair and replacement of degraded or failed components can be extremely costly. For example, when a turbine disk is degraded by fatigue in the bore of the component, the whole disk is replaced, at a cost of \$40K. Considerable savings might be effected by use of new materials with improved properties and with production methods that are more reliable. Furthermore, as described in the body of the report, changes in design to permit replacement of only the degraded part of the component may also lead to significant decreases in costs.

In terms of strategic implications, the fate of the F-16 fighter may be considered. At present, a serious failure involving a crack in the aft fuselage frame at the point of joining to the tail plane has been discovered. The solution is either to strengthen the frame—undesirable, but required in case of imminent threat—or to replace the rear frame assembly. The problem is that only a small fraction of the number of frames required to refit the fleet is available, and there is a significant probability that up to 700 planes will be grounded. This is a strategic nightmare, since fleet readiness is impaired markedly. In replacing these rear frames, new materials will be used, namely Al-Li alloys, which will be more reliable than the older alloys that were used originally. Also, these new alloys have lower densities and hence result in weight savings, which is an additional benefit.

1.4 Strategic Issues

Importantly, new capabilities, such as stealth, nonchlorine containing propellants, superemitters, and composites will allow missions to be performed with minimum detection and loss of aircraft and personnel.

1.5 Payoff From Novel Materials Development

There has been extremely exciting progress in computational methods to describe materials behavior, which will change the way materials will be developed and processed in the future. The progress is such that we envision predictive capabilities that will permit the design of new materials by computation, similar to the design development of the Boeing 777 aircraft. There are two advantages in this scenario: 1) The cost of alloy and materials development will be drastically reduced by eliminating expensive experimental programs of testing, and 2) brand new materials may be predicted and synthesized, which would not necessarily have been discovered by experiment. Coupling of computational and experimental methods will lead to detailed understandings of the properties of materials over many orders of magnitude of dimensional scale, atomic-, nano-, meso-, micro-, and macrostructure, as well as over a very wide range of time constants from atomic frequencies to hours. Concurrent to this computational development, there is an ongoing strong effort in new schemes for processing and synthesizing

new materials. These materials are synthesized from the developments at the atomic/molecular level, are typically nano-scaled materials and composites, and offer revolutionary sets of properties. Successful implementation of these programs will lead to not only the application of new materials to existing aircraft platforms, but also the development of novel designs and technological approaches allowed by the unusual behavior of these materials to aircraft and space and missile systems.

2.0 New Comprehensive Materials Policy and Infrastructure

2.1 Introduction

The Technological Importance of New Materials

Many materials have emerged during the 20th century, enabling technologies that impact directly on our defense systems. In the context of the Air Force, the discovery of a synthetic route to aluminum metal and other materials with high strength to density ratios for airframes, synthetic rubber for tires, and large silicon single crystals for computers have all been key discoveries of this century. The potent technology-enabling power of new materials is obvious if one considers a hypothetical 1995 world in which these three materials and the processes for their large-scale synthesis were not known but are to be discovered during the next 50 years. Fifty years is, in fact, the historical time span over which these three materials emerged during this century. There are many other materials discoveries in this century that might be considered in this illustration, including systems such as lightweight organic composites, high-temperature titanium and nickel alloys, piezoelectric materials, capacitors, high-temperature ceramics, synthetic diamonds, and many others.

Our capabilities in chemical synthesis, characterization of structure and properties of materials, and computation are rising exponentially. Thus, there is virtual certainty of successfully discovering even more new materials and process technologies in the next 50 years. However, U.S. capabilities, working independently in the three areas needed for new materials and process discovery (synthesis, characterization, and computation), will not easily lead to success. The key to maximizing the probability of success is for the interested parties, the Air Force being one, to develop a well-thought-out new comprehensive materials policy.

Over the past century, the discovery and invention of new materials occurred largely in synthetic chemistry laboratories. The large-scale synthesis of aluminum and other metallic systems, synthetic rubber, ceramics (silicon nitride with potential for high-performance engines), and the epoxy matrices of composite materials are all obvious examples. More recently, as the field of materials science and engineering has developed, more structural components have entered the field of new materials discovery. These new elements bring an appreciation of the impact that microstructure or nano-structure has on the characteristics of materials systems and of the critical role that materials processing plays in defining these materials systems. Silicon chips are a good case in point. Silicon was known at the dawn of aviation, but the exotic electronic properties of the low-defect density single crystals that led to the information age were not known until more recently.

It is impossible to predict the technical breakthroughs that may emerge in the next 50 years, but it is possible to envisage potential discoveries. It is reasonable to believe that systematic coordinated research by scientists of many disciplines will lead to many if not most of those discoveries. Furthermore, the high-risk nature of investment in new materials research and the current industrial climate in the U.S. will require greater amounts of federal funding for basic

research and exploratory development (i.e., 6.1 and 6.2) to maintain the critical mass required to successfully invent and transition technology-enabling materials.

There are several reasons to believe that materials science breakthroughs might be more difficult to attain over the next five decades. One is simply the current technological sophistication, which makes the targets much more specific and the required novel properties extremely demanding. Another is the number of requirements that new materials will have to satisfy in order to be acceptable to designers. Two key requirements for all materials will be the environmental impact of their preparation and disposal and the closely coupled requirement of implementation cost. The combination of these two cost factors, with acquisition cost, reflects a new or renewed interest in affordability as a design factor. Before describing what might enhance future mechanisms of new materials discovery, it is useful to consider what could be considered at this time as typical of the "technological gems" the Air Force will find in the arena of new materials and processes.

High Aims in New Materials for the Air Force

Consider a new generic class of structural polymers for ultralight airframes that does not require carbon fibers for reinforcement, and is processed by "reversible sintering." This type of processing, presently unknown, would be somewhat analogous to ceramic sintering or powder metallurgy techniques, and would impact greatly on the cost relative to current day composites. More importantly, however, its reversible nature, possible given the molecular nature of the material, would offer the possibility of recycling airframes for other uses if not for aircraft. The basis for this concept is offered in Section 13. Another example would be finding revolutionary photonic materials that utilize photons instead of electrons, and that may increase by orders of magnitude the rate at which we transmit, process, and store information. With such materials, switching speeds can be 10,000 times faster than current electronic silicon-based technologies. Based on current knowledge, these materials are likely to be fully or at least partly organic composite in nature. Thus, they would significantly affect the weight and possibly the size of devices on aircraft, satellites, missiles, or rockets, impacting also on the number of new technologies that could be accessed with these materials. Again, some thoughts are offered on this subject in Section 13. One last example could relate to solid energetic materials that would be molecularly designed to have nanometer- or micron-sized regions of all key ingredients. The vision would be to generate the ability to design single-component solid propellants and explosives with microstructural control and with the capability of being processed as macroscopically ordered structures, for example, nano- or microtubes of oxidizer in fuel matrices oriented in a common direction within a charge. Alternatively, consider layered structures self assembled from a fuel-oxidizer block copolymer. Such materials may bring spatial control of focused energy, homogeneous energy dissipation and safety, as well as enormous increments in specific impulse given their densities and other factors detailed in Section 10 of this report. Self-assembling materials as described by George Whitesides in the September 1995 *Scientific American*, may enable not just materials, but these revolutionary materials systems, and perhaps self-assembled devices and machines. The generic concept here for such new materials could probably also be applied to the fuels area.

2.2 The Evolution of Mechanisms for Materials Discovery

Generic Evolutionary Changes for All Materials

As mentioned previously, some of the Air Force-critical materials of this century, such as aluminum produced in large scale and synthetic rubber, were discovered in chemistry laboratories. In these two cases, and in others as well, a target was being pursued. Aluminum was known in the 19th century as a laboratory curiosity, but because of its low density there was interest in finding a viable methodology for its synthesis in large scale. In the case of synthetic rubber, a material like it, natural rubber, was already known and was determined to be a technologically desirable substance for military purposes during the Second World War. Thus, the transition from polyisoprene to vulcanized polybutadiene was in a sense a biomimetic discovery. This begs the question of whether or not a material like rubber, which is critical for the landing of aircraft, would have been invented in the absence of polyisoprene in nature. The point is how different will be the mechanisms for materials discovery in the future, in that the infinite number of synthetic permutations will have to be guided by at least a rudimentary knowledge of how molecular structure is connected to physical properties. This type of expertise does not exist in the classical chemical laboratory. Also, the expansion of our knowledge base has been such that an exponential rise is occurring in the number of possible permutations for new materials. For example, in the early part of the century, there was little awareness of the potential of engineered composite materials. Also, our organic synthesis capabilities have been increasing steadily over the past few decades, thus increasing the number of possible structures that could be explored. Thus, a permutation explosion will exist for new organic structures, ceramics, metallic alloys, intermetallics, and composites. For this reason, on the experimental side, the future mechanisms of materials discovery will have to include rapid property-screening methodologies with very small laboratory-scale quantities, milligrams to grams, and also will have to be closely coupled to a scaleup resource when a promising new material is identified. On the theoretical side, there is no question that the "dry" search for new materials using computers will aid the exploration, and this will raise the probability of critical discoveries. Both rapid screening of new materials with small quantities and the computational search for new structures are important evolutionary changes in the mechanisms for materials discovery.

Combinatorial Libraries: One Possible Mechanism for Materials Discovery

In the context of the permutational explosion in metals, ceramics, organics, and composites, how will the scientific community proceed to search for technologically important new materials? For example, how should we search through structural space for superconducting solids at temperatures approaching room temperature, highly efficient luminescent materials for displays, nonlinear optical materials for photonics, polymeric structures of high compressive strength and stiffness, powerful adhesives for adverse environments, and for many other technically important materials? It is clear that, at the present time, the theoretical and computational resources, including thermodynamic data and models, to fully predict these structures of technological importance, are not in place anywhere in the world. Over the past decade, chemists and biochemists have developed the so-called combinatorial approach to search for specific molecules, particularly for drug development. This approach generates "combinatorial

libraries" consisting of large arrays of specific families of molecules to test for molecular binding characteristics or catalytic activity. The application of this approach to the search of superconducting solids was reported very recently.¹ This work described methodology for parallel synthesis of spatially addressable arrays containing superconducting copper oxide thin films. Libraries containing more than 100 materials were generated by sequential sputtering of various precursors on different substrates, using masks to vary the chemical composition. The final materials were produced by thermal processing and then screened for superconductivity using rapid scanning probes.

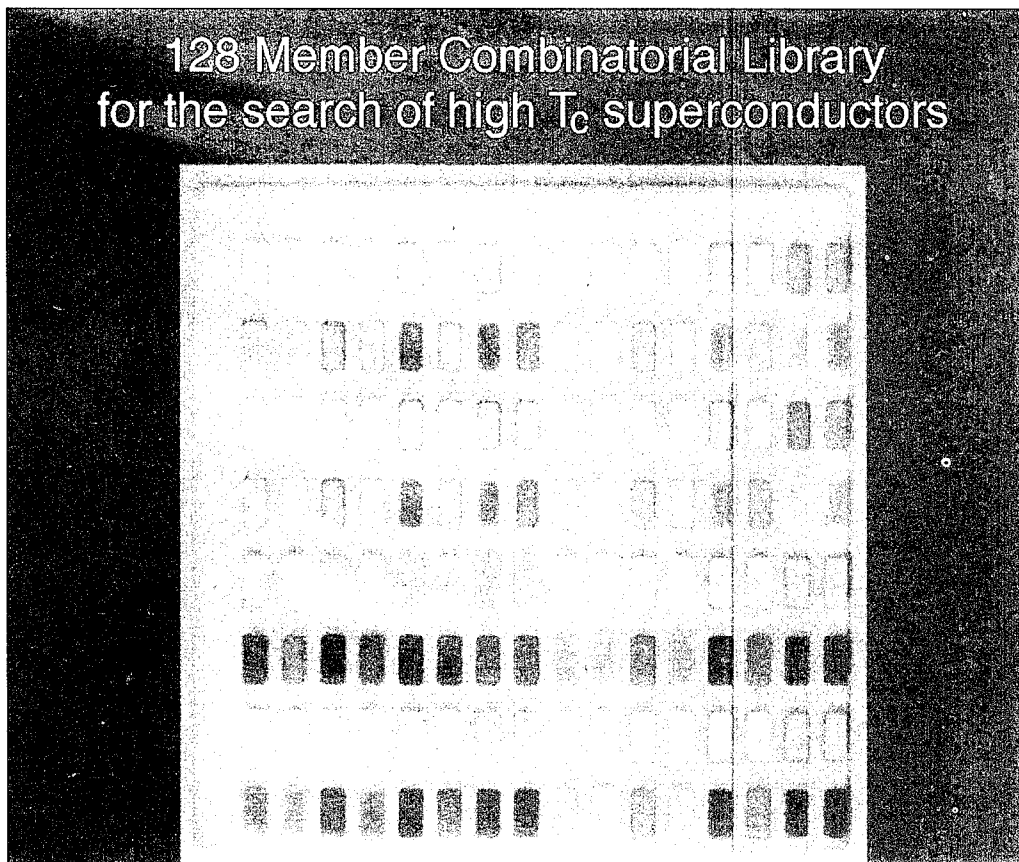


Figure 2.1 A Combinatorial Library Design to Search for High-Temperature Superconducting Materials

It is reasonable to assume that this type of empirical search for new materials could be extended to other types of solids considered to be critical for Air Force technologies. These

1. *Science*, Vol. 268, p. 1738 (1995).

would include nonlinear optical materials for sensors and rapid information processing, advanced magnetic materials for the more electric aircraft, luminescent materials for aircraft panel displays, energetic materials, conducting polymers, intermetallic alloys, or even single or multicomponent composite structural materials. However, each different physical property will require the development of different rapid scanning probes, which may have to be new technologies in their own right. Furthermore, the three-dimensional hardware required to search for new materials in large arrays containing hundreds or thousands of compartments may be quite challenging. It will also be necessary to find methodologies that will allow in situ organic chemistry to be performed in materials libraries. Such reactions would include polymerization schemes, as well as the chemical synthesis of monomers or oligomers. Finally, the simulation of materials processing in the microenvironment of the combinatorial library is not a trivial objective but should be explored. This is, of course, necessary in order to access microstructural factors and not simply chemical composition in a new materials library.

It is unlikely that combinatorial libraries alone will lead to the successful search of new Air Force-critical materials. However, it may be useful to couple empirical combinatorial efforts with computation in order to select the correct homologous sets of materials that should be investigated. Another approach involving computers coupled to combinatorial libraries would be to use genetic algorithms to optimize the property being searched and in this way guide the experimental array to be investigated. When promising materials are identified through combinatorial libraries, it will be critical for investigators to have access to a scaleup infrastructure. In fact, this coupling should be considered a critical issue in any Air Force decision to fund exploratory work for new materials and must be an integral part of a new materials policy.

2.3 Scaleup of New Materials and U.S. Industrial Capabilities

Scaleup Procedures

The full potential of a new material for technological implementation cannot be assessed without scaleup of mass by at least three orders of magnitude relative to the amount typically produced by the original discoverers. In research dealing with organic materials, which tend to be the most synthesis-intensive, once a synthetic pathway has been identified, researchers will produce less than one gram of the substance. Even though a materials target might have been identified, the driving force of the investigation is often the development of new chemistry. A similar situation is encountered in inorganic synthesis targeting the discovery of new chemical precursors for ceramic materials.

Conventional characterization of structure and sometimes physical properties, which does not require large quantities, is often done in-house or through external collaborations and quite frequently is the end of the loop for that particular material. The infrastructure to pursue scaleup of what appears to be a promising material as defined by the original target is in most cases nonexistent. This particular situation is very common in both academic and government laboratories, and sometimes even in industrial laboratories. Traditionally, however, U.S. chemical industries have had scaleup capabilities for their own internal explorations.

Scaleup efforts are not trivial to undertake, since they most likely will involve not only chemists but also chemical engineers, materials scientists, and mechanical engineers. In a scale-up effort, chemists and engineers need to work closely because often the synthetic pathway that

works for laboratory-scale synthesis cannot be implemented in large scale. A redesign of the pathway, often suggested by the specific problems faced in scaleup, needs to be implemented. The number of chemical reactions required to reach the final product must be minimized, and the yield of each reaction has to be optimized. This is clearly necessary, since the final of the yields for the new material is given by the product of yield in the six various reactions of the pathway.

The U.S. Industrial Problem for New Materials Exploration

At the present time the United States faces a major problem with regard to exploration of new materials. R&D efforts are being downsized substantially in all areas, but the exploration for new materials followed by in-house scaleup is possibly affected even more than other technical areas. For example, software and silicon device industries seem to be in a relatively healthy state with regard to R&D, and, of course, computer-based service industries are extremely popular. The sector that transforms raw materials into high value-added materials is definitely weakened in our country. Over the past decade, chemical industries such as Celanese Corporation, and engine companies such as Allison, and others, have been sold to foreign multinationals. Those chemical industries that still retain new materials interest will only pursue systems that can be produced in the billion-pound scale needed for consumer goods. On the other hand, the sizing materials that bond fibers and matrices in composites, and make up hardly a few percent by weight of a structural composite, do not justify a serious exploratory effort for a large chemical company. Yet molecular explorations for sizing materials could improve significantly the performance and reliability of composites used in advanced airplanes; novel sizing materials could also be used to improve fire retardancy of composite vehicles, develop self-monitoring composites for microstructural damage, and perhaps even self-healing of damage. To summarize, in the context of new materials, our infrastructure for discovery in all classes of materials is eroding rapidly.

The global picture in the United States for the discovery of new materials, which would impact directly on the technological superiority and effectiveness of the Air Force on the battlefield over the next fifty years, does not appear to be encouraging, in 1995. A new materials policy in the scientific establishment of the Air Force is therefore of critical importance. To design this policy, the declining interest in this area within U.S. industry must be accepted as a reality, and the origin of the problem must be understood. Without pursuing a detailed economic analysis of the problem, it is probably safe to assume that the slowing innovation in new materials from industry is simply an issue of high-risk capital investment. For the sake of technological lead, the Air Force and other DoD agencies must therefore invest funds in this area.

2.4 The New Materials Exploration Loop: A 6.1 Funding Model for the Air Force

The model proposed is to fund new materials research at Air Force laboratories, research establishments, and academic institutions that would be scrutinized carefully for in-house or external network capabilities for closing the new materials exploration loop. The first step is conventional, and should be a serious evaluation to determine if the proposed exploration is highly innovative and targeted for Air Force-specific needs. However, the new elements in the policy should include requirements that demonstrate real, budget-committed connections to a

structure-property screening capability and, most importantly, a second connection to a scaleup capability. The scaleup effort should probably be funded with 6.2 funds, but the basic premise in the proposed loop is to establish an early coupling of 6.1 and 6.2 funding that seems to be critical for the area of new materials to be successful. A final requirement before the 6.1 investment is made should be a vision by investigators, bearing evidence of reality, of identifying an industrial establishment that could implement the production of proposed concepts. The connections for structure-property screening and scaleup could exist in-house or be established externally in industry, other government laboratories, or academic institutions. The importance of a connection to a scaleup capability is, of course, the fact that many properties of new materials remain undiscovered because of limited availability of the novel material.

The basic philosophy of the new materials loop is the fact that proof of concept and application appear to be the necessary driving forces at present for industry to consider investing in the development of new materials. It is in this context that the concept could be regenerative to the national new materials infrastructure. It is also clear that coordination with other DoD agencies is of key importance in this particular area. A part of the overall vision for the Air Force is also to create an internal mechanism to accelerate the acquisition of the many forms of data needed once a new material with technological advantage is clearly visible. A diagram of the new materials exploration loop is shown in Figure 2.2.

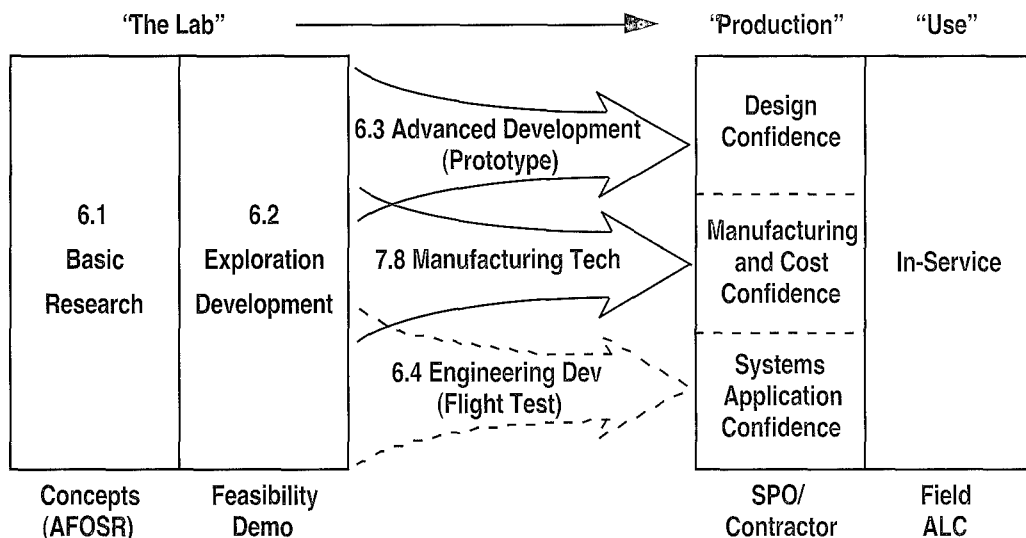


Figure 2.2 New Materials Exploration Loop

2.5 Scaleup Stations for New Materials

From an R&D standpoint, scaleup of new materials is a unique activity for the following reasons. At academic institutions, and even at private research institutions, and government laboratories involved in basic research, scaleup of materials is not regarded as an intellectually challenging, creative activity. In academic institutions, for example, it is difficult to involve creative graduate students in scaleup work. In fact, it is often difficult to integrate with current

degree programs research on scaleup of new materials. This is particularly true in chemistry programs. At the same time, in chemical engineering programs, where there used to be some emphasis on scaleup research, there has been a declining interest in the subject. The situation in industry has already been described; therefore, serious consideration must be given to the establishment of scaleup stations at either Air Force or academic laboratories. In these stations, promising new materials would be scaled-up by two or three orders of magnitude relative to basic research laboratory scale. The advantage of establishing these stations in laboratories, where the truly exploratory synthesis and characterization work is being conducted, is fairly obvious. The colocation would offer the possibility of a very beneficial synergistic interaction for the final outcome. At academic institutions, these stations should employ primarily professionals and technicians to address the incompatibility issue between scaleup efforts and academic materials synthesis research leading to a degree. The downsizing of industrial R&D efforts has created a surplus of highly trained personnel with technical degrees that could be employed for this important effort.

2.6 Commercial Payoff in Materials Innovation

There is great potential for commercial payoff in new materials discovery, since they seldom have unique applications. In contrast to specific devices, the potential commercial payoff is almost guaranteed, since new structural and functional materials permeate automatically into many other sectors of the world's economy. Among many examples, one could cite two that demonstrate this principle: the use of aerospace metals in orthopedic surgery and the use of advanced composites in sporting goods.

2.7 Conclusions and Recommendations

- A strong program of 6.1/6.2 funding for Air Force-relevant new materials exploration needs to be established. This program should be established under the guidelines of a new materials exploration loop described above with the objective of inducing some regeneration of a new materials infrastructure.
- We need scaleup stations that will support synthetic and characterization activities in, and the capability of, academic and government laboratories in new materials research.
- While the next 50 years might be totally infertile worldwide with respect to technological implementation of new materials, or may produce revolutionary discoveries, an important policy question to address is whether or not U.S. government institutions, the Air Force in particular, will take the risk of *not* investing in the exploration for new materials. The risk is to be assessed considering that other important countries, and potential adversaries, are investing in new materials exploration, especially Japan, Germany, France, Korea, China, and several emerging countries in the Third World, as well.
- The absence of a U.S. government-supported effort in new materials augments the risk to technological lead, since U.S. industry is only weakly involved in this exploration at present, and is unlikely to be strongly involved in the foreseeable future.

- There is great potential commercial payoff in new materials discovery, since they seldom have military-unique applications. In contrast to specific devices, the potential commercial payoff is almost guaranteed, since new structural and functional materials permeate automatically into many other sectors of the world's economy (e.g. composites in aircraft, sporting goods, and orthopedics). However, advanced materials of specific interest to the Air Force frequently represent a market that is too small to interest commercial suppliers. Accordingly, it would be foolish and inappropriate for the Air Force to rely solely on commercial suppliers for its advanced materials needs. This argues strongly for a robust in-house materials R&D program and possibly even production capability.

3.0 Materials in the Current Air Force

3.1 Introduction

It is often said that those who fail to heed the lessons of history are condemned to repeat them, and this is no more true than in politics and technology. It therefore behooves us to examine the role of materials in the past and current Air Force, with the goal of identifying the roles played by advanced materials in the development of Air Force systems. In particular, we seek to identify reasons why certain materials were introduced into aircraft systems, to identify the factors that controlled their rate of introduction, and to ascertain the impact of these materials on aircraft operation from an historical perspective. For example, we often hear that a new material was introduced to improve performance, but improved performance means different things to different people. Thus, we all accept that new materials have allowed for greater airspeeds (e.g., titanium in the SR-71), but have they improved payload?

In this chapter, we explore these issues from an historical perspective by examining the performance characteristics of a large number of military and civil aircraft extending from World War I to the present day. Much of this analysis has been made possible by the generosity of Richard N. Hadcock, RNH Associates, Inc., who kindly allowed us to use statistical data on various aircraft systems prior to their publication in book form.

3.2 Structural Materials

The first aircraft to fly, the Wright Flyer in 1903, was fabricated largely from composite materials. The choice of this material was dictated by various factors, including weight, strength, cost, and, of course, availability. Over the two decades that followed this historic event, wood and fabric reigned supreme with only a few excursions by designers into the use of metals for systems other than engines, bracing, controls, and landing gear (Table 3.1). From an historical

Table 3.1 Airframe Structure Definitions: 1915-1940

Construction Type	Elements
Composite Structure	<ul style="list-style-type: none"> • Wood, steel, or aluminum framing • Steel bracing wires (internal and external) • Fabric or aluminum non-stressed skins
Stressed Skin Construction	<ul style="list-style-type: none"> • Wood, metal or composite load-carrying skins supported by wood, metal or composite internal structure (spars, ribs, bulkheads, or frames)
Transition from composite to alclad stressed skin construction accomplished by major companies	<ul style="list-style-type: none"> • Germany 1918-1930 • United States 1930-1936 • France 1932-1938 • United Kingdom 1930-1939 • Japan 1934-1938 • USSR 1922-1944

perspective, it is important to note that wood is a biological composite material containing cellulosic fibers embedded in a natural resin. Likewise, fabric, principally linen as used in the early days of aviation, is a refined material in which natural fibers have been woven into a cloth. After being stretched over frames, the cloth is impregnated with resin to make the composite taut and impervious to air and water. Interestingly, this process has a lot in common with modern day composite manufacturing, but, of course, today the fibers and resins are high-performance synthetic materials. Nevertheless, the comparison is striking, and it illustrates that the real change over the past 90 years has been in the materials.

As the performance of aircraft improved, new materials were required to support greater aerodynamic stresses. These materials were high-strength steels and aluminum alloys. However, penetration of these materials into the aircraft industry was not rapid (Table 3.2). Indeed, as late as the Second World War, some high-performance military aircraft still made extensive use

Table 3.2 Aluminum Alloys in Airframes: 1912-1995

Year	Alloy	UTS (ksi)	Aircraft	Applications	Remarks
1912	1100 Pure Hard	24	Reissner	Wing, canard	Corrugated Al skins
1915-1919	Al Cu Mn "Duralumin" (17-S)	50-55	Germany: Dornier Junkers France: Bréguet Britain: Short	Wings, fuselages, tail units, struts	Alloy invented by Alfred Wilm, 1908 Some corrosion and cracking problems
1920	Alcoa 17S and 14S products	45-55	U.S.: Stout 1923	Complete airframes: corrugated skins	"Alclad" has excellent corrosion resistance
1926	Alcoa "Alclad" Al clad 17S sheet	50	Ford Trimotor 1926	Formed sheet or extrusions, substructure	Ford/Stout construction infringement of Junkers patents No European sales permitted
1931-1955	2024 Al-Cu - bare - clad sheet - forgings Equivalent European and Japanese alloys	64 56	U.S.: Northrop Douglas Martin Boeing Foreign: all major manufacturers	Complete airframes: stressed-skin, semi-monocoque, and integral structure	Standard material for WWII aircraft
1940-1995	7075-T6 Al-Zn -bare -clad sheet -forgings Equivalent European and Japanese alloys	80	World-wide use of 7075 and foreign equivalents	Complete airframes: compression-dominated stressed skin, semi-monocoque, and integral structure. Used in combination with 2024	Japan: Used in "Zero" spars in 1940 U.S.: Used for reinforcement of B-29 "Enola Gay" in 1945 Standard military aircraft material, 1946-1990
1971-1995	7075-T76 Al-Zn As above	75	Preferred to -T6	Used in place of 7075-T6	Improved stress corrosion resistance to 7075-T6
<p>Note: Aluminum construction was finally accepted for airframes by most aeronautical engineers and aircraft users about 1935. This was 20 years after the first use of "Duralumin" in 1915 by Prof. Claude Dornier for the Rs.I flying boat lower fuselage covers and struts.</p>					

of wood (e.g., the deHavilland Mosquito, troop-carrying gliders, and later the Spruce Goose of Howard Hughes' fame). The first use of structural metals in the aircraft industry had to await a crucial materials development: a corrosion-resistant aluminum alloy in the form of Duralium. Metals then became extensively used in high-performance military aircraft, but their penetration was not complete until the end of WW II. Subsequent alloy development produced materials of higher strength and better fatigue resistance that allowed aircraft to fly faster and higher and carry heavier loads. Surprisingly, when one considers the multitude of possible alloy systems, only a handful of aluminum alloys penetrated the industry, including "pure" aluminum (Alloy 1100), Duralium, Alcoa 17S, Alclad (Al clad 17S sheet), Alloy 2024, Alloy 7075-T6, and Alloy 7075-T76, which exhibits improved resistance to stress corrosion cracking compared to the T6 heat of the same alloy. Part of the explanation for the slow transition of new materials into aircraft prior to WW II is that the airplane industry is very conservative, particularly when it comes to the introduction of new materials into man-rated systems. Thus, designers insist on having extensive property databases before specifying new materials in airframes and engines. This conservatism was largely justified, as evidenced by the historical lack of involvement of new materials in aircraft accidents, but it did result in a lack of flexibility in developing new airplane systems.

It is interesting to note that the problems experienced in the introduction of metals into aircraft were well recognized at the time. For example, in 1935 it was noted that:

"The fundamental reason for the structural difficulties encountered in metal airplane structures was the lack of suitable alloys, technique of heat treatment, fabrication inexperience, and cost"

and

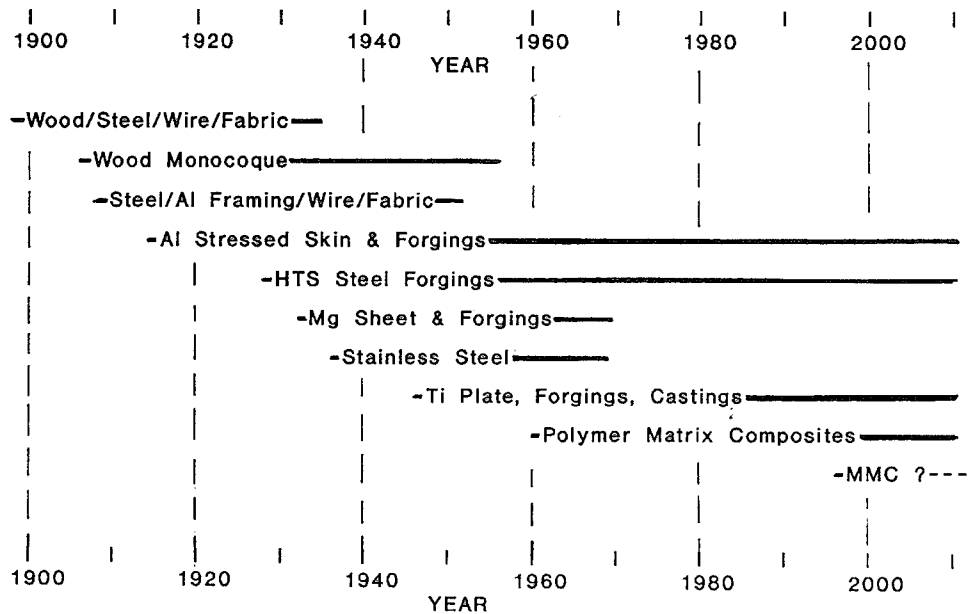
"The gradual transition to the metal structure has not been of rapid rate. The period of transition has been forestalled by the scarcity of sound engineering data and the method for economical production"²

This statement could easily be made in 1995 with respect to current attempts to introduce advanced composite materials into aerospace systems. We note that this problem is not unique to the aerospace industry because identical difficulties arise in any industry where reliability is of paramount importance. For example, efforts to introduce aluminum into the automobile industry as a replacement for steel have been met with strong opposition, even though the savings to the consumer in terms of improved mileage has been well documented. Likewise, efforts to introduce composites into automobiles, even into expensive ones, have met with little success.

So far, we have described only two of many materials that appear in aerospace systems. A partial list of aerospace materials, together with their times of introduction, is given in Figure 3.1. One notes that over the past 50 years, only two new major structural materials, titanium and polymer matrix composites, have been introduced. Despite their high cost, both were introduced, because they allowed quantum leaps in performance.

2. Willis L. Nye, *Metal Aircraft Design & Construction*, Aviation Press, 1935.

AIRCRAFT MATERIALS & STRUCTURES



RNH Associates, 1995.

Figure 3.1 Aircraft Materials and Structures

Historically, materials have been introduced into military aerospace systems because they offer the designer improved performance. One performance factor that has increased markedly since the days of wood and fabric is the specific tensile strength, as shown in Figure 3.2. One sees the superior tensile strength of graphite fiber-reinforced plastic, even when compared with titanium, and this explains the great current interest in this material. However, strength degrades with increasing temperature, so that a material that provides satisfactory performance at ambient temperature may not do so at high Mach numbers. This is illustrated by the data shown in Figure 3.3, in which the specific tensile yield strengths of a variety of materials are plotted as a function of temperature. These materials include alloys Ti-6-4, Weldalite 049, Al 2618, a polymer matrix composite Celion 3000/PMR-15, and three metal matrix composites 2124/SiC/15w, 8009/SiC/11p, and 2124/TiB₂/15p(XD). Note that the quantity that is plotted on the ordinate is the specific tensile yield strength, which is the yield strength divided by the density. Thus, low-density materials may have excellent specific tensile yield strengths, even though their total yield strengths are low. The superior performance of Weldalite 049, which is an aluminum/lithium alloy, at low temperatures is evident, and it is this property that has attracted designer attention to aluminum/lithium alloys in general over the past decade. At higher temperatures, particularly at temperatures above the range corresponding to Mach 2.4 operation, this alloy fares poorly and is no better than Al 2618 and titanium diboride metal matrix composite.

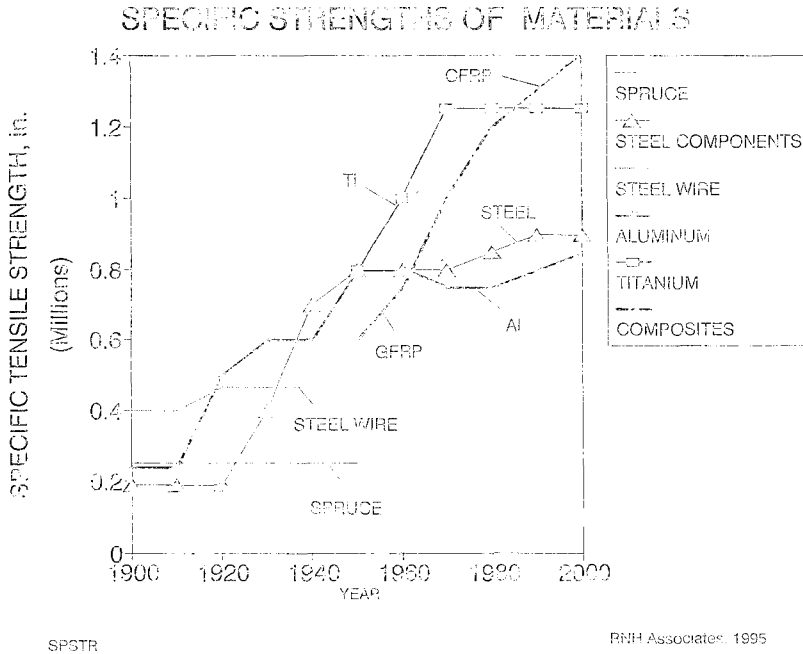


Figure 3.2 Specific Strengths of Materials

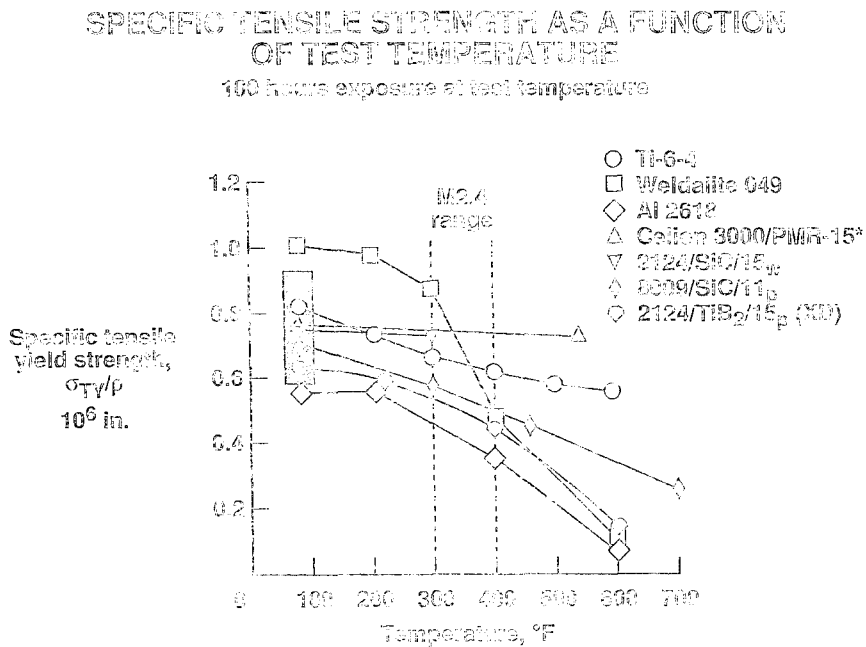


Figure 3.3 Specific Tensile Strength as a Function of Test Temperature (100 hours exposure at test temperature)

The distributions of materials in pre- and post-World War II aircraft are shown in Figures 3.4 and 3.5, respectively. The replacement of wood by aluminum in the prewar aircraft extending over a decade from 1923 to 1933 is clearly illustrated in Figure 3.4, as is the fact that the penetration of aluminum alloys into aircraft structures was essentially complete by 1933. With a few exceptions, the SR-71 and F-22, aluminum alloys have accounted for about 70 percent of the structural weight of aircraft from 1934 to the present day. The exceptions are important because they are examples of systems in which performance demands drove the choice of exotic materials (titanium in the case of the SR-71 and titanium and composites in the case of the F-22), despite the high cost.

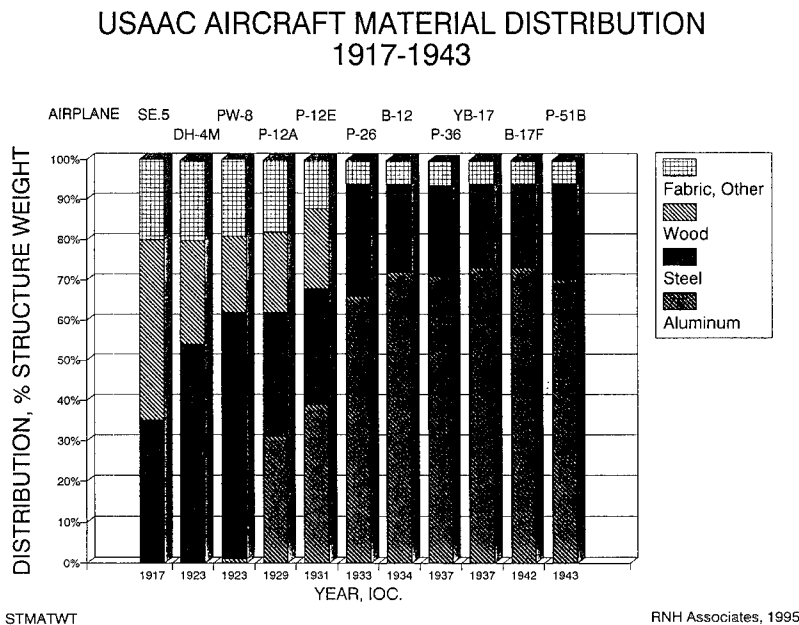


Figure 3.4 USAAC Aircraft Material Distribution 1917-1943

The influence of performance on the choice of materials is better illustrated by a plot of the distribution of materials, as a function of maximum airspeed, as shown in Figure 3.6. One should note the rapid decline in the use of aluminum and the introduction of titanium in U.S. fighters, attack aircraft, and trainers as the maximum Mach number exceeds 2.4, due to the rapid increase in structural temperatures with increasing airspeed (Figure 3.7). The same trend holds true for bombers and transport aircraft (Figure 3.8).

Much has been said and written about the use of polymer matrix composites as structural materials in modern high-performance aircraft, but it is worth examining the record to ascertain how extensively these materials are actually used. Data on this issue for fighter and attack aircraft and for transports, are summarized in Figures 3.9 and 3.10, respectively. As far as fighter and attack aircraft are concerned, the composite fraction of the structural weight has not changed significantly since the early 1980s. Even composite aircraft, such as the AV-8B, Rafale, B-2A, and the F-22A, incorporate only about 30 percent of their structural weight as

USAF AIRCRAFT MATERIAL DISTRIBUTION FIGHTERS, ATTACK & TRAINERS, 1955-1996

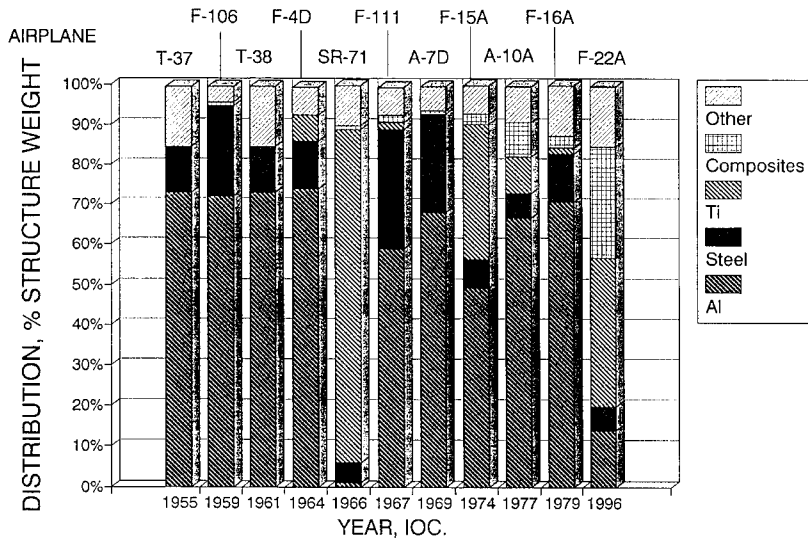


Figure 3.5 USAF Aircraft Material Distribution vs. Year, IOC (Fighters, Attack & Trainers, 1955-1996)

USAF AIRCRAFT MATERIAL DISTRIBUTION FIGHTERS, ATTACK & TRAINERS, 1955-1996

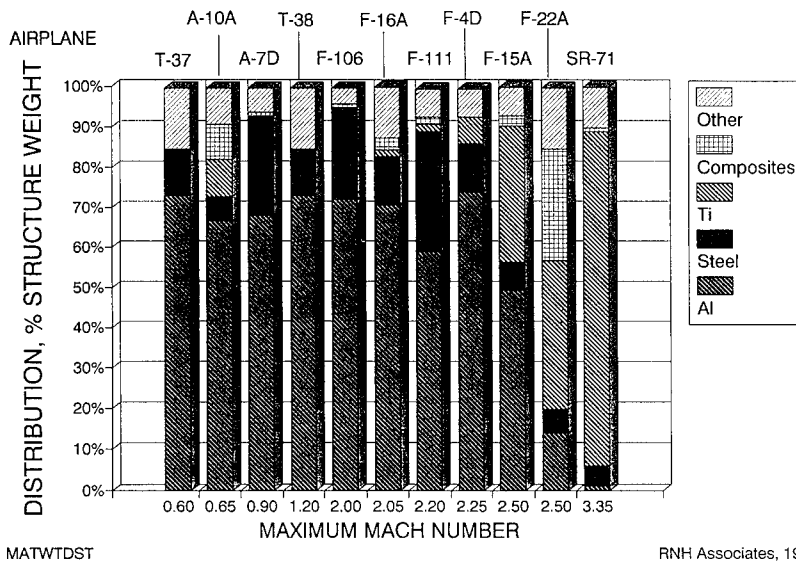
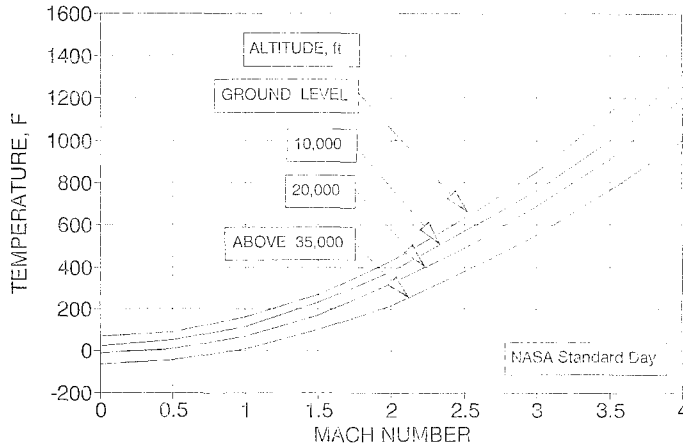


Figure 3.6 USAF Aircraft Material Distribution vs. Maximum Mach Number

AIRCRAFT STRUCTURAL TEMPERATURES ADIABATIC WALL TEMP, F.



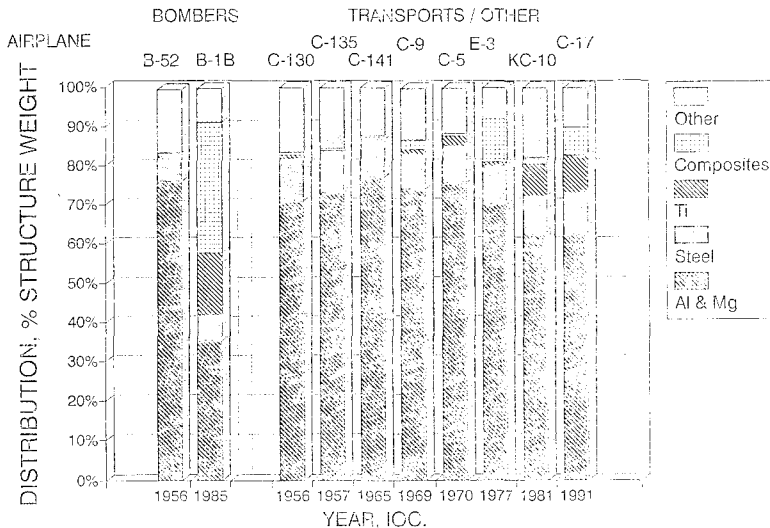
STRCTEMP

RNH Associates, 1995

Figure 3.7 Aircraft Material Structural Temperatures vs. Mach Number

polymer matrix composites. Of course, because of the lower densities of the composites, compared with steel, titanium, and aluminum, the volume fraction of the airframe that is composite is considerably greater and may exceed 60 percent in some cases. It is important to note that in the case of the systems shown in Figure 3.9, the driver for the use of composites is performance

USAF AIRCRAFT MATERIAL DISTRIBUTION BOMBERS & TRANSPORTS, 1953-1991



MATWTDST

RNH Associates, 1995

Figure 3.8 USAF Aircraft Material Distribution vs. Year, IOC (Bombers & Transports 1956-1996) Maximum Mach

COMPOSITE STRUCTURE: COMBAT AIRCRAFT
ADVANCED COMPOSITES, % STRUCTURE WEIGHT

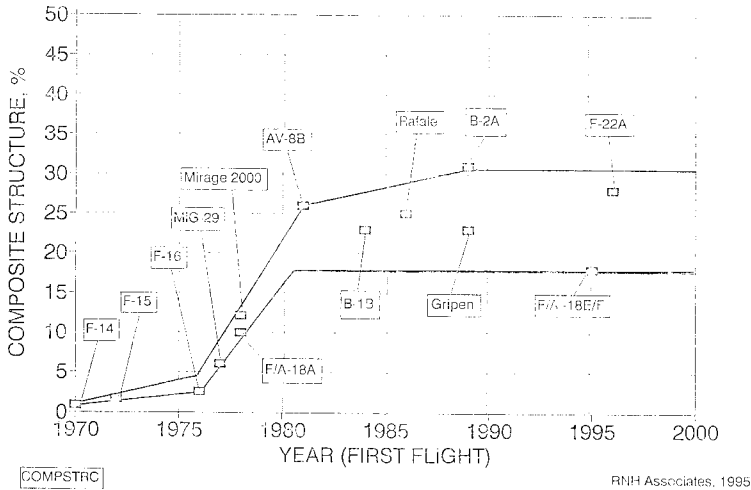


Figure 3.9 Composite Structure: Combat Aircraft (Advanced Composites, % Structure Weight)

in the form of weight, ability, useful payload, and speed. In the case of transport aircraft, where cost and reliability are the predominant factors, composites account for no more than 20 weight percent of the structure, and even then they have been used more extensively in European than in U.S. aircraft, as shown in Figure 3.10.

COMPOSITE STRUCTURE: TRANSPORT AIRCRAFT
ADVANCED COMPOSITES, % STRUCTURE WEIGHT

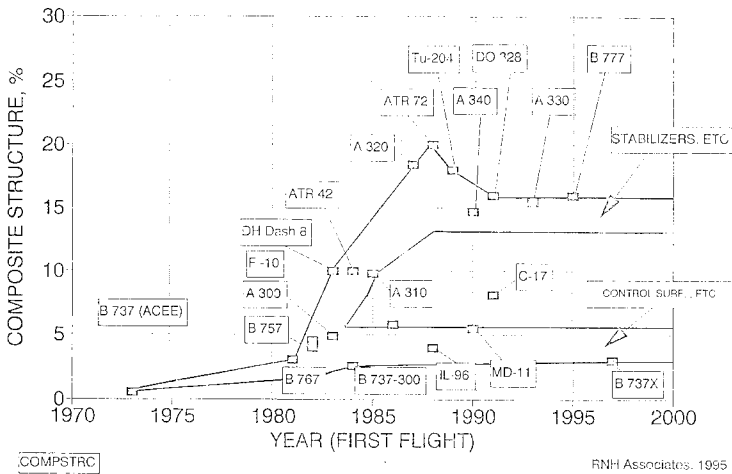


Figure 3.10 Composite Structure: Transport Aircraft (Advanced Composites, % Structure Weight)

A critical performance parameter for any aircraft is the fraction of the takeoff gross weight (TOGW) that is useful load. The trend of this parameter for fighter aircraft from 1917 to 1979 is given in Figure 3.11, showing that the fraction of the TOGW that is useful load has doubled over this period. Interestingly, this gain has not been due to savings in the structural weight or the weights of various systems avionics, but rather has been achieved because of dramatic improvements in the performance of propulsion systems. The most dramatic improvement in the latter occurred upon the introduction of the jet engine (see P-51 vs. F-100), illustrating that system changes can have as dramatic an effect on performance as materials changes.

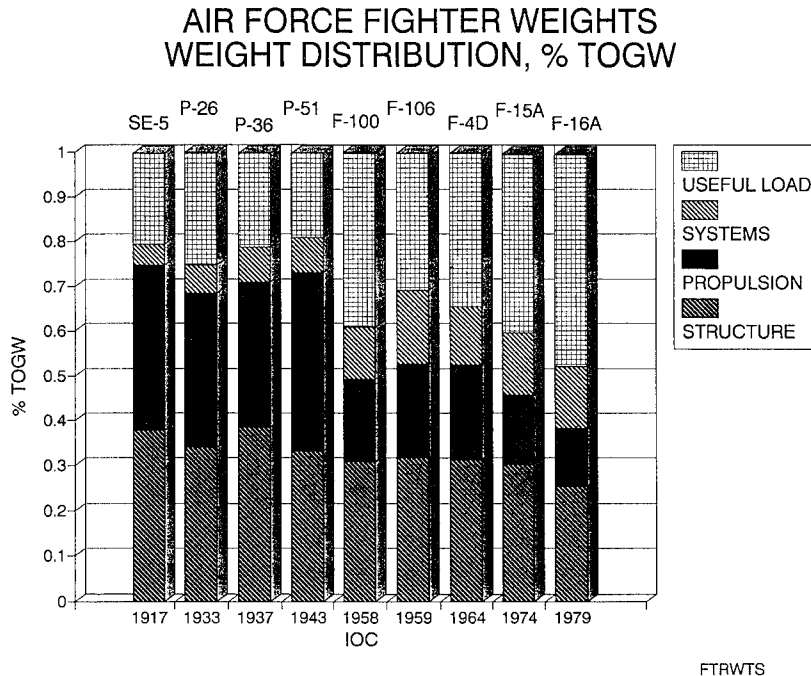
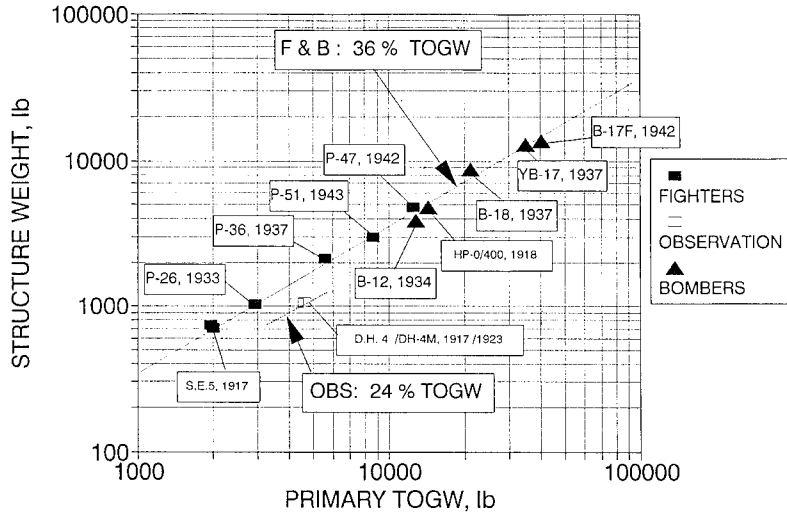


Figure 3.11 Air Force Fighter Weights (Weight Distribution, % TOGW)

An interesting observation is that new materials have historically had relatively little effect on the relationship between structure weight and TOGW. This is clear from Figure 3.12, which shows that prewar aircraft follow the same correlation, regardless of whether they were manufactured primarily from wood or aluminum, and from Figure 3.13, which shows postwar aircraft that used a much wider range of materials. A comparison of these correlations shows that a significant improvement in the payload characteristics occurred between 1943 and 1955. This timeframe does not coincide with the introduction of any new structural material or new structure type, but it does coincide with the introduction of higher power-to-weight propulsion systems in the form of jet engines, which, of course, also employ new materials. Note, however, that the advantage of turbine power plants, as far as the relationship between structural weight and TOGW is concerned, becomes smaller as the takeoff gross weight increases. Finally, it is important to emphasize that the use of advanced materials has had a dramatic influence on other performance parameters, such as the maximum Mach number and observability, as previously noted.

MILITARY AIRCRAFT STRUCTURAL WEIGHTS 1917-1943

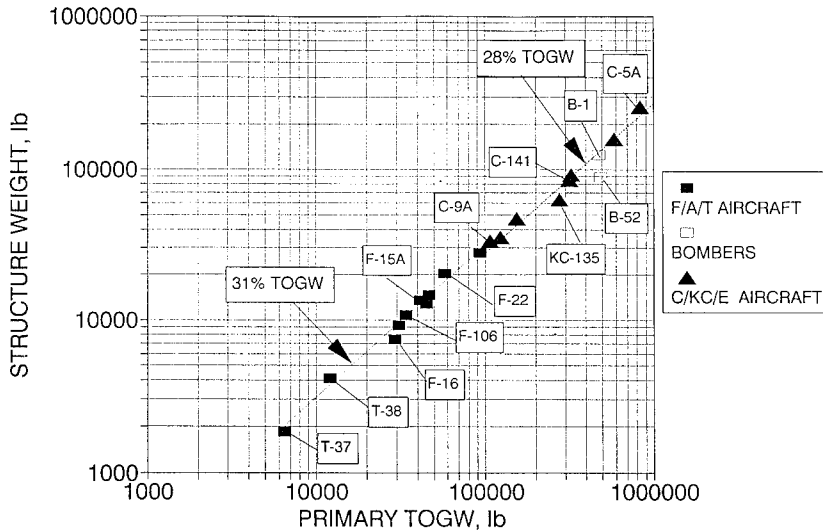


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RNH Associates, 1995

Figure 3.12 Military Aircraft Structural Weights 1917-1943

MILITARY AIRCRAFT STRUCTURAL WEIGHTS 1955-1996



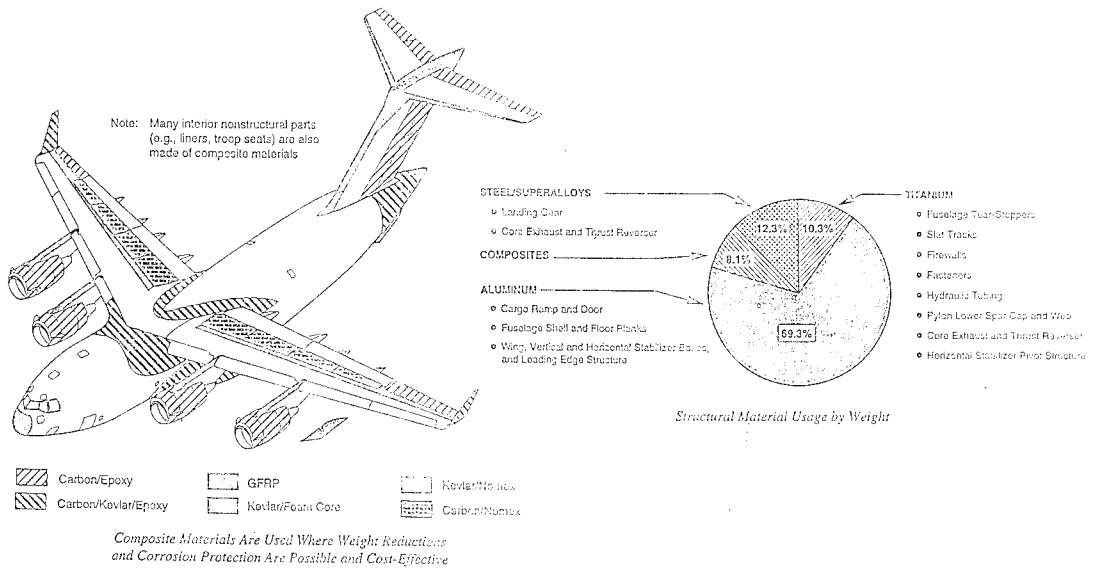
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RNH Associates, 1995

Figure 3.13 Military Aircraft Structural Weights 1955-1996

Just where are various materials being used in current aircraft? Because each aircraft is unique, it is impossible to generalize, but reference to a specific example illustrates the trends.

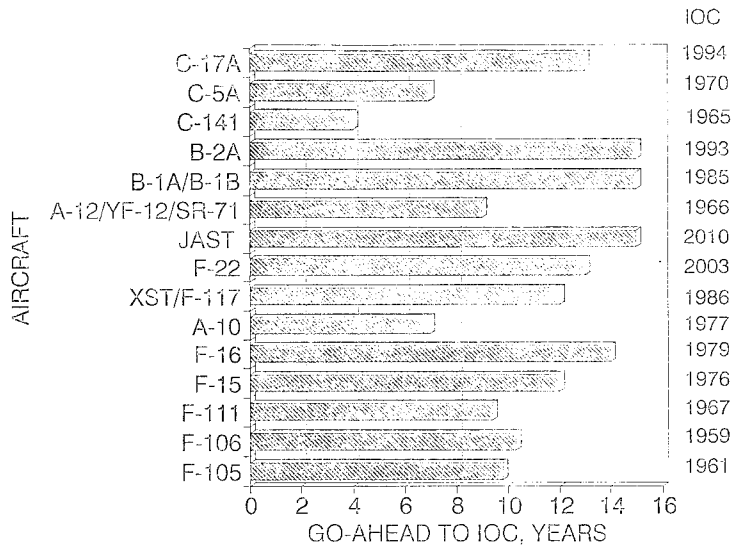
C-17A STRUCTURAL MATERIAL USAGE



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Figure 3.14 C-17A Structural Material Usage

USAF AIRCRAFT DEVELOPMENT CYCLES



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Figure 3.15 USAF Aircraft Development Cycles

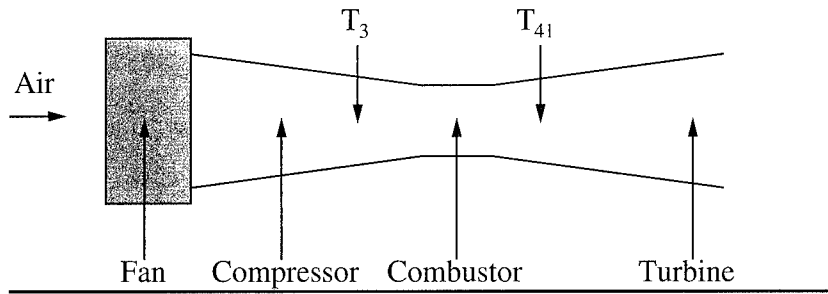
The case that we have chosen is the C-17A, the Air Force's new heavy-lift transport. As shown in Figure 3.14, almost 70 percent of the structural weight of this aircraft is aluminum alloys, with the "advanced" materials in the form of composites and titanium accounting for only eight percent and ten percent, respectively. In general, new materials are introduced in noncritical components, or into components of high redundancy (e.g., engine cowlings, winglets, tail cones, and radomes), partly to gain manufacturing experience and partly to accumulate flight hours. However, this implies that the time required to introduce a new structural material into aircraft is governed, to a large extent, by the development cycle, which is currently between 10 and 15 years (see Figure 3.15). Assuming that several generations of aircraft are required to introduce a new structural material, it is not difficult to see that many decades may pass between the first manufacture of a material and its extensive use in an airframe.

The final issue we wish to discuss is cost, because no relevant analysis can be conducted without considering this factor. The dramatic increase in the cost of military aircraft, particularly after WW II, is evident by the fact that the F-22 costs an order of magnitude more per pound than did an F-86. Conversely, the per-pound cost of civil transport aircraft has risen only modestly by a factor of two over the same period. It is difficult to attribute this difference to the introduction of advanced structural materials, because the composite content of a modern airliner is not commensurably different from that of a modern military aircraft (see Figures 3.9 and 3.10). A more likely explanation for the cost discrepancy lies in procurement procedures, specifications, and in the much more sophisticated avionics that are characteristic of military systems.

3.3 Propulsion Systems

The second major system in an aircraft is the propulsion system. Prior to the mid-1940s, propulsion was due exclusively to the internal combustion engine (ICE). ICEs developed dramatically in the period from 1935 to 1945, but by the end of WW II, ICEs had achieved a maximum power-to-weight ratio at a great cost in increased complexity. At that point (1938-1940), a revolution occurred with the development of the turbojet more or less simultaneously in England and Germany. Not only was the turbojet a much simpler device, but it offered dramatic improvements in the power-to-weight ratio (commonly expressed as thrust-to-weight ratio). Since these early times, the performance of the turbojet and its derivatives, turbofans and turboprops, has improved dramatically, and much of this improvement can be attributed to better materials. The driver for advanced materials in propulsion systems has been higher thermodynamic efficiency, which translates into higher combustion temperatures, lower specific fuel consumption, and reduced weight. The evolution in engine operating parameters is summarized in Figure 3.16 together with projections into the future.

Of particular importance has been the evolution in the turbine blade alloy temperature capability, as shown in Figure 3.17. However, the development of better alloys, particularly nickel-based superalloys, is only part of the story because the most dramatic improvements can be attributed to materials processing and component design. In the case of turbine blades, it was the introduction of monolithic single-crystal structures with internal air cooling that led to the great increases in efficiency. Reductions in weight have been achieved by using lightweight/



Year	Overall Pressure Ratio	T_3 (°C)	T_{41} (°C)	ByPass Ratio
1970	15:1	590	1345	5 - 6
1994	38:1	695	1425	8 - 9
~ 2006 HSCT	25:1	620-705	1540-1650	~1
~ 2010*	75:1	815	1760	12 - 15
Concorde	20:1			

* Cannot make this engine due to materials limitations

Figure 3.16 Time Series of Engine Operating Parameters

high-stiffness materials for compressor blades. The introduction of graphite/polymer composites into the RB-211 is perhaps a lesson in the dangers of introducing a new material into an engine when sufficient flexibility in cost and delivery schedules is not available. Nevertheless,

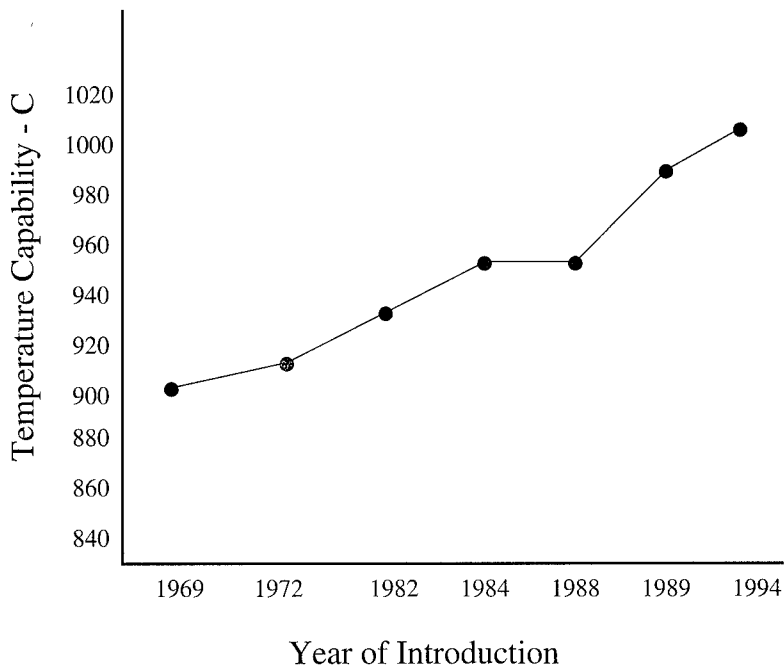


Figure 3.17 Turbine Blade Alloy Temperature Capability

new materials will continue to be introduced into engine systems with lightweight/high-stiffness materials, such as the intermetallics and metal-matrix composites, leading the way. The introduction of these materials, together with evolution in design (e.g., in the use of a single fluid for lubrication and propulsion), offers continued and dramatic improvements in engine performance.

3.4 Fuels and Lubricants

There are perhaps few Air Force materials that have changed as little over the past 40 years as fuels. The standard fuels, ranging from JP-4 through JP-8 and derivatives thereof, are basically refined hydrocarbons of the kerosene type. They lead to coking, are susceptible to combustion instabilities, and have a minimal potential for cooling. Likewise, current lubricants can be traced back several decades and, again, are hydrocarbon derivatives of synthetic esters and fluorinated ethers. While considerable development has occurred in lubricants, the current philosophy is to modify the properties of contact interfaces. This philosophy would be abandoned upon the introduction of magnetic bearings.

Dramatic developments are now occurring in fuels and lubricant technology, and these developments are discussed at great length later in this report. Briefly, the development of high-heat-sink fuels, endothermic fuels, and chemically reacting fuels offers great advances in propulsion technology and should result in greatly reduced fouling, maintenance, emissions, and signature, as well as increased component lifetime. The concept of a single fluid for lubrication and propulsion would also have a major favorable impact on Air Force operations, and this technology is now in the research stage.

With regard to missiles and rockets, little has changed in propellant fuel and oxidizer technology over the past three decades, except for the more extensive use of liquid hydrogen as a fuel. Our solid propellants are still based on ammonium perchlorate as the oxidizer and aluminum-filled hydrocarbon polymers (e.g., polybutadiene) as the fuel. The need for higher specific impulse propellants is well recognized, not only for improving performance, but also for reducing cost, but introduction of new technologies has been slow. As a case in point, we note that the superoxidizer, ammonium dinitramide, has been fielded by the Russians in several missile systems, but has yet to be incorporated into any U.S. missiles or launch vehicles. Part of the problem is a reluctance on the part of system designers to depart from time-proven technologies, even if significant increases in performance can be achieved. Equally important is the poor prospect that new propulsion systems will be sponsored and fielded by the military in the future.

Gas turbine engine lubricants currently used by the Air Force are based on polyesters that are capable of operating to 400°F. Other important fluids include polyalphaolefin-based hydraulic fluids and dielectric coolants. Both liquids and solids are utilized in space lubrication, coatings are utilized in several applications, and greases are used in some expendable engines. There is also current interest in biodegradable hydraulic fluids, and the technology is presently available for aerospace nonflammable hydraulic fluids.

3.5 Vision Protection

The development and proliferation of laser technology in the 1980s and early 1990s pose a serious threat to low-flying aircraft, in that ground-based lasers can be used to attack the pilot. For

instance, it has been demonstrated that a shoulder-fired laser aimed with a telescopic sight can incapacitate a pilot of an F-4 undergoing evasive maneuvers at a distance of 14 km. Because of the rapidly developing power capabilities of lasers brought about by advances in nonlinear optical materials technology, it is not difficult to envisage the seriousness of this threat to current and future Air Force operations. As of 1995, the only currently available protection against this threat are dye systems (goggles), which are effective against three wavelengths during daytime missions only. Development of more effective protection systems is an area of active research, and many new concepts are currently being explored.

3.6 Pyrotechnics

The principal line of defense for Air Force pilots against heat-seeking missiles is flares, which are ejected from the aircraft when a threat is perceived or detected. Current flares are magnesium-based systems that are tailored to simulate the emissions from a jet engine. This technology has been effective against first and second generation seeker systems, but seekers are now being developed, or have been fielded, that lock on to emissions at wavelengths outside the flare spectrum, or that can distinguish between the trajectory of a flare and an aircraft.

4.0 An Air Force of Aging Systems

4.1 An Aging Fleet

Continuing trends toward reduced procurement of new aircraft is forcing the USAF to extend the operational life of its current weapons systems. This trend is expected to continue for the foreseeable future (see Table 4.1).

Aircraft Type	Number of Aircraft	Average Age	Projected Retirement
C/KC-135	638	33	2040
B-52	94	34	2030
C-5A	77	25	2021
C-141	248	29	2010
C-130 (20 years or older)	439	30	2030
F-15	940	12	2020
F-16	1727	7	2020

Table 4.1 Fleet Life Extension

This unanticipated extension is placing ever greater emphasis on the ability to find, characterize, and ameliorate the deleterious effects of fleet operations. In addition, most systems are being asked to operate with changed mission requirements that were not envisioned when they were originally procured. In the future, radical improvement in the life management of the aging fleet will be fully dependent upon the ability to identify and characterize changes in materials and structures throughout their lifetimes.

One is immediately struck both by the broad variation in ages and by the distribution of ages of weapon systems in the current inventory. It is important to note that the length of service of an aircraft is not the only indicator of its "age." Both time-dependent and time-independent deteriorating processes are at work on the fleet. An example of a time-dependent process would be corrosion, where environmental conditions would have to operate over a period of time to have a significant effect, whereas a time-independent process such as stress corrosion cracking is directly related to the imposition of structural stress on the material. Time-dependent processes such as corrosion can be affected by design practices such as the use of corrosion prevention coatings, whereas time-independent processes can only be affected by changes in systems use. Design practices for each weapon system are commonly dependent upon the specifications in place at the time of manufacture.

The operators of older systems such as the KC-135 are generally confronted with corrosion as it affects the economic life of the aircraft. Another important consideration with an aging fleet, is that multiple problems will occur with increasing frequency. To highlight how broadly based problems with the aging fleet are, current systems considering or conducting serious structural modifications, due to the affects of aging, range from the C-130 Special Operations Force aircraft wing/fuselage structural elements to the F-16 fuselage structural frames, and to the B-1B horizontal stabilizer internal spars.

Whereas most components in an airframe are not removed and replaced on a regular basis, most turbine engines are routinely disassembled during programmed depot maintenance (PDM) cycles. This offers the opportunity to carefully inspect critical components. In an effort to extend the useful life of the F100 turbine engine, the Air Force developed and has implemented the Retirement For Cause (RFC) program for this engine's disks and other flight-critical high cost components. The advantages and disadvantages associated with this effort are currently being weighed as they might be applied to other turbine engines. Given the large numbers, the high costs, and the extremely critical nature of most of the components, the Air Force is attempting to significantly enhance its understanding of the behavior of critical components in fleet aeropropulsion systems. Given earlier successes in low cycle fatigue life prediction, behavior and life prediction methodologies are now being addressed.

On a total system basis, retrofits, replacements, and upgrades are critical elements in all efforts to extend the life of the aging fleet. This is a particularly effective strategy for onboard electrical, electronic, and electro-optical systems, since these tend to be replaceable on a unit or modular basis. Electronic, optical and magnetic materials technology is the enabler for this concept of life extension. As an example, the F-15 will have at least two complete avionics suite replacements before the airframe is finally retired.

4.2 Materials and Structural Integrity

Careful, detailed understanding of the behavior of materials subject to structural loads is at the heart of the Airframe Structural Integrity Program (ASIP) used by the Air Force to manage the flying fleet. In the 1994 SAB Summer Study on Life Extension and Mission Enhancement for Air Force Aircraft, the Materials Degradation Panel discussed the main focus of the ASIP as being to ensure that aircraft are being operated in the most economical manner possible. The ASIP has evolved over the years, primarily through the efforts of the Aeronautical Systems Center, into a process that develops aircraft that are tolerant to both manufacturing and service-induced damage throughout their design life and usage.

Experience has shown that it is rare for an Air Force aircraft to be retired because of structural degradation due to fatigue cracking. This type of degradation normally occurs on a single component of the aircraft rather than the entire aircraft. The damage tolerance approach is directed towards repair, modification, or retirement of a component only when in-service inspections require that one of these actions be taken.

There have been many cases of structural modification to preclude retirement of the aircraft. It is believed the damage tolerance approach incorporated in the integrity process in the 1970s is still the cornerstone for protecting the safety of aging aircraft. The operational usage of

Air Force aircraft is almost always found to be considerably different from that assumed in design. This is primarily the result of increased weight and more aggressive mission profiles. Many aircraft, such as the C-130 and F-15E, are flying in low-level environments where the damage from cyclic loading is many times worse than for high-altitude missions.

As a weapon system ages, it is exposed to multiple threats to its integrity. Threats to integrity can take on many forms. Metallic structures may be compromised through the initiation and propagation of cracks while composite structures frequently suffer from environmentally driven weakened adhesive bonds and matrix degradation. Electronic component life is greatly influenced by the robustness of the device with respect to the environment. The Air Force must maintain the fundamental capability to understand the chemistry and physics of failure of materials in order to provide quick, responsive solutions to failures that occur in the aging fleet. Given the success of the ASIP program, the Air Force has expanded its structural integrity efforts to include both turbine engines and mechanical systems, annotated as ENSIP and MechSIP, respectively.

4.3 Characterization

Behavior and Life Prediction

Destructive characterization of materials behavior plays a vital role in the development of new materials and in understanding the behaviors of materials currently in service. Current applications make increasingly more aggressive use of demonstrated materials properties. In addition, new applications will require a better understanding of materials response over the lifetime of the system. This includes being able to correlate changes in microstructural features with the eventual changes in the materials system that result in changes in the overall structure. For some applications this is called understanding the "effects of defects." The current need for this technology is best exemplified by the problems in the fleet caused by the F100 fan blade failures attributed to high cycle fatigue. In this situation, several different failure mechanisms are being investigated. The fundamental characterization of the failure mechanisms of emerging materials becomes an essential part of their transition. Current modeling technology does not permit failure prediction and current lab level testing capabilities are not yet able to duplicate all of the critical dynamic modes felt to be contributors to the failures.

Deterministic Prediction of Damage - Modeling Combined Corrosion and Fatigue

The aging aircraft community should move to the development of deterministic models for the nucleation and growth of damage. No reliable empirical method exists for even qualitatively predicting the nucleation of damage. The nucleation process involves a large number of variables that are almost always very poorly defined and characterized. The number of degrees of freedom in this problem is such that a purely empirical description of the nucleation process is unrealistic. Our contention is that deterministic models are required to provide a framework within which the seemingly disparate observations can be rationalized, and which might then be used as the basis for the prediction of nucleation times.

Deterministic methods for predicting the nucleation and growth of damage are now beginning to emerge from corrosion science. However, for the prediction of damage, complete determinism is currently excluded because of limitations in our knowledge of the basic laws and because of the complexity of the systems. On a more practical level is the lack of fundamental data, requiring that even the most deterministic algorithms be calibrated against a few known, well-controlled cases. However, even this is much more efficient than the empirical methods, which require huge data bases to capture all of the constitutive relationships.

The technical community that deals with aircraft problems has never had a strong representation in electrochemistry and corrosion science, so that damage and failures have tended to be addressed in terms of purely mechanical phenomena. There is a critical need for engineers to recognize environmental effects in the development of damage. The basis of damage tolerance analysis (DTA) needs to be expanded to include environment effects on the development of damage in a much more realistic and effective manner. Current materials qualification test protocols do not capture all the of the environments in which weapons systems currently operate. The panel strongly recommends that handbook data for new aircraft stress levels and fatigue lives be based on fracture mechanics parameters developed for corrosive environments. Along with the expansion of the DTA methodology, the SAB Materials Degradation Panel report of the 1994 SAB Summer Study recommended that the Air Force develop deterministic corrosion damage prediction technology based on damage function analysis (DFA). It was also predicted that DFA, as a stand-alone damage prediction technology, would eventually supersede DTA as the understanding of corrosion mechanisms became more complete. Further, the panel recommended the continued education of key personnel to enhance their understanding regarding the effects of corrosion on the acceleration of fatigue crack growth rates, and therefore on the availability of aircraft now and in the future.

Nondestructive Inspection/Evaluation

Crack detection. Current Air Force efforts in crack detection address the recently identified problem of multiple subcritical cracks in aircraft that can link up to compromise structural integrity. The current focus is on the rapid detection of first layer and second-layer cracks under fasteners. The detection of small second-layer cracks with conventional low-frequency eddy current methods is generally limited by the presence of structural features near the fastener hole. These features create eddy current signals that can mask crack indications. Responses due to probe tilt, off-centering, and fastener-related responses can also hinder crack detection. Current methods include principally hand-held probes, with a limited number of semi-automated systems. In the future, robotic handling of electromagnetically based inspection systems will allow automated scanning over large areas. The focus will be on the ability to identify small, subcritical, widespread cracks that could interact in a catastrophic manner.

Corrosion detection. Most corrosion is found visually, both in military and commercial aircraft. Therefore, corrosion that does not produce any visual indications may be missed. Current efforts have shown that some locations in the aircraft have hidden and inaccessible corrosion that do not produce visual indications. It must be concluded that some aircraft corrosion could go undetected, be missed, be hidden from view, or that aircraft disassembly would be required to uncover the inaccessible corrosion. Further, it must be concluded that in these hidden and/or inaccessible areas, the corrosion will continue to grow until it causes or produces

some visually observable indications that someone detects, or misses, or it continues to grow until the material is degraded to the point that cracks nucleate under normal operating loads and grow to a detectable length.

Corrosion detection in hidden and inaccessible structures is a key USAF Air Logistics Center need. The Air Force has several ongoing efforts to develop corrosion sensing technology. This technology will be evaluated on KC-135 components before disposition to flight test aircraft. In addition, multiple exploratory development new start efforts are underway with follow-on advanced development, culminating with initial availability in fleet in the late 1990s. In the near future, methods will be available to verify materials losses of between one percent and five percent due to corrosion. This will allow changing the maintenance philosophy of removing corrosion whenever it is found to monitoring corrosion loss until maintenance economics necessitate remedial action. This will be one of the cornerstones in allowing the Air Force to utilize condition-based maintenance (CBM) instead of the current approach of PDM. In the more distant future, methods will be available to detect nascent corrosion. These may involve a combination of very small, wireless imbedded sensors and indicator systems such as thin film, bimetallic, galvanic sensors. The identification of areas for tracking or immediate remediation will further improve CBM and further reduce costs due to corrosion.

High resolution digital radiography. X-ray inspection is moving from analog (film) data acquisition to digital data acquisition. Recent advances in high resolution x-ray detectors; high fidelity, low light-level camera systems; image enhancement techniques; and robotic inspections have been spurred by the development of new fiber-optic scintillating face-plate technology for x-ray detection that can be used in conjunction with a high resolution, low noise, wide dynamic range, cooled charge-coupled device (CCD) for imaging. This capability allows x-ray data acquisition with film resolution, 10 to 20 line pairs per millimeter, along with much higher dynamic range, 4000 vs. 200 to 500. This means that data for both thick and thin structural components can be acquired in the same data set.

Current methods have shown the feasibility in identifying tight fatigue and corrosion induced cracks. The development of digital radiography is directly tied to improvements coming in the fields of image processing and computer data storage, both of which will continue rapid growth for the foreseeable future. The digital data set has the advantage of allowing sophisticated processing methods to be employed to identify potential defects and the disadvantage of a massive amount of information that must be archived for subsequent use over the life of the system. Development of advanced particle accelerators for medical use will benefit neutron radiographic inspection processes. New accelerator designs are producing neutron fluxes comparable to reactor fluxes and are capable of being transportable. In the near future, advances in x-ray detection system development will be used in all the active depots. This will lead to the use of image processing and computerized accept/reject criteria as more is learned about defect signatures.

The ability to do multilayer, in-depth inspection will reduce the costly downtime associated with current radiographic methods. Rapid, robotic inspection will reduce the maintenance downtime caused by the need to clear the hangar. The overall result will be improved defect sensitivity, enhanced speed (factors of 3 to 10 are possible because of scanning techniques and wide dynamic range), and reduced inspection materials costs (no film or processing chemical

expenses). In addition, the ability to inspect directly through the paint will reduce the need to remove the paint to allow inspection, certainly an important corollary effort to the "Paint for Life" philosophy being pursued by the Air Force.

In the more distant future, advancements will come in the imaging devices, resulting in much more compact, lighter weight detection heads. Automated quantification and recognition of features will further enhance accept/reject methodologies. Portable neutron sources will allow both neutron and x-ray inspection modalities to be conducted with the same detector package, further enhancing the ability to discriminate corrosion and cracking in the structure. Absolute alignment of the detectors will allow image processing equipment to do subtraction to show the locations subjected to the combined effects of corrosion and fatigue.

Massive amounts of data. One of the problems presented by accurate large area, high resolution crack and corrosion detection in the future is that massive amounts of presumably digital data will be generated. This data will most likely be stored on either magnetic or optical media. The requirements for long term storage of inspection data means that archiving of the data will have to be addressed aggressively. Advancements in computer processing and storage capabilities should provide the needed technology base for the Air Force.

Automation. Because NDE inspections are completed during scheduled maintenance periods, the amount of time available for these inspections is limited. Manual inspections introduce potential avenues for inspection errors, including operator fatigue, data evaluation, data translation, and reproducibility. Automation of ultrasonic and eddy current methods can improve flaw detection resolution, reduce inspection times, and reduce errors inherent in the manual process, with results available in a fraction of the time required to complete a manual inspection. Automated probe positioning relieves the operator of the tedious task of moving the probe and improves data repeatability. Recently a portable, semi-automated scanner and related electronics package (for acquiring and imaging data) has been demonstrated that will enable maintenance personnel to perform inspections of large metallic and fiber-reinforced composite surfaces in a fraction of the time required by current off-the-shelf equipment. This scanner provides production quality C-scan (two lateral dimensions) presentations in a portable package and can be adapted for ultrasonic or eddy current evaluation methodologies. Future efforts in automated NDE are critical for the affordable operation of the aging fleet. This would include all NDE modalities, with near term emphasis on eddy current, ultrasonic, and x-ray methods.

Remote inspection. In many cases, components may develop structural defects in inaccessible portions of the structure, necessitating significant disassembly to perform the required inspection to validate the defect. A recent problem with cracking on one of the spar caps inside the wing of the F-15 forced removal of the wing skins to allow eddy current validation. Recent cracking problems in one of the fuselage bulkheads in the F-16 made for very difficult access for inspection validation. With the increased use of composite structural elements, it is likely that there will be a need for inspection to validate a potential delamination deep in the heart of the wing or fuselage structure. The use of active optical inspection methods such as laser generated ultrasound through flexible fiber optics and MEMS offers the opportunity for future inspection of internal structures without requiring disassembly. This would be accomplished via a "design for inspection" approach that would provide small access ports similar to those that are currently provided for conventional optical borescope access. Given this design feature, the

active fiber optic system would thread itself through the structure, conducting inspections or materials characterizations at key points throughout the structure. The end result will be verification of structural anomalies without the high cost of current disassembly methods.

4.4 Life Extension via Retrofits and Upgrades

A critical consideration in extending the life of existing platforms is the replacement, retrofit and/or upgrade of onboard systems and subsystems. These can lead not only to life extension, but also to increased capability, concurrently with increased maintainability, reduced life-cycle cost and in some cases, pollution prevention. This is a particularly effective strategy for electrical, electronic and electro-optic systems, and these are enabled by the related materials technologies. Examples include high-performance and/or low cost transparency materials, frequency conversion materials (second order nonlinear optical materials) for infrared countermeasure systems, and high-performance magnetic materials, which are enabling for high-performance aircraft on shaft starter/generators, which in turn would eliminate the need for hydrazine and a large amount of ground support equipment.

Future aircraft platform concepts need to encourage "plug-in" upgrades and retrofits, in a concept similar to the "universal bus" concept for spacecraft. This will enable higher performance Air Force systems by allowing for more rapid transition of new technology to existing systems.

4.5 Coatings and Inhibitors

Aircraft coatings and corrosion inhibitors offer significant challenges. Coatings are multifunctional, providing air vehicles with three main attributes: 1) survivability, 2) corrosion protection, and 3) cosmetic appearance. Current coatings for aluminum-skinned aircraft consist of a chromated surface pretreatment, a chromated paint primer layer and paint topcoats, each of which performs several crucial functions. Here, the term "coatings" refers to the aircraft coating structure as a system and includes all the individual elements of the system from the surface treatment to the topcoat paint. The term "paint" refers to a single organic coating comprised of a binder, solvent, pigment, and additives. The surface pretreatment provides passivation of the metal surface, incorporates corrosion inhibitors, and creates a surface topography for maximum primer coating adhesion. The organic primer coating also incorporates corrosion inhibitors and serves as an adhesive layer between the metal substrate and the topcoat layers. At mechanically stressed or damaged areas such as fasteners, rivets, expansion joints, and scratches, the surface pretreatment/primer system provides active corrosion protection from exposure to environmental factors (e.g., water, acids, and solvents). The paint topcoat layers provide signature control and protection against erosion and mechanical abrasion, in addition to providing acceptable cosmetic appearance. The surface treatment/primer coatings are intended to remain intact throughout the PDM cycle. Mission-related topcoat layers are intended to be applied and removed as needed, based on the mission. However, current actual practices have aircraft being repainted, primer as well as topcoats, well ahead of the PDM cycle because of poor appearance due to degradation.

Current materials and processing technology for organic coatings is based on a formulation chemistry involving extensive utilization of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs). Current Air Force corrosion inhibitor paint chemistry relies on the

heavy use of metal chromates (Cr [VI]) in the form of strontium chromate which are incorporated into both the surface pretreatment and the primers as highly effective corrosion inhibitor additives. Environmental regulations are forcing paint materials and processing technology to move away from the use of formulation chemistries involving VOCs, HAPs, and chromates. These ingredients will soon be substantially reduced or eliminated from the paint tech base. Estimates indicate that aircraft painting/stripping/ repainting and handling the hazardous waste associated with these materials and processes costs the Air Force in excess of \$150M per year, and the hazardous waste costs are rapidly increasing. Corrosion-related problems are the number one maintenance cost to the Air Force (estimated \$700M per year but suspected to be much higher, because of the way "corrosion" is defined) and paint-related corrosion consumes about 15 percent of this cost. Currently, there are no known high-performance coatings with extended durability, and little is understood about paint degradation phenomena. Presently, there are no known alternatives to dichromates as corrosion inhibitors. None of the materials currently under investigation seem to work as well as chromates.

The Air Force has established goals for coating systems from now to beyond the year 2003 which call for: 1) life extension of coatings to a permanent foundation layer, and 2) chromate-free corrosion prevention. To meet these Air Force requirements, establishment of a revolutionary new coating materials and processing technology base is required. The future tech base must be founded on a knowledge base created by basic research. A chromate-free foundation layer coating would require invention of a new corrosion inhibitor chemistry utilizing elements having atomic weight less than zinc and would utilize a high solids paint chemistry involving no VOCs. Improved coating materials would utilize formulation concepts such as pigmented polymeric beads and ultraviolet light resistant binders to achieve cleanability, durability and extended life. Application techniques for such a coating would involve processes such as high velocity thermal spray and include tight process controls based on robotic control and qualitative process algorithm (QPA). Concepts such as self-healing, optical detection of corrosion, microencapsulated inhibitors, and corrosion-activated inhibitors will be actively pursued and will require new polymers to be designed with such end requirements in mind. Mission coatings would still need to be applied and removed as needed, but these coatings would also undergo tremendous changes, including self-healing and tailored, on-demand low observability.

4.6 Structural Repair

Repair of cracked and corroded structures has always been challenging. Not infrequently, conventional mechanically fastened patches are not practical. Since the early 1960s, high modulus, high strength fiber-reinforced composites have been used to repair metallic structures. The patches are designed for the specific application and either cocured or secondary bonded to the surface. The high modulus patch dramatically reduces the stress in the vicinity of the crack, effectively extending the life of the component. For thin fuselage structures, the use of multilayer metal/composite patches offers advantages in providing a closer match with the thermal coefficient of expansion of the structural element being patched. In the future, as systems continue to be forced to operate beyond their original design, expanded use of patch repairs will allow the managed reduction of strain in structural "hot spots" that would otherwise begin to fail before the rest of the structure. Careful consideration will have to be given in the design of the patch to

prevent forcing excessive strains into the surrounding structural elements. Given the excellent fatigue performance of fiber-reinforced composites, it is conceivable that very significant extensions in the structural life are possible.

4.7 Direct Fabrication of Replacement Components

Replacement of damaged components is never easy or inexpensive, especially for aging systems for which there may be no digital data that would allow fabrication via modern automated methods. Digital metrology via methods such as x-ray computed tomography allows the direct fabrication of components via a variety of approaches that have flowed from stereolithography. The end result is that in the future the maintenance of older systems will be greatly enhanced if enough work is done to continue to develop the combined opportunities of digital metrology, CAD/CAM engineering, and process modeling. The resulting novel processes with computer process development and control will allow fabrication of custom parts directly in the depot at very low cost.

An ancillary activity to direct fabrication of complete replacement components is replacement of only that portion of the component that has been damaged, referred to as refurbishment technology (REFTECH). In many cases, this would allow retention of the majority of the economic cost of the component while restoring it to useful performance. An excellent example of the opportunity possible is the turbine engine disks that are removed due to low cycle fatigue exposure. In many cases, these very expensive components may only have damage in very limited areas. If this material could be removed and replaced via a process such as vapor deposition, plating, or even the insertion of a thin layer of new material, the cost savings would be enormous. This is not a particularly new concept, but one which must be explored as the Air Force strives to extend the economic life of its weapons systems. One of the key limitations in the past has been the inability to inspect beyond the boundary of the old and new materials, thereby preventing normal in-service nondestructive inspection to validate structural integrity. Implementation of REFTECH will require extensive coordinated programs for design, structural testing, advanced materials and process development, and advanced inspection technologies to realize the savings possible.

5.0 Environment and Life Cycle Considerations

5.1 Relationship of Environmental Issues to National Security

There is clearly a relationship between the environment and national security as seen within the following definition of national security. It is defined by the Office of the President as “the sovereign responsibility to remain a free and independent nation and protect our fundamental values, institutions and people.”³ Security is achieved through a combination of political, economic, military, and social strengths.⁴ Within this definition, environmental considerations can affect national security in four fundamental ways:

- Pose a direct threat to the health or well-being of the American people
- Contribute to regional instability
- Enhance (or detract from) the economy
- Threaten our social stability

In her testimony to Congress in 1994, Sherri Wasserman Goodman, Deputy Undersecretary of Defense for Environmental Security, pointed out that “the values supported by a healthy environment—life, liberty, freedom from fear and want—are the same ones we stand ready to fight and die for.”⁵ Because the United States has abundant resources and a generally healthy environment, direct threats to our health and well-being are more likely to be those that impact the global commons, such as ozone depletion or global warming. There may or may not be irrefutable evidence that these are valid phenomena, but there is enough doubt to regard them as valid environmental threats and suggest that we respond as we would to a military threat: with vigilance, gathering of intelligence data, and preemptive action in proportion to the threat, such as eliminating our use of ozone depleting chemicals (ODC) and carrying that message abroad.

Environmental problems have the potential to create significant regional instability and ultimately, regional conflict. To the extent that a particular conflict threatens U.S. national interests, there is a direct connection between the state of the environment and national security. As the world’s resources are depleted and polluted they become increasingly scarce and more valuable. As the premium on resources increases, the possibility for conflict over the use or pollution of the resources becomes more likely.

For example, upstream pollution of the Danube River is a source of great concern for the downstream nations. Air pollution from high-sulfur coal burned to generate electricity in the Czech Republic crosses the border and creates problems in neighboring countries. Depletion of fisheries worldwide threatens the primary protein supply of a large percentage of humanity. Just as diplomacy and the encouragement and support of international organizations are used to avoid regional instability, preemptive and peaceful resolution of environmental crises is a valid U.S. national security activity. However, this task requires a system of global monitoring and

3. U.S., Office of the President, *National Security Strategy of the United States*, 1993, (Washington, D.C.: GPO), p. 3.
4. U.S., Industrial College of the Armed Forces, *National Security Strategy Syllabus*, 1993, Washington, D.C.: ICAF), p. 4.
5. U.S., Department of Defense, “DoD’s New Vision for Environmental Security,” *Defense Issues*, Vol. 9 No. 24, (March 1994), p. 1.

analysis to collect and assess environmental data. Sophisticated sensors, such as those developed by the Air Force for other applications, will be vital for environmental surveillance.

Environmental considerations can act as a drag on the economy or serve to stimulate new markets and increase American competitive advantage. When compared with the environmental standards of other economic superpowers, such as Japan, ours are not unique. The relative advantage from lax environmental standards currently enjoyed by some emerging economies will be short lived. The differences in environmental standards will gradually vanish, based on emerging evidence that environmental improvement in industry enhances efficiency, reduces costs and ultimately increases competitiveness. Those economies that are embracing "sustainable development" are strategically positioning themselves for optimum future competitive advantage.

DoD and the Air Force have been at the forefront of developing remediation technologies and pollution prevention processes that could contribute significantly to U.S. competitiveness in a growing international market. One effort is the attempt to leverage the Strategic Environmental Research and Development Program (SERDP) to strengthen partnerships with industry, regulators, states, and the public for the field testing of new technologies. SERDP was established by Congress to support basic and applied research and development of environmental technologies. SERDP is actively supporting cutting-edge technologies, such as the electron beam scrubber that turns dirty high-sulfur coal emissions into a potential commercial product. Although development of new products for the market has not been a traditional DoD or Air Force mission, through environmental technologies and process development work, they can play a role in increasing U.S. international competitiveness while developing methods to control emissions, prevent pollution, and remediate past problems.

There is an additional issue, that of "environmental justice," that needs to be addressed. This emerging concept poses the question of social equity in the distribution of environmental burdens. Environmental justice considerations could have a fragmenting effect on society or an integrating influence, depending on how well we accommodate the concerns of that portion of the population that perceives itself as carrying a disproportionate environmental burden. Although this is not a traditional DoD or Air Force concern, there is a greater need to address the issue more energetically. Emphasis must be placed on efforts to select materials more carefully, with a bias toward those with greater environmental friendliness, conducting the research needed and then implementing pollution prevention methods and evaluating life-cycle costs for all materials and systems to place greater emphasis on final disposal.

5.2 Impacts of Environmental Laws and Regulations

Budget

With over 100 active and formerly used facilities on the Environmental Protection Agency (EPA) Superfund National Priorities List, the major portion of DoD's expenditures to date have gone to support cleanup efforts. This amounted to approximately \$4.5B in FY 94 and FY 95. However, even total costs to date are relatively small compared to the ultimate liability, which is potentially huge. Using a DOE example for comparison, cleanup costs at the Hanford reservation are estimated at \$100B to \$200B over a 20 year period.

Readiness

As the Air Force devotes more resources to environmental compliance and remediation, it must evaluate the impact on future readiness. If the total DoD budget continues to decrease while environmental expenditures increase, the sacrifice would come from current operations, training and maintenance, because DoD currently funds environmental efforts from operations and maintenance (O&M) monies. While only a small fraction of the current DoD budget (about 0.2 percent of FY 94 budget) has been directed to environmental issues, this percentage is expected to grow even as total budget authority declines. These direct costs do not include indirect expenses, such as having to conduct training at a more distant training facility due to environmental restrictions.

Despite the diversion of resources to environmental issues, records show that readiness rates remain healthy across all Services. How long this will continue is speculative, and any degradation would manifest itself over time and be somewhat difficult to detect, except retrospectively. Because environmental costs come from previously allocated funds, there is an opportunity cost associated with each expenditure. Although it is not possible to know what opportunities have been foregone, there is certainly some marginal cost for environmental requirements. Because these are often added on as unplanned costs, the prospects are great for minimizing such costs through pollution prevention and life-cycle analysis focused on material selection and system disposal.

Going beyond funding, it is critical to view the impact of environmental requirements in a strategic sense. We have probably entered the first phase of a major shift in national security thinking, involving planning to operate in a green future. The insight of Sherri Wasserman Goodman, Undersecretary for Environmental Security, supports this contention as revealed in her testimony to Congress in 1994.

“At first the notion of a green weapon system may seem absurd, but in reality it is not. These systems spend most of their lives in a peacetime role and often remain in the inventory for 30 years or more. During that time maintenance and refurbishment performed by contract and at our industrial depots use large quantities of hazardous materials and generate large quantities of waste.”⁶

Mobilization Capabilities

Related to readiness is the ability to mobilize the elements of material power. Although it may seem obvious that increases in the environmental regulation of both private industry and the federal government would have a negative influence on our ability to mobilize, this is difficult to quantify.

The defense industry's efforts to cleanse itself have advanced to the point that there will be little impact of environmental compliance on its ability to mobilize. Industry processes have already incorporated these requirements, reflecting responses to current regulations. In addition, Executive Order 12856, of 3 August 1993, establishes a formal exemption mechanism for relief from environmental regulation in the interest of national security. In a crisis, regulatory

6. Prepared Remarks to the Defense Subcommittee, House Appropriations Committee, March 23, 1994.

impediments could be removed temporarily. The only area that will still be impacted is the production of ODCs. Since the nation is ceasing production of these materials, even if regulations are waived, the lack of production capability will result in significant delay.

On the other hand, expansion of U.S. environmental regulations to overseas activity could have substantial, negative impact. Adding more and more Federal agencies to the review process for overseas actions (e.g., deployments, exercises, relief efforts) certainly will cause delay and could jeopardize operations. There could be a particularly negative impact on foreign military sales (FMS). Skepticism about the desirability of U.S. systems products and training will have an adverse impact on the industries producing them. If we are going to rely on FMS to help maintain parts of the defense industrial base, then we must plan for alleviating these concerns.

A perspective on the effect of environmental concerns on mobilization is provided by Operation Restore Hope. Disposal of hazardous waste generated in Somalia, disposal of captured vehicles, and application of dust control agents were all issues driven by environmental concerns. In the case of the dust control agent, instead of using readily available waste-oil as is the practice in the region, over 4,000 barrels of a petroleum-free dust suppression agent were shipped from the United States to Somalia, 500 barrels by air. Although not a high impact issue itself, the potential impact of such issues on future operations and mobilization efforts is sobering.

5.3 Pollution Prevention

Prosperity without pollution has become the fundamental environmental theme of the 1990's. The new paradigm—pollution prevention—serves as the keystone of federal, state, and local environmental policy. Support for this approach is broad-based, and includes environmentalists, industrialists, law-makers, academicians, government regulators and policy-makers, and the general public. Pollution prevention is the environmental ethic of the 1990s. It replaces two decades of national and state environmental policies based on pollution control. It represents the latest step in the evolution of environmental policy in industrialized nations, especially the United States. That policy over the past twenty years has progressed from a narrowly focused preoccupation with regulatory command and control of "end of pipe" releases, to a more practical waste management technology, and ultimately to the more enlightened economics of waste minimization.

The advent of waste minimization was a watershed in the evolutionary process. It redirected the attention of industry, regulators, and environmentalists away from "end-of-the-pipe", and "fence-line" micro-environmental releases, back through the industrial facility or treatment process being controlled, right up to the plant or laboratory door and into the conference rooms where planning begins. The additional problems of non-point source pollution provided further impetus to revisit the basic processes and systems polluting the environment.

Pollution prevention emerged as the theme around which to establish a framework to protect the environment; in part, to confront the economic realities of the enormous costs associated with hazardous waste treatment and disposal. The good sense of the pollution prevention concept was clear, because past improvements in one medium invariably resulted in contamination of another. Transferring pollutants between environmental compartments no longer was a viable solution. The successful control approaches of the 1970s and 1980s in dealing with mac

ro-environmental pollution of air and surface waters no longer were sufficient. A new, more flexible paradigm, that allowed creative solutions, jointly developed by industry, government, and environmentalists, would have to be put in place. The new framework, with a defined hierarchy of possible responses—source reduction, recycling, treatment and disposal—provides industry, government and the environmental groups an array of options from which to seek acceptable solutions.

For the Air Force and the industries it relies on, pollution prevention is an attractive environmental strategy for several reasons. If no pollution is generated, there are no pollutants to be controlled and managed. Future problems and risks are avoided. The old policies and methods resulted in billion dollar site remediations. Preventing pollution before it occurs has the added feature of preventing exposures to the community at large and to the workers charged with the management of pollution.

The Pollution Prevention Act of 1990 was designed to reduce the amount of industrial pollution in the United States by: 1) establishing a source reduction program at EPA; 2) calling for increased technical assistance to industry by EPA and states; and 3) requiring additional reporting on:

- Quantity of material (prior to recycling, treatment, or disposal) entering any waste stream or released to the environment.
- Quantities of material recycled and treated at the facility and elsewhere.
- Quantity of material released in one-time events not associated with production processes.
- Information on source reduction activities and methods used to identify those activities.
- Production ratio/activity index.
- Projections of future activities.

These reporting requirements, and the underlying challenge of pollution prevention and source reduction, are major concerns for the Air Force and its suppliers.

A significant potential benefit of industrial pollution prevention is economic. When wastes are reduced or eliminated, savings in materials result and more product is produced from the same starting materials. Re-examination of manufacturing processes as part of a pollution prevention approach can produce a variety of unanticipated benefits, such as conservation of energy and water and improved product quality. Given the escalating costs of waste handling, a program promoting source reduction can provide a major incentive to industrial firms. A dominant cost savings can be realized from significantly reduced future liability for future pollution.

On the environmental side, the advantages of pollution prevention include improving the effectiveness of managing reduced waste streams, minimizing the uncertainty associated with the environmental impact of released pollutants, avoiding cross-media transfers of released pollutants, and protecting natural resources. Finally, pollution prevention is consistent with the public's right to know and right to know more laws, and with increased public scrutiny of industrial practices.

Notwithstanding the fact that pollution prevention is the most effective way to reduce risks and avoid liabilities associated with producing the materials and products essential to Air Force operations, by 1999 the Air Force must reduce pollution by 50 percent (from FY94 levels). With 80 percent of hazardous material generation tied to weapon systems production, maintenance and disposal, the most effective way to reduce pollution is to design and engineer as much hazardous material and pollution generation out of a system as possible in the early stages of the acquisition process. However, to meet the 1999 goals, the opportunities to affect pollutant reduction through involvement in new system design will be few and the need for solutions to retrofit into existing systems will predominate.

Outside the short term challenge of meeting the mandated 1999 goals, the longer term opportunities to develop new materials and processing techniques and then the manufacturing methods themselves, which are vital to new weapons systems, must be addressed by considering pollution prevention at every phase of development. As U.S. businesses continue to place more emphasis on up-front costs, as well as on pollution prevention, there could be a short-term loss in their competitive advantage vis-à-vis their international competitors. U.S. industries apparently have made the decision that these short-term costs will be offset by the long-term benefits of owning more technologically advanced, efficient, and "environmentally friendly" plants. However, their selection of which materials, processes, and manufacturing methods they should invest in will be extremely cautious, tending to favor those with highest potential to profit from commercial application. The downselecting process by U.S. industry then could result in unfulfilled Air Force needs. Additionally, some new methods will need to be developed to treat wastes that survive pollution prevention planning efforts, because the commercial sector cannot economically and competitively take on the development risk.

The above are supporting reasons why the Air Force must build its environmental applied research capabilities to world class status. Inevitably Air Force/industry partnering will result, where the Air Force will need to shoulder a substantial amount of the pollution prevention process development risk. This will produce added long term benefits for the Air Force, because it will possess as well the treatment process know-how to apply to weapons systems operations, maintenance, and refurbishment. As U.S. policy has moved toward a process-oriented approach that focuses on pollution prevention, the U.S. environmental industry itself has changed. The thousands of small businesses formerly devoted to serving the command and control environmental industry has shrunk, and now about 25 major corporations dominate the U.S. environmental industry market. The Air Force cannot afford to rely on this reduced talent resource.

The realization that pollution prevention will ultimately cost less than remediation has given impetus to technological innovation. The development of new environmentally sound technologies and processes is of interest to developed and developing countries alike.

The importance of technology and process innovation as a contributor to economic competitiveness, as well as to environmental protection, makes technology development a significant element of the U.S. environmental agenda. The need to incentivize such development and innovation is leading the U.S. to undertake long-needed regulatory reform on one hand and, on the other, to give mandates to the national laboratories, the DoD laboratories, the National Institute of Standards and Technology (NIST), and ARPA to pursue environmental technology development. The 1995 budget provided more than \$2B for environmentally-related research and development.

The promotion of innovative environmental technology promises to increase environmental protection in a more economically efficient way. It is also expected to stimulate the development of new commercial products and markets for the U.S., such as clean cars and new techniques and uses for recycling and resource reclamation.

5.4 Life-Cycle Assessment (LCA)

An apt definition of LCA that captures the intent of the assessment process, identifies it as an attitude that displays an acceptance by manufacturers of their share of responsibility for the environmental burden caused by their products from design to disposal. Thus the LCA is a quantitative tool, which ensures that real rather than superficial environmental improvements are identified. Pollution prevention through LCA is a substantial change from evaluating waste management options that look mainly at single issues, such as recyclability or reduced toxicity. Figure 5.1 offers a notional look at pollution from a weapon system viewpoint.

An LCA is a snapshot in time of input and output. It can be used as an objective technical tool to identify environmental impacts associated with a specific product, process, or activity, and to evaluate opportunities to reduce the impacts. The LCA is a holistic approach that analyzes the entire system around a particular product, process, or activity. It encompasses extracting and processing raw materials; manufacturing; transportation and distribution; use, reuse, and

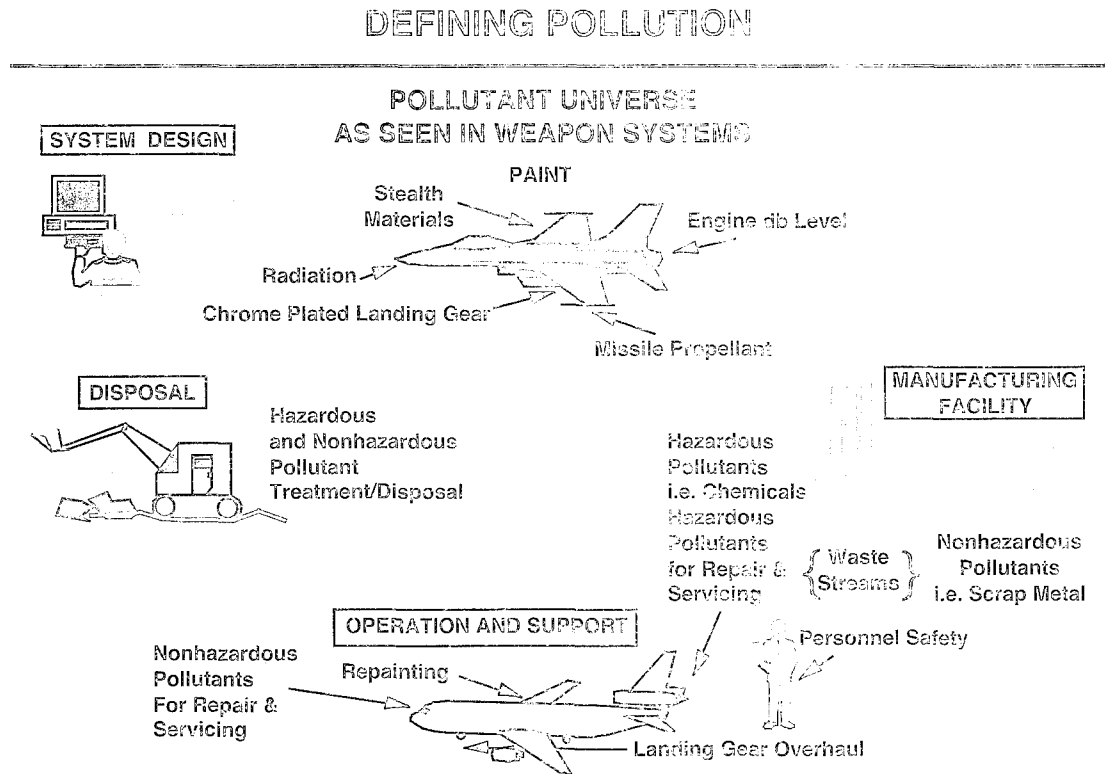


Figure 5.1 Weapon System Pollution

maintenance; and recycling and waste management.⁷ It also factors in the downstream and upstream effects of product use.⁸ The Society of Environmental Toxicology and Chemistry (SETAC) defines LCA as looking holistically at the environmental consequences associated with the cradle-to-grave life-cycle of a process or product.

Another approach involves looking at how waste can be reduced or eliminated, starting with the point of generation in the manufacturing operation, to its processing, treatment, or ultimate disposal as a residual hazardous waste.⁹ Pollution prevention can take place at any stage in a product life-cycle, and changes at any stage can have positive or negative effects on waste generation at other stages.

LCAs can assist in evaluating proposed changes to product process designs, so that trade-offs can be identified. For example, an apparent improvement to a product that decreases air pollutants, but which results in increased water-borne pollutants, could be identified by an LCA. Any potentially offsetting effects of the water-borne pollutants could be accounted for in an overall environmental assessment of the product, process, or activity.

5.5 Product Stages and LCAs

The process of evaluating the environmental impacts and releases of a specific product as it goes through various stages of development is depicted in Figure 5.2.

For the raw material acquisition stage, an LCA considers activities that involve removing materials from the Earth, such as crude oil. The second stage is material manufacture, which includes processing raw materials, for example, turning crude oil into polymeric resin. In the product fabrication stage, the processed raw materials are made into products. For example, polymeric resin is melted and formed into a number of products, such as plastic bottles.

Many activities take place during the next stage: filling, packaging, and distribution. Transportation, however, occurs throughout all the life-cycle stages and is not accounted for as a single activity during distribution. The next stage—use, reuse, and maintenance—incorporates how the product is used after the point of sale. The last stage, recycling and waste management, assesses how the product is ultimately disposed of, including recycling. Figure 5.1 depicts the stages of production life-cycle assessment.¹⁰

Generally, LCAs are thought to be costly and time-consuming, because they are inherently complex and data intensive, subject to technological change, and depend on data that often are proprietary. This can be particularly true of LCAs for public use, those which rely on published and public data sources, and which are intended to compare one consumer product to another. However, in 1990, SETAC concluded an LCA workshop recommending that complete LCAs should be composed of three separate but interrelated components:

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7. Fava, J. A. et al. "A Technical Framework for Life-Cycle Assessments" Society of Environmental Toxicology and Chemistry Workshop held in Smuggler's Notch, VT, August 18-23, 1990.
 8. "Background Document on Clean Products Research and Implementation," prepared by Franklin Associates Ltd., Inc., for U.S. Environmental Protection Agency, Cincinnati, 1990, EPA/800/2-90/048.
 9. Hunter, J.S., and Benforado, D.M. "Life-Cycle Approach to Effective Waste Minimization," 3M Company, paper presented at the 80th Annual Meeting of APCA, New York, NY, June 21-26, 1987.
 10. Curran, M.A., "Broad-Based Environmental Life-Cycle Assessment", *Environmental Science and Technology*, 1993, Vol. 27, pp. 430-436.

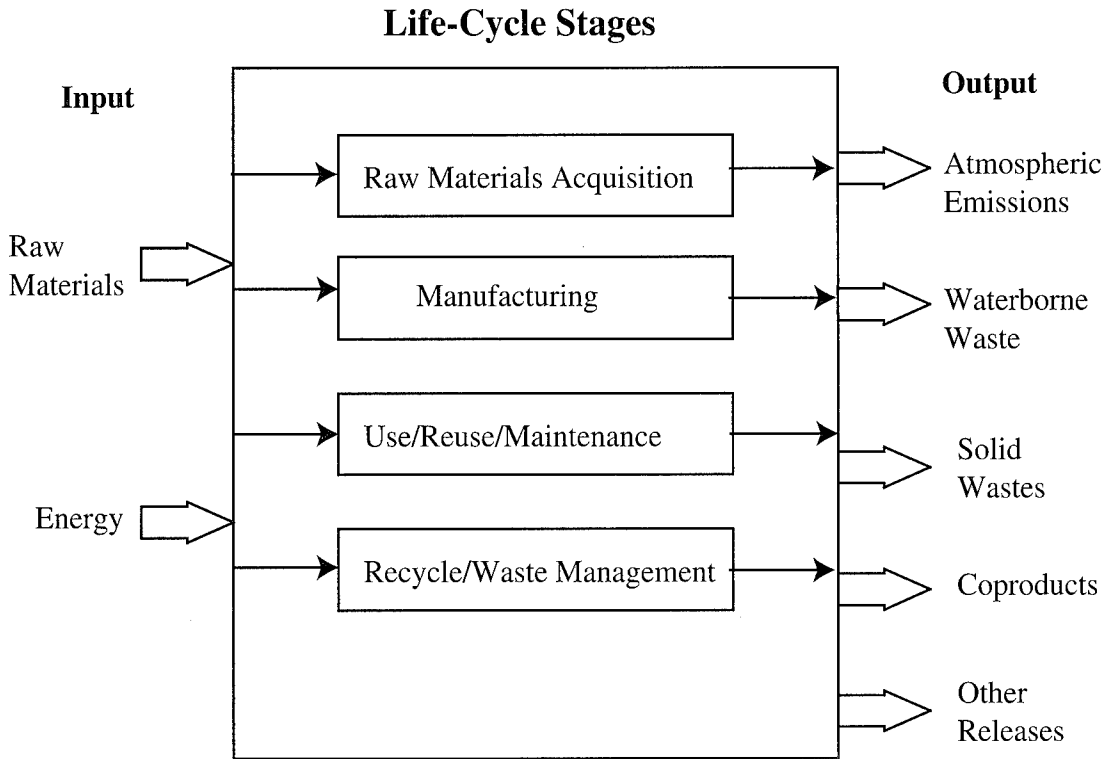


Figure 5.2 Defining System Boundaries

- Life-cycle inventory
- Life-cycle impact analysis
- Life-cycle improvement analysis

In addition, others have pointed out that it is far more feasible to formulate approaches that influence the choice of materials from which products are made.¹¹ For example, energy concerns in the 1970s motivated the U.S. Bureau of Mines to sponsor studies on the energy demands of major U.S. industries. Rather than examine the energy needs for the plethora of products made from aluminum, for example, this study instead inventoried the energy required to make aluminum itself.

This type of focus on materials can help guide product design, and it can offer opportunities for manufacturers who want to avoid unanticipated future regulatory and cost burdens as they evaluate alternative process modifications and material substitution options. Even if it turns out that cross-pollutant and cross-impact comparisons can never be satisfactorily resolved, the inventory phase of LCAs remains a valuable method for directing attention to pollution reduction opportunities regardless of their relative harm. It is not necessary for all LCAs to

11. White, A.L., and Shapino, K., "Life-Cycle Assessment. A Second Opinion," *Environmental Sciences and Technology*, 1993, Vol. 27, pp. 1016-1017.

include impact analyses. Their inclusion depends on the objectives of the study and the intended use of the information.

It is important that the LCA identify and measure both direct and indirect environmental, energy, and resource impacts associated with a product, process, or activity. Direct impacts might include emissions and energy consumption of a manufacturing plant. Indirect impacts include energy costs (by the functions of the product), impacts caused by extraction of raw materials used to make the product, and by product distribution, use and disposal. It is becoming increasingly apparent that indirect impacts, particularly post-manufacturing ones, often dwarf direct impacts. Improving the environmental performance of products of processes requires that they be designed to reduce post-manufacturing impacts.

It was noted at the 1993 conference at the Massachusetts Institute of Technology, "Life-Cycle Assessment: From Inventory to Action", that when indirect impacts are taken into account, conventional wisdom about the environment—the reduce, reuse, recycle hierarchy—may no longer apply. Recycling may consume more resources than it saves if, for example, recyclables must be transported long distances for processing or sale. Reducing toxicity may result in environmental costs if, for example, switching from chlorinated to water-based solvents requires increased energy use that generates additional solid waste.

Graedel, Allenby and Conrie have reported this year on using matrix approaches to carry out abridged LCAs.¹² The central feature of the abridged assessment system is a 5 x 5 assessment matrix, the Environmental Responsible Product Assessment Matrix, one dimension of which is the life-cycle stage and the other is environmental concern (Table 5.1). In use, the Design for Environment (DFE) assessor studies the design, manufacture, packaging, in-use environment, and likely disposal scenario, and assigns to each element of the matrix an integer rating from 0 (highest impact, a very negative evaluation) to 4 (lowest impact, an exemplary evaluation). In essence, the assessor is providing a figure of merit to represent the estimated result of the more formal LCA inventory analysis and impact analysis stages. The process is purposely qualitative and utilitarian, but provides a numerical end point against which to measure improvement. Once an evaluation has been made for each matrix element, the overall Environmentally Responsible Product Rating (R_{erp}), is computed as the sum of the matrix element values:

$$R_{erp} = \sum \sum M_{ji}$$

Because there are 25 matrix elements, a maximum product rating is 100.

The matrix scoring system provides a straight forward way to compare options for improving a complex manufactured product or an industrial manufacturing process. In using the method for assessing generic automobiles, at least two aspects of modern (1990) automobile design and construction were identified as retrogressive versus that (1950s) from the standpoint of their environmental implications. Both are apropos to Air Force weapon system manufacture.

12. Graedel, T.E., Allenby, B.R., and Conrie, P.R., "Matrix Approaches to Abridged Life-Cycle Assessment," *Environmental Science and Technology*, 1995, Vol. 29, No. 3, pp. 134A-139A

Table 5.1 Environmentally Responsible Product Assessment Matrix

	Environment				
Life-Cycle Stage	Materials Choice	Energy Use	Solid Residues	Liquid Residues	Gaseous Residues
Premanufacture	(1,1)	(1,2)	(1,3)	(1,4)	(1,5)
Product Manufacture	(2,1)	(2,2)	(2,3)	(2,4)	(2,5)
Product Packaging and Transport	(3,1)	(3,2)	(3,3)	(3,4)	(3,5)
Product Use	(4,1)	(4,2)	(4,3)	(4,4)	(4,5)
Refurbishment-Recycling-Disposal	(5,1)	(5,2)	(5,3)	(5,4)	(5,5)

One is the increased diversity of materials used, mainly the increased use of plastics. The second aspect is the increased use of welding in the manufacturing process. In the vehicles of the 1950s, a body-on-frame construction was used. This approach was later switched to a unibody construction technique, in which the body panels are integrated with the chassis. Unibody construction requires about four times as much welding as does body-on-frame construction, plus substantially increased use of adhesives. The result is a vehicle that is stronger, safer, and uses less structural material, but, one that is much harder to disassemble, recycle, or throw away.

The Air Force should concentrate on conducting life-cycle inventories for the materials and processes that go into the systems it uses. These limited LCAs will reveal substantial numbers of opportunities to investigate material and process substitution possibilities with the potential to reduce or prevent pollution. In addition there should be established on an expedited basis a group within the Air Force Laboratory system charged with developing the database and, particularly, the methodologies for performing LCAs for all current and future materials and systems.

6.0 Computationally-Driven Materials Development

Computationally-based materials design and manufacture were envisioned in the earliest days of quantum mechanics. Implementation awaited the advent of modern computers. Only now are we on the threshold of a modeling era that pervades the materials fields. This is not merely the application of computers to existing materials technologies and equipment automation, but rather using computers to change the way materials problems are approached.

In the new paradigm modeling will be integrated throughout the materials sciences and often applied by the modeling non-specialist. For example, before performing traditional experiments, the organic chemist of the future regularly will execute a series of computational experiments. Physical experiments will often be more focused and defined, and sometimes no physical experiments will be needed to obtain required information. The same will hold true for many of the phases of materials development.

More efficient development of new materials, better control and improved properties in known materials, more environmentally friendly synthetic schemes, improved opportunities for meeting multiple requirements, substantially improved understanding of materials, dramatic reductions in resources expended on unproductive materials R&D avenues, improved quality control and lower costs in manufacturing, and more precise troubleshooting of future problems can be expected from this revolution. Inasmuch as materials are often the critical limiters in AF systems, the impacts to be realized are broad. The AF must nurture these changes.

Materials modeling is enormously complex. The scheme illustrated in Figure 6.1 summarizes the hierarchical and interdisciplinary natures of material development. At the left of Figure 6.1 are depicted the atomistic models, including first principles quantum mechanical methods. Progressing up the chain to finite element methods, one is less concerned about atomic details and more concerned about bulk properties. The next stages include the realm of modeling processes, and ultimately system modeling, which is beyond the scope of this report. For a new material to go from a laboratory curiosity to an engineering material, the entire spectrum must be spanned. This journey can require 20-50 years, substantially longer than the plant design analogy cited above. Computationally driven materials development encompasses all the phases in Figure 6.1, and is changing the practices of the disciplines shown at the bottom of Figure 6.1 as they relate to materials development.

In materials sciences only limited specific applications of materials modeling are currently in use. While examples of multimillion dollar corporate decisions based on molecular simulations exist, revolutionary change is still on the horizon. Two requisites to induce this revolution are 1) broad based computer simulations as reliable as experiments, and 2) acceptance by the practicing community of the results from such techniques. The latter entails a cultural change which will occur as the methods prove themselves. Whereas theoretical results competing with experimental findings are not uncommon in certain fields of physics and mechanics, this is generally not the culture in materials development. In the materials sciences, simulations that can challenge experimental findings have been rare. The focus should then be on "What bottlenecks are inhibiting such a revolution in materials sciences?"

The greatest limiting factor in modeling has traditionally been computer power, but this is often no longer the case. Even the higher-end personal computers are capable of modeling

Computationally Assisted Materials Development

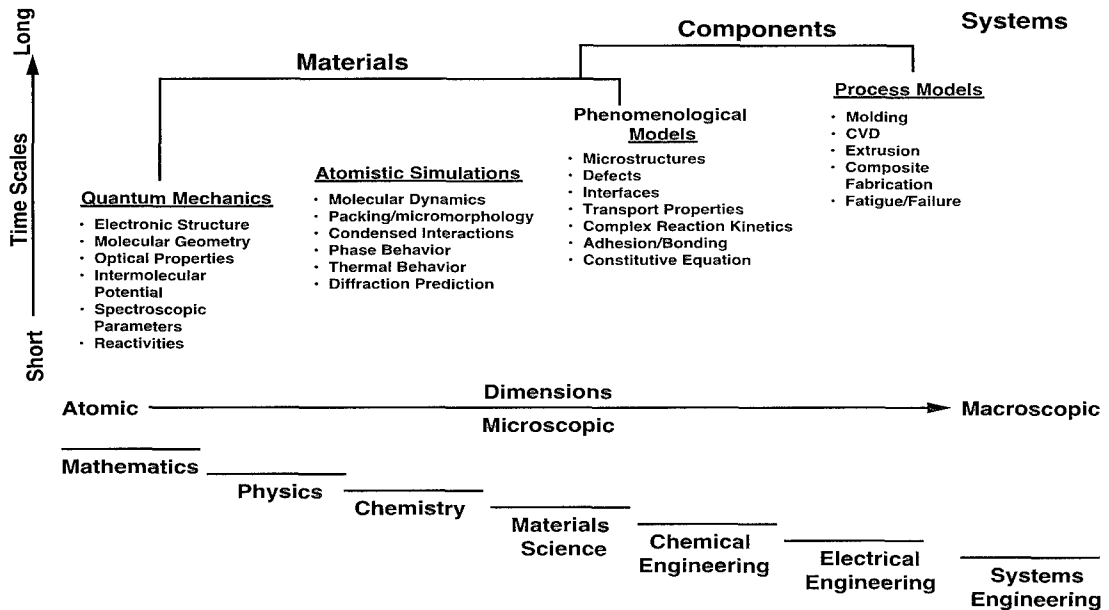


Figure 6.1 Computational Assisted Materials Development

problems that a few years ago were reserved for mainframe and supercomputers. This is not to say there isn't a place for large computers. Many computationally-limited problems exist, but the trend is clearly toward high-end workstations at the desktop. The advances in computer technologies and falling computer price/performance ratios will continue and facilitate application of modeling methods at the desktop. The workstation at the desktop will be particularly useful for the materials scientist for synthesis as well as being useful for prediction of properties and behavior.

Increasingly, software is more limiting than hardware. Software modernization is a concern. Significant programming advances, such as current efforts in massive parallelization, seem to be funded, at least while the techniques are new, revolutionary, and offer dramatic improvements. But more evolutionary software enhancements are lagging in their implementation into codes. To understand this we consider typical transition paths.

Most materials codes originate in academic laboratories and are either directly distributed to other researchers or are commercialized. Academic researchers find it difficult to raise funds to revise old codes. Research funds are typically awarded for programming new and exciting things, not for optimizing integral evaluation and other routines first developed 25 years ago. Likewise, computer scientists don't receive funds for incorporating newer programming methods into old software, but rather for developing new programming methods. The companies, for those codes that are commercialized often don't have the resources to devote to updating old

products. Hence, many codes have archaic, inefficient segments with no viable mechanism for rewriting old codes to take advantage of newer program technologies. Significant enhancements in applicability and capability could be realized with such modernizations. Complete rewrites are not needed, but rewriting the bottlenecks, memory or computationally inefficient and resource intensive routines would be beneficial.

The most important and numerous advances are yet to be made in coding property calculations and in method development. Often one is interested in a property or process for which no adequate software exists. This may be a matter of the software not having been written, but more often the underlying theoretical methods to calculate such properties simply don't exist. The theory hasn't been reduced to programmable logic. In these areas the Air Force can provide direction and leadership by investing in areas where software and methods are lacking but are needed for Air Force programs. Indeed, this leadership has been demonstrated. About 1989, none of the common first principle codes were capable of calculating nonlinear optical properties for molecules. At that time interest was generated from the Air Force in nonlinear optical materials research, and soon thereafter techniques were developed and implemented that could calculate some nonlinear optical properties. These codes are now broadly applied in academic, government, and industrial laboratories. Still, very little of the potential has been realized in other properties simulations.

Cross-discipline interaction is a must. The theoretical and modeling communities should address problems that span the spectrum of materials development. Certainly technique development, coding, and validation will remain the domain of the specialist and these must all be nurtured, but the utility to the non-specialist must also receive high priority. Too often the modeling results are in arcane terms, and are focused on modeling and theoretical minutiae. Cross-fertilization—true teaming—should be encouraged. One mechanism to encourage this interdisciplinarity, as now being implemented at one Air Force laboratory, is to not isolate modelers as separate groups, but rather to incorporate them into the overall research teams. This has the advantage of focusing the modelers on specific problems, though it does run the danger of neglecting methods development, which often takes years. Too often modelers do not know the most important questions to address, while experimentalists are unaware of the capabilities and limitations of modeling.

Data fusion—incorporating information from lower level calculations to higher level users, experimental and modelers—promises to be a challenging problem. For example, some questions must be addressed at the atomistic or molecular level, but that degree of detail is neither needed nor desired at the higher level. If these linkage issues can be addressed, materials could be straightforwardly tailored to specific engineering applications.

The vision of this section of the overall report is to anticipate what areas the Air Force should emphasize and what relationships the Air Force should foster. For technical emphasis, the criterion should be to support those modeling techniques that are key to critical Air Force materials technologies. Several areas for emphasis are discussed below.

6.1 Propellants and High Energy Materials

There has been and continues to be much modeling effort in this technology area. The modeling has been focused on designing new materials; however, there is not enough cross-disciplinary interaction. Modeling areas to be emphasized are 1) solvent and chemical environment interactions with high energy molecules, 2) improved methods of mapping out reactions, and 3) methods to model and understand kinetics in multiphase systems. There is much effort in the quantum field addressing solvent interactions, so this needs sustained emphasis and incorporation into the energetic materials efforts. Discovering unusual reactivities, especially by modeling techniques, is a wide open field. Perhaps high energetic materials is an ideal place to emphasize and develop methods for this. The actual experiments are difficult, dangerous, and often ambiguous. Since many of the molecules are small to moderate size, some advanced, experimentally competitive techniques are quite applicable. What is lacking is a reliable technique that can quickly and efficiently generate reaction paths. This is a daunting task, and will require long term support. Since reactivities, especially in propellants, often depend critically on grain size and processing parameters, incorporating these factors into models is critical.

6.2 Magnetic Materials

The importance of magnetic materials is noted elsewhere in this report. Molecular magnetics are relatively new, yet very little if any modern modeling has been done. The codes and techniques are scattered or are nonexistent. For example, there are no known codes that can calculate or estimate bulk magnetic susceptibilities for molecular magnetic compounds. Little is understood in how to design a molecular magnet. If modeling techniques were developed, they could provide the needed insight.

6.3 Epitaxial Growth Processes

Epitaxial processes underpin the electronics industries. These include chemical vapor deposition (CVD), which is used for the majority of established semiconductor thin film growth processes, and molecular beam epitaxy (MBE), which will be used to produce the next generation electronic and inorganic optical materials taking advantage of quantum effects. The most advanced simulations are of gas-phase materials, yet very little atomistic modeling has been applied to the relevant gas-phase processes in CVD. In MBE, there are no gas-phase interactions due to the ultrahigh vacuum environment; instead an understanding of surface processes and energetics on an atomic scale are of importance in establishing the growth conditions for high quality films. Some preliminary computational work has been done in this area but much more is needed. Additionally, organic based photonic and electronic materials are emerging technologies, and vapor deposition may play an important role. Again, the modeling could make a substantial contribution to the development of the materials processes. Note that modeling could be employed virtually from the ground up for electronic and nonlinear optical materials. Early attempts at this philosophy have been initiated for inorganics, but organic materials should also be well suited to this approach.

6.4 Materials Level Modeling

Great strides are being made in modeling the behavior of composite materials, for example in understanding weaknesses induced by holes. This is a critical area to the Air Force,

because of the lack of civilian leadership in this area. The field has a history of highly empirical models with expensive experiments required to even parameterize the computer models. This is changing; better deterministic, hence more predictive, models (rather than parametric fits of experimental data) are forthcoming. Other areas, such as a priori prediction of matrix-reinforcement interface properties, are still distant, and so are methods in other composite materials areas. However, this is a critical technology to the Air Force, and support of it must continue. With the downsizing of the industrial base, the cohesiveness and coordination is centered about the Air Force laboratories. The savings and capabilities of future systems stand to benefit greatly from this work.

6.5 Ceramics, Alloys, Intermetallic Compounds, and Interfaces

Atomistic simulations are not well advanced for these systems. For ceramics, alloys, intermetallics, and interfaces, the modeling situation is not even close to the level of sophistication and application of the organic materials. New techniques, such as the density functional methods, are being pursued, but much remains to be done. Very few dynamic properties can be modeled, and often the models are highly simplified and parameterized. What this field requires is sustained effort in general, and for the Air Force leaders to give focus on important areas.

6.6 Photochemical Modeling

In the relatively short term—five years—the ability to model excited-state and photochemical properties from first principles will mushroom. Relatively little detail is known about excited state structures and reactivities. Indeed, it is almost impossible to get this information experimentally. Most synthetic chemists will avoid photochemical processes if possible, since such processes are difficult to control. Much of this difficulty may stem from the lack of detailed understanding in the field.

In the near term, modeling may start to change this status. While practical applications will be further out, the possibilities are exciting. For example, the same excited states and reactive species often play roles in degradation processes such as stress-induced reactions or photochemical degradation. Modeling may realistically be capable of addressing the problems and lead to materials solutions to chronic maintenance problems. One possibility is designing materials to give readily detectable signals when failure or degradation occurs. Another potential area is the use of holographic masking and photo-assisted reaction schemes for semiconductor thin films. These procedures could lead to an increased integration of different components on the same chip, and may even largely replace expensive processing steps, such as traditional masking and photolithography. This would result in substantial gains in capabilities at reduced cost.

6.7 Bulk Properties

Data fusion—linking of lower-level data, experimental, theoretical, or both, into calculation of engineering properties of interest—is a key component in computationally-driven materials development. For example, how do the coefficient of thermal expansion (CTE), dielectric constants, thermal characteristics, and interfacial behavior vary with chemical composition or processing conditions? While many of these may not be calculable in the near term, specific

properties and behavior will succumb to modeling. There is effort to link quantum mechanics with molecular mechanics, but much remains to be done. Cross-discipline efforts should be fostered.

6.8 Defects, Dynamic Behavior and Transport Properties

In many materials, either the interesting properties or the limiting behaviors are dominated by defects. The easy problems in modeling are to handle defect free, ideal materials. That is valuable for both understanding and predicting ultimate properties. However, increased emphasis is needed for defect modeling. Some defects, such as charge carriers in organic conductors, are amenable to current methods. Others, particularly when intermolecular interactions and dynamic behavior are key components, are much less advanced. This is particularly true when dynamic electronic behavior is involved. Dynamics based on computational fluid dynamics (CFD) continuum models or molecular dynamics (i.e. sophisticated ball and spring) atomistic models are well developed. Only now is time-dependent electronic behavior being addressed. Here, computer power is highly limiting and efficient codes are sorely lacking.

6.9 Synthesis and Reactivities, Synthetic Paths

Pioneering work has been done in modeling the synthesis of organic materials, particularly the famous retrosynthetic schemes. Much of this effort has been driven by the pharmaceutical industry. Modeling reaction conditions, synthetic paths, and reaction catalogs are lacking for other classes of materials—intermetallics, ceramics, alloys and polymers. Great benefit can be derived from more effort here. It can be experimentally tedious to determine mechanistic details, and yet these details are necessary for optimizing reaction and processing conditions.

6.10 Atomistic Catalyst Modeling

Our society relies upon catalysts. The quest for efficient, cheap, reliable catalysts is common to almost all chemical development. This area is fraught with difficulty, in that catalytic activity depends upon many parameters. Not surprisingly, modeling in this area is driven by particular industries, especially the petrochemical industry. No government nurturing seems needed there. However, in areas of Air Force interest, such as propellant manufacture or catalysts for curing composites, application of existing or new modeling tools could facilitate the development of lower-cost processes.

6.11 Modeling Heterogeneous Materials

Atomistic and continuum models are focused on homogeneous materials. As discussed above, defects are beginning to be modeled. What is virtually neglected is heterogeneous materials. Simply put, the methods used for modeling organic molecules are quite different from those used to model intermetallic compounds, ceramics, or glasses. This is understandable, since the bonding in organic molecules, inorganics, glasses, metals, and ceramics differ. Further, hybrid materials have emerged with new and revolutionary properties. Much remains to be done here, especially in understanding interfacial behavior, predicting and designing interfacial behavior, and the a priori prediction of phase transitions and degradations.

6.12 Advanced Synthesis and Processing

Spectacular strides have been achieved in recent years in the pharmaceutical industry toward automation of drug discovery. Combinatorial chemistry is the term used to describe efficient, highly automated methods in which tens of thousands of compounds are synthesized and tested for pharmaceutical activity in short times. Certainly this is possible with peptides since peptide synthesis is a well understood, defined chemical process. These techniques might also be applicable to the less well defined areas. One distinct possibility is in alloy testing. Again, some of the synthetic automation techniques and logic for testing large numbers of samples could be applied to quickly optimize alloy composition for specific applications. Overlapping with robotics applications, emphasis should be placed on automating well defined chemical and processing steps. While this is done on the industrial scale, little has been done in automation for materials development. An achievable goal would be automated synthesis for materials screening on a broad basis.

6.13 Solid State Materials

Out of the possible solid-state materials, only a few have found technical application. Indeed, until recently solid-state physics has not been emphasized in the U.S., and technological leadership has come from Europe and Japan. Beginning in the 1980s, the NSF recognized this cultural shortcoming, and increased its emphasis in this area of materials science. Modeling in solid-state physics, with the exception of modeling simple metals and semiconductors, is relatively unadvanced. Part of the difficulty arises in that many engineering properties depend upon particle size and processing conditions, which tend to be material specific. Given the range of possible materials and applications, sophisticated (i.e., beyond the Huckel independent electron model) methods should be brought to bear. Likely techniques will be applicable from other areas, but the Air Force can provide leadership in areas and topics of interest.

Solid-state theoreticians are continuing to develop full-range computer codes that can treat an almost limitless variety of semiconductor combinations, and which have the predictive power to model several physical phenomena: absorption, lifetime, mobility, third-order nonlinear susceptibility of quantum wires, to name a few. At present, these models continue to be specific to the materials and device of interest. In the future, these models need to become more universal, so that there are not separate models for each combination of semiconductor multilayers such as Si/SiGe or GaAs/GaInP. Another challenge of modeling in the future will be in the areas of lower dimensional structures, quantum wires and dots, and superlattices involving new materials combinations. As the complexity of the layered material designs continues to grow beyond simple two-layer heterostructures, the models predicting the properties of these materials will also have to advance. In particular, the area of quantum electronics continues to spawn new or improved device concepts for devices from infrared detectors to laser diodes, whose properties will continue to challenge modelers for a long time into the future.

6.14 Summary

In summary, computer-driven materials development is not directed toward a specific system, but toward materials technology. Materials is a pervasive technology, and the advances outlined above will lead to dramatic changes in the entire enterprise. As such, the Air Force has

a keen interest in nurturing these developments, incorporating them into its internal and extramural programs, and leading the modeling technology in selected areas while leveraging off-the-shelf technologies as they become available. Unlike most revolutions, this one is slow in coming, but it is nevertheless very real. It portends dramatic changes in how materials will be developed and emphasizes the efficient use of resource dollars. Ultimately, materials and processes must be translated from the computer to the real world.

7.0 Structural Materials (Integration of Materials and Structure)

Structural, including engine, materials have been largely responsible for the major performance improvements in Air Force systems by optimizing certain physical and mechanical properties, such as density, strength, and stiffness. Future structures are likely to require multifunctional capabilities in single components. The use of structural materials such as composite materials will enable this capability.

Composite materials are themselves "structures." Because of their functionality, composite materials have helped narrow the chasm between the disciplines of design and materials. Structural design and materials science must become even more integrated in the future as materials' properties are graded and locally altered to meet multifunctional requirements in structures. Furthermore, the structures must meet the mission requirements for the full life cycle or must be designed for easy or even self-identification of developing flaws and simple repair. Such structures must also be economically manufactured in terms of the total life-cycle costs.

7.1 Materials Payoffs in the Future

The selection of a material is determined by its combination of properties, ease of manufacture, useful lifetime, and total cost. For aircraft structural materials, most airframe materials traditionally have operated near ambient temperature. However, aeropropulsion and hypersonic airframe components must operate at high temperatures, some for several thousands of hours, others only for minutes. Space structural materials must survive excursions to both low and high temperatures. There are frequently other requirements, such as electrical conductivity, optimized thermal management, or dimensional stability (low thermal expansion), which might be combined with the structural requirements. The questions are: What are the trends in materials properties, and what are their payoffs?...What materials might or already provide improved properties?...What is the physical basis for these properties?...What new directions might materials development take to achieve these properties?...Can we fabricate, repair and dispose of them economically?...What enhanced or new systems capabilities will these new materials provide?

Lower Weight

For a given modulus and strength, the material with the lower density will give a lower weight structure, all other factors assumed equal. Density always provides a first power weight saving: half the density, half the structural weight. This truth accounts for the use of aluminum, and the trend from aluminum to composites. Aluminum is about 50 percent more dense than a carbon fiber / epoxy matrix composite. Polymeric materials, with their very low density, are even more attractive. If polymers were available with suitable mechanical properties, an additional weight savings over present composites could be realized, plus the simplicity of polymeric fabrication. Addition of light-weight elements in metallic alloys usually decrease density. Additions of lithium to aluminum decrease density more than proportionately and even increase stiffness. Performance improvements equal to approximately one-half of those attainable with present composites are possible, yet with the normal advantages of metals. Processing of this reactive material has been costly, and corrosion has been a problem. Addition of aluminum to

titanium, nickel, or niobium in larger quantities to form low-density intermetallic compounds offers weight savings of up to 50 percent, often with even potentially better mechanical properties. These trends will probably continue with weight savings of up to 50 percent.

Stiffer, Stronger Structures

High strength and stiffness require strong chemical bonds, with each atom having as many covalent bonds as possible. The moduli of metals increases linearly with density, such that the specific modulus—stiffness/density—is constant to two significant figures. Beryllium is an important exception, as it has a modulus one-third higher than steel, but with one-fifth the density. Covalently bonded materials have the potential of providing up to 15 times the specific modulus of the common engineering metals. High specific modulus elements are bunched around carbon in the periodic table and include boron, compounds of beryllium, boron, carbon, nitrogen, oxygen, aluminum, silicon, yttrium, and titanium.

Most of these elements are among the most plentiful available, although boron and beryllium are rare. Graphite has the highest specific modulus in the directions of the chicken-wire structure basal planes with about five times the modulus, at less than one-third the density of the common engineering. However, the specific modulus normal to the planes has only one-third the value of the common engineering materials. Carbon fibers having sufficient strengths for structural applications have only achieved about one-third of the theoretical modulus, while carbon fibers with nearly theoretical modulus, but substantially reduced strengths, have been made for other applications. Carbon fibers with 100 percent higher modulus should be developed, with balanced tensile and compressive strengths, to fully exploit the increased modulus. Cost issues surrounding these fibers would have to be monitored to keep them financially attractive.

Theoretically, a high modulus material with high bond strength should also have high tensile strength. Since the most attractive materials from a specific modulus/strength view exhibit brittle failure, the challenge is to develop a material with very small flaws. There are two microstructures that might allow ultrahigh strength: single crystals, or nanocrystalline to amorphous materials. The nanocrystalline approach has been most attractive for near-ambient temperatures because of relatively rapid processing speeds and quick achievement of adequate tensile strengths. The fiber or film form allows more rapid processing with finer microstructures, but more importantly has a small volume and surface area which gives high strength because of the smaller probability of finding a major flaw. Fibers usually increase in strength with decreasing diameter. However, there is a lower limit to diameter: 1) health, (i.e., carcinogenic behavior of small diameter fibers), and 2) manufacturability (i.e., fiber breakage due to aerodynamic drag during spinning). There is also an upper limit due to processing and handling. Practically, fibers can be made in the range of 3 micrometers to 200 micrometers, which also depends somewhat on the process. Fine diameter carbon fibers have been made commercially with a 7 GPa (1 Msi) tensile strength or two times more than commonly used fibers. Hence, twice the stiffness and strength, in both tension and compression, should be attainable, but some novel effort is required. Once again, costs must be contained to make these fibers attractive.

Films provide stiffness and strength in two dimensions. While they are attractive for providing stiffness, a crack can propagate across a whole film, whereas a layer of fibers requires fracture of each fiber. Lamellar structures would provide in-plane isotropy with an increase of

approximately 80 percent in stiffness, given the same materials used in fiber form. However, a more reasonable increase is 25 percent, in order to retain a desirable fracture behavior. Very thin lamellar structures in metals have shown experimentally very high strengths and surprisingly up to 30 percent higher modulus. For different reasons, thin ceramic lamellar are predicted to have significantly higher strengths and improved toughness. Both these latter areas are at the research stage. Film or lamellar structures will first appear where a planar, albeit curved, geometry can be exploited. First applications will probably be in aeropropulsion, but skin structures are also likely uses.

Longer Lifetime

Airframes are being used substantially longer than their original design lifetimes. Furthermore, structural loads are increased due to new mission profiles, armament, and electronics. Deleterious effects on durability and lifetimes can be expected. New systems must be designed for much longer lifetimes, and present systems must be monitored and repaired.

Mechanical failures can occur from simple overload of the structure. Increasing the strength of the material, if possible, alleviates this problem. However, a very strong material may be sensitive to initial flaws introduced during fabrication or service. A major improvement in the strength of materials has arisen from our ability to reduce the size and number of flaws. An important factor has been the development of techniques that can identify very small flaws in complex structures, but improvements will be required in resolution for effective application of high strength ceramic materials. Although intertwined, mechanical failures often occur from the inability of the material to withstand multiple loadings well below the initial failure load, which is frequently exacerbated by corrosion.

Composite materials can have extremely high strength, and modest damage tolerance. For two-dimensional structures such as skins, delamination between composite plies in resin matrix composites is the limiting design parameter. To improve resistance to out-of-plane loads, a variety of techniques have been examined. Stitching has been used, but has adversely affected in-plane properties, such as compressive strength. A more uniform strengthening, which might be more generally applicable, is desirable. Several techniques have shown promise, such as whiskerizing, but have not been implemented. Development of these methods should be pursued. However, improving interlaminar strengths may cause the failure mode to change to in-plane, a potentially more catastrophic failure.

Composite materials have also been touted for their excellent fatigue resistance. That is true if the loads are predominantly carried by the fibers, but not if carried by the fiber/matrix interface or by the matrix. Hence, a composite structure may have little likelihood of a fatigue failure in most of its structure because fibers are carrying the load, but may be very sensitive to fatigue in certain other regions. Careful design is required, and a change in concept from black aluminum to visualizing a composite as an ensemble of ropes loosely coupled together must occur. Free edges and cutouts must be minimized because they are sources of delamination and fracture. Assuming proper design, resin matrix composites generally provide run-out (no failures after more than 10^8 cycles) at 60 percent (2-D isotropic) to 90 percent (uniaxial) of the tensile strength. This is typically about a two-fold or better improvement in stress over structural metals. Composites do not perform as well in compression or torsional fatigue as the matrices and interfaces must carry major loads. Run-out loads may be limited to as low as 20-25 percent

of the single load strength, which is poorer than structural metals. Fatigue in metal and ceramic matrix composites is also observed to be excellent when properly designed, even though extensive microcracking occurs. This may require replacement of the part for loss of stiffness, even though the retained strength may be adequate for the mission.

In summary, composite materials can offer dramatic performance improvements due to characteristics such as longer fatigue lifetimes. Substantial improvements in composite materials, such as improved fibers, are possible, with a resultant improvement in the performance of system components. Attention needs to be paid to improved composite-specific design practices and to the prevention of service-induced damage.

Higher Temperature

The higher operating temperature for airframes in sustained supersonic flight makes aluminum and epoxy-based carbon fiber composites marginal, except for lower Mach numbers. Higher temperature metals such as titanium and higher temperature carbon-fiber composites based on imides are currently acceptable for higher Mach numbers. New resin systems with carbon fibers, metal matrix composites, and intermetallic alloys appear satisfactory up to temperatures of approximately 500°C. They are in different stages of development and maturity, but are all likely to find application in aerospace systems.

Materials in the temperature range from 500°C to 1500°C are covered in the section on gas turbines. Even apparently small increases in operating temperatures of a gas turbine have a major impact on specific fuel consumption and thrust to weight ratio. However, increases in operating temperatures are limited by the melting points of the presently-used alloy systems. Future improvements must come from the application of ceramic materials.

Materials for applications above 1500°C are limited. Graphite has a sublimation temperature of about 3700°C and the best mechanical properties at high temperature. Graphite begins to creep at 2200°C, but can be used in lightly loaded structures up to 2800°C or even higher. A problem is that an appreciable vapor pressure exists at temperatures above 3000°C, and this may give rise to an appreciable loss of mass. The major problem with graphite is oxidation in oxidizing atmospheres, which begins at temperatures as low as 350°C and at 700°C for pure and highly perfect single crystal graphite respectively. Much effort has been expended on oxidation protection schemes for graphite, but the fact remains that it does oxidize, and the vastly different coefficients of thermal expansion cause cracking in oxidation resistant coatings and infiltrants.

Substantial progress has been made towards solving these problems, and some parts have withstood 500 hours of cyclic oxidation, but other similar parts have survived for only 50 hours. Oxidation performance depends on the exact temperature cycle, as lower temperature oxidation is often more severe than at higher temperatures. Silicon-based protective systems are limited by the loss of the protective silica film at temperatures above 1740°C and 1 atmosphere. Oxidation protection systems for higher temperatures are based on alumina or hafnia formers. Both are not as good at lower temperatures, but French results with alumina formers have been remarkably good up to 2000 C. Hafnia forming systems are limited to about 2400°C, because the volatility becomes appreciable for long term applications approaching 1000 hours. However, hafnium diboride, with a 3250°C melting point, has been found to provide

improved short term, very high temperature oxidation resistance with better low temperature resistance. All these coatings have significantly higher thermal expansion coefficients than graphite, and cracks can occur upon cool-down. Passing an inert or possibly even a fuel gas through a coated carbon/carbon composite may allow active protection.

Oxide materials appear to be attractive for oxidative conditions. However, the most creep-resistant oxide—yttrium aluminum oxide—starts creeping at 1500°C. Hence oxides could only be used in nonload-bearing applications at high temperatures. Melting points and volatility also become a problem. Oxides generally have high thermal expansion coefficients, and relatively high moduli, which makes them susceptible to thermal shock. For relatively short times (hours) and for temperatures above 2500°C, careful design of stabilized hafnia liners may be attractive. The yttria stabilizer, which prevents a phase transformation, evaporates relatively rapidly by 2500°C and its use probably would be limited to a single mission.

Oxide materials are attractive for thermal barrier coatings and reinforcing fibers. For example, multilayered coatings of alumina and zirconia are very effective in decreasing the temperature of parts. The physical understanding of this performance is not understood, and improvements can be expected in the future. Oxide fibers can be used for lower temperature applications. Oxide fibers have suitable thermal expansion coefficients for potential matrix materials. Thermochemical compatibility of the matrix and fiber has been a problem, however.

Non-oxide ceramics fill an important niche between superalloys and graphite. They offer higher operating temperature and good oxidation resistance. Silicon carbide has the potential of adequate creep resistance to 1550°C and to 1800°C in single crystals. The fracture toughness of monolithic silicon carbide is low and formation of a composite is probably required for extensive application. Silicon nitride is much tougher and stronger than silicon carbide, but is probably limited to 1400°C because of creep. Both are limited by active oxidation above 1740°C and more practically to about 1650°C. The development of silicon carbide composites for jet engines would provide large increases in combustor and turbine temperatures compared with the incremental improvements with superalloys. However, the choice of superalloys (or their replacements) with thermal barrier coatings, or ceramic matrix composites is not obvious.

Other fibers that have thermochemical and thermomechanical compatibility with potential matrices, such as titanium diboride, would provide lower density with higher operating temperature than the nonreinforced matrix.

Hypersonic vehicles using air breathing engines will surely be an important part of the offensive and defensive weaponry of the future. They will use ramjet/scramjet engines and be capable of speeds up to the Mach 25 to achieve access to space. In the near term—the next ten years—non-man-rated vehicles will be built to serve as precision scalpels to expediently neutralize ground targets and air and spaceborne targets. These vehicles would be powered with scramjet engines that use conventional hydrocarbon fuels, making them capable of being incorporated easily into the Air Force warfighting infrastructure, and both the airframe and the engines would be fabricated from materials that are currently being researched.

In the further term—within 25 years—man-rated vehicles operating in the same speed regime would require the same types of materials, but the reliability would be significantly improved as production experience is gained with building the non-man-rated systems. These

vehicles could have a variety of roles, ranging from high-speed battlefield fighter aircraft to long-range, global-reach bomber transport aircraft. Ultimately, they could eliminate the need for overseas bases, in the sense that they could reach any part of the world in a few hours.

In the far term, routine access to space will be accomplished using single-stage-to-orbit (SSTO) vehicles. Present trends indicate that these vehicles would be powered by air-breathing engines for most of the flight, with a rocket being used for the space portion. It may well be the case that some new generation of thrust production becomes available, but a clear requirement will continue to be a low airframe structural weight and an efficient, lightweight air-breathing propulsion system. The types of materials used for the near- and middle-term applications will probably include nickel-based superalloys, advanced refractory alloys, intermetallics, metal matrix composites, intermetallic matrix composites reinforced with ceramic fibers, ceramic and carbon-carbon composites, and lightweight thermal insulation materials. In addition, for both the engines and airframe, high thermal conductivity materials such as copper-based alloys, beryllium-based alloys and carbon-carbon composites will be needed. Almost all of these materials will require coatings to provide protection against oxidation and the other environmental conditions associated with high speed flight through the atmosphere. Advanced processing methods will be used to produce the necessary lightweight structures that in some cases will contain arrays of coolant passages through which fuel will flow to serve as the temperature control of the structure.

For the far-term applications, advanced versions of current materials will be needed. These may include super-lightweight materials such as beryllium composites or very high temperature-resistant materials such as fiber-reinforced ceramics, nanostructures, functionally graded materials, multilayer coatings, high-temperature electronic materials, high thermal conductivity materials, high-temperature transparencies, etc. It is clear that materials will be an enabling technology for hypersonic vehicles of the future.

To realize the extraordinary benefits of significantly increased temperatures, superalloys, refractory alloys, intermetallics; ceramic, carbon and intermetallic matrix composites, creep-resistant fibers; environmentally stable, crack-stopping interfaces; and high strain-to-failure matrices must be developed. These are not trivial, cheaply solved problems.

Thermally Conductive/Thermally Dimensionally Stable Structures

Heat dissipation from electronics modules and space structures is a major problem. Dimensional stability of platforms and antennae when subjected to temperature fluctuations is often required. An increasing demand is also being placed on heat exchangers in aircraft. Future heat exchangers need to have increased efficiency and reduced weight.

High thermal conductivity is often associated with electrical conductivity, but the best thermal conductors near room temperature are phonon (lattice vibration) conductors. The best thermal conductors will be pure elements with strong bonding in a highly perfect single crystal. Isotropically pure diamond has the highest theoretical and experimental thermal conductivity with a conductivity/density ratio over a magnitude better than copper. Diamond films offer much improved thermal conduction for semiconductor heat sinks, such as tungsten/copper laminates, or substrates such as beryllium oxide, aluminum nitride, or alumina. Diamond-film fabrication improvements can be expected to allow large areas to be coated, at higher deposition

rates, and at lower temperatures, but possibly not all simultaneously. Chemical vapor infiltration of diamond powder preforms would allow more massive and complex parts to be fabricated. Diamond fibers have the potential of providing high stiffness and strength as well as high thermal conductivity. Diamond fibers would probably have the best compressive properties of any fiber for use in composites if a suitable interface was achieved.

Graphite provides almost the same specific thermal conductivity as diamond but only in the two dimensions of the planar structure. When combined with a carbon matrix, the resultant composite has the highest thermal conductivity of any composite material. Carbon-fiber/aluminum provides more than twice the conductivity of aluminum with 15 percent less density. Reliability of electronics and weight savings could be achieved by direct replacement of present thermal conductors with these materials. While life-cycle costs may be reduced, the initial cost of high conductivity carbon fibers—\$2000 per pound—limits their application. Part of the high cost is caused by the small production volume associated with high-temperature processing. Certainly, a great reduction in costs is possible with changes in precursors and increase in production volume. Decreasing the cost nearly two orders of magnitude is conceptually possible, but would require improved chemistry to be developed. This also may allow the thermal conductivity to double, approaching the theoretical value.

Thermal conduction in composites for space structures could be enhanced if diamond fibers were available. Thermal conductivity, stiffness, and compression would be the major considerations and all are well satisfied by diamond. An alternate is a lamellar structure using diamond films, which may be cheaper and provide two-dimensional conductivity. Carbon fibers might be developed that would meet all the requirements. However, high thermal conductivity fibers and structural carbon fibers are a more likely optimum.

Strong bonding and an open structure, typical of covalent bonding, tend to produce low thermal expansion coefficients. Negative thermal expansion coefficients are frequently observed in rod layer and other anisotropic structures. Negative coefficient materials can be combined with a positive coefficient material to provide a zero expansion coefficient, at least over a limited temperature range. Often this can be done with one material, since the different expansion coefficients can be in two directions within the crystal. Graphite and magnetostrictive materials, including some alloys and titanates, are examples. High-modulus carbon fibers have a small negative coefficient at room temperature that can be used to produce structures with near-zero thermal expansion and high stiffness. The problem again is poor compressive strengths. A different fiber architecture is required, but it has not been proved that a better balance of properties can be achieved. Stiff rod-like polymers also have a negative thermal expansion coefficient along the rod. However, the transverse thermal expansion and the moduli have not allowed near-zero expansion for angle-ply composites. Large changes in properties are not required to achieve zero thermal expansion. The problem is that these aligned rods buckle under very low loads in compression. Most designs require balanced tensile and compressive properties. While the problem appears to be inherent to the material, the payoff is sufficiently high for both polymeric and carbon fibers that any innovative but sound idea should be funded.

Future Materials Chemical Compositions

Considerations of density, stiffness, strength, thermal conductivity and thermal expansion all lead to more emphasis on the lighter elements in the center of the periodic table. Aluminum,

magnesium, carbon, beryllium, silicon, titanium, yttrium, and their compounds with oxygen, fluorine, and nitrogen provide the highest potential improvements. Additions of light elements to form intermetallic compounds of titanium, the iron group, niobium, and perhaps several others offer lower densities, higher operating temperatures, and sometimes improved oxidation resistance, but usually with a loss of ductility. Progress in achieving a modicum of ductility in some of these systems can be expected.

Desirable Microstructural Architectures

A material's properties are partially determined by its composition and crystal structure, and also by its microstructure. The size, shape, and orientation of the crystals in a solid have a primary effect on a material's properties. The improvement of materials will continue by finding new materials compositions and optimization and control of the microstructure. The ability to control microstructure on a finer scale will undoubtedly lead to unexpected changes in properties. However, finer control of properties by placement of materials, as in fiber-reinforced composites, leads to a higher level of architecture. Designers in the future will dictate this top level of architecture, by specifying the orientation and number of plies in a composite, for example, as well as by integrating sensors to measure stresses or failure. In addition, this design flexibility allows anisotropic elastic properties which provide bend/twist and tension/torsion couplings. While well-known, the only application has been to increase the stability of the forward swept X-29 wing. The perception that anisotropic composites must warp with temperature or humidity is incorrect. Finally, variation in the orientation of fibers need not be limited to twist between the plies. Curvature and splay within a ply allows the stresses to be kept within the fibers, minimizing the loads carried by interfaces and the matrix to increase the safety of the structure.

7.2 Processing and Fabrication Technology

Processing and fabrication of materials into structures is of importance here, because of the cost and performance requirements of the final structure. Processing of a material generally includes synthesis or reduction of a compound to a metal, refining, and forming to an intermediate product such as powder, pellets, or billets. Processing also includes such things as rolling, injection molding, and sintering. Fabrication usually involves machining and the building-up of a structure, frequently from mill forms, such as bar, sheet, or forging. The dividing line between processing and fabrication is ill-defined, and has become more diffuse with the introduction of composites. Processing and fabrication costs are varied, depending on the part. For example, the cost for a large number of injected molded parts can be largely for materials. By contrast, the materials cost when fabricating a small number of complex parts is usually a small fraction of the total cost. Even with a composite, carbon fiber prepreg is made to structure at three to six times the material cost. Airframes fit the second case quite well, as serial numbers are small and complexity is high. Obviously, any process that can take a raw material and directly produce a final shape that requires a minimum of machining is desirable.

Bulk Materials

Parts may be short and squat, or thin, such as skins. The processing and fabrication techniques may be quite different for the different categories. For short and squat parts, direct

casting to shape is very cost-effective. Traditionally, cast properties have not been as good as wrought products. However, computational programs for the design of the casting process and new compositions, which can produce desired microstructures, have reduced (and even eliminated, in some cases) the difference in the properties. Powder processes also allow near-net shape processing and allow high-strength, rapidly solidified compositions and structures to be retained. The process can be economical, even with the added cost of the powder. However, for reactive metals and some ceramics, powder costs and handling are very high.

Direct spray-up of molten metal droplets into the final shape including skin structures eliminates intermediate steps, and maintains the benefits of rapid solidification. This general trend of building up materials, rather than machining away, will continue, as subelements can be easily added throughout the process. Sensors, actuators, electrical conductors, or insulators can be directly placed within the structure. Sensors could measure stresses and temperatures during service, which can be directly input to deterministic lifetime prediction models. Spray-up, electron-beam (e-beam) evaporation, and other techniques would also be directly applicable to lamellar composite and functionally graded structures. The one-dimensional gradings usually implied by functional gradients will become generalized to three dimensions in the future. Stress concentrations caused by discontinuous changes in the material properties will be eliminated or at least moved to a much finer scale.

Composite fabrication costs have been relatively high. A major part of the problem is that the design makes for expensive processing. For example, redesign of a carbon/carbon part for manufacturing would include the incorporation of channels in the preform to enable rapid mass transport and high deposition rates. The extremely long deposition times could be reduced by a magnitude, while retaining the economies of scale inherent in using large furnaces.

Prototype Fabrication

Prototype parts have traditionally taken many months for fabrication and are extremely expensive. The major cost driver in this environment is tooling. Designs often had to be modified after the first prototype, and a second or several more variants had to be fabricated. Today's computer design of parts can check fits and clearances easily, but a prototype must still be fabricated, if only to serve as a model for mold manufacture. Free-form fabrication enables direct mock-up or real fabrication of a prototype part from computer input. Several techniques exist at present, but stereolithography will be described.

In this case, a platform is placed just below the surface of a photo-polymerizable polymer, and a computer-controlled laser beam cures the liquid polymer on the platform, but just in the regions where material is desired. The structure is built-up layer by layer. The plastic part can be used as a nonworking model or as a model for mold fabrication. The total time can be hours to 1-2 days, depending on the size and complexity of the part. Replacement of out-of-stock parts is also facilitated. Hip joints are tomographically scanned into a computer, worn regions redrawn to original shape, and a stereolithographic part is made in plastic. A titanium hip replacement is then cast in a mold made from the model. The part fit to the patient is much improved. The Air Force should make use of this technology to help maintain aging hardware.

Today's properties obtainable with directly used free-form parts do not match those from other processes. However, tomorrow's properties may allow direct fabrication of the final part, without using an intermediate model.

Production Fabrication and Minimum Touch Labor

Airframes still require "touch" labor. The low production numbers and complexity of structures has made automation difficult to justify, due to high nonrecurring capital expenses. However, the decision also results in a large, highly skilled work-force. The difficulty in hiring highly skilled, highly paid employees in the future, given our lack of apprentice schooling, will cause accelerating use of automation. The ease of implementing these complex tasks will ease with time because of continued development of computational software.

Composite fabrication of complex parts has been manual labor-intensive, and the cost of quality has been relatively high. Given the costs of composite parts, few get scrapped, and rework and reinspection are cost penalties. Numerous processes exist that have not been fully exploited to minimize touch labor, to rapidly process material, and therefore to reduce fabrication costs.

Discontinuous fibers have been largely neglected in high-performance composite structures, because of the possibility of compromising mechanical properties. While these materials do not display significant decreases in in-place static tensile properties, effects of compression loading, temperature, combined temperature and stress, and time dependence have not been thoroughly characterized for complex structures. These materials allow for easy molding of sheet materials to form relatively complex shapes with either thermoplastic or thermoset resins. Simple application of the technique is difficult, as the fiber movement during forming must be controlled. The understanding of the deformation and the development of simply used software for design of dies and processing control will speed the application of this technique. Short discontinuous fibers can be aligned into preformed sheets by paper-making technology with only a 10 percent to 15 percent decrease in composite tensile properties parallel to the fiber axis. More importantly, the slight misalignment of fibers increases the often limiting transverse properties by 50 percent. Reaction injection molding of the preforms in a mold produces a net-shape part. Obviously, simpler shapes could be reaction injection molded with continuous fiber preforms as well. Textile technology could be applied to minimize cut edges on preforms, and directly weave "2 1/2 dimensional" structures. These materials are not made rapidly now, but would allow integration of sensor fibers into the structure.

Tape lay-up and broadgoods will continue to be developed. However, the use of high-throughput, limited-geometry technology such as pultrusion, braiding, and filament winding will increase. Versatility of these processes will be expanded by such techniques as fast-winding of a simple shape and subsequent deformation to a more complex geometry. Again, application will depend on the development of simple software that automatically handles the "inverse" deformation of the final geometry back to an easily wound shape.

Autoclave curing is a relatively inexpensive, but time-consuming process. Principal recurring cost factors are vacuum bagging and loading labor costs. The autoclave provides heat for curing the resin and pressure for consolidating the composite to minimize internal voids, to eliminate gaps between pieces, and to provide a good outer surface. It does not maintain tight

tolerance on thickness. It does not provide a uniform heating cycle for uniform curing of thick parts. Given these deficiencies and expense, non-autoclave processes are highly desirable. Molds can provide pressure and tight dimensional tolerances, but are expensive and limited in size. As fabrication experience increases, tolerances of prepregs and tows can be expected to improve, and the necessity of using high pressures for curing will be reduced. Elimination of vacuum bagging is desirable, and will be eliminated or at least simplified as defects in materials and manufacturing are reduced. More novel pressurizing systems, such as foam in-place and structural foams, which pressurize skins against molds, will probably be used more commonly. Better foam materials, such as high modulus, low density carbon foams, will provide higher structural efficiencies with either closed or open cell structures. Heat is generally required to cure high performance resins, but UV or e-beam curable resins are available. UV may not penetrate the part sufficiently for cure, but e-beam can, and both are used in commercial applications for electronics. The use of low-energy curing resin systems offers the potential for dramatically reducing costs, because they allow much cheaper tooling materials to be used.

High-temperature composites usually require quite different processing. One approach is to apply resin matrix technology by using polymeric precursors to carbon or ceramic matrices. The major problem, if low-porosity and high-strength matrices are required, is that multiple reimpregnations are required, because of the shrinkage and cracking that occur with the density increase from polymer to ceramic. Conceptually, the fibers and matrix could be processed together to better match processing shrinkages. Up to the present, coprocessing has not produced good mechanical properties. If innovative concepts for overcoming the problems emerge, they should be funded.

Chemical vapor infiltration of composite matrices has often given the best mechanical properties. Little has been done to determine fiber and filler architectures that would produce a more pore-free structure, and simultaneously allow rapid and complete infiltration. Many schemes for more rapid deposition have been proposed and investigated, such as forced flow and temperature gradient. However, processes that can be used with complex arbitrary shapes should also be developed, such as liquid and supercritical precursors.

Molten liquid impregnation is one of the few really low-cost techniques for high-temperature composite fabrication. The major limitation is the lack of really desirable systems that can be processed this way.

Finally, processing and fabrication costs could be reduced if structures were designed for manufacturability as well as for performance. Similarly, life-cycle costs could be reduced if structures were designed for inspection, repair, and disposal.

Bonding, Joining, and Fastening

The potential weight savings to be gained by using composite materials is often halved by the necessity of joints. Better design of the structure may ameliorate these losses, but better ways to connect structural elements can provide large weight savings. Adhesive bonding would make aerodynamically smoother skins, but reliability of adhesively bonded structures and repairs has limited its usage to secondary structure and lightly loaded parts. Cocuring of composite parts is more attractive, because a continuous polymeric phase forms through the interface. This allows a lower part count, particularly of fasteners, for final assembly. The lower fastener

count is important for carbon fiber composites, because the structure is weakened by fasteners, but more importantly because of the high cost of titanium fasteners required to prevent galvanic corrosion. Replacement of these costly fasteners by substituting an adhesive bond with the carbon-fiber equivalent of Velcro to aid in assembly and to provide strength between the plies would be desirable. Bonding, joining, and fastening are often neglected areas, as they are not as flashy as other areas. However, the payoffs in initial weight and lifetime of the structure make advancements in this area important.

7.3 Repairing Structures

Structures should be designed for inspection and repair. Sensors will be incorporated in the structure to monitor and record the history of the structure, so that a life-prediction model can predict the safety of the present structure. Ready access for inspection of structures that can not be monitored onboard should be designed-in. Similarly, the design of a large integrated structure should allow simple cutout or patching of a failed or weakened region at a minimum cost.

Active Repair of Cracks

Traditionally, materials have been repaired actively by a person performing the repair. The crack might be welded, diffusion bonded, or glued. An economic impetus will probably develop to try to repair subcritical cracks, and particularly invisible cracks. Techniques that might fill these cracks, such as a smart glue, or gas or vapor transport to a crack-tip with local deposition of the repair material at the stress concentration, could prolong the lifetime of structures.

Surface Roughness

Slip bands and asperities can initiate fatigue cracks. Surface roughness analysis will be used to identify the initiation of these regions, which then would be smoothed by local polishing using wet or dry chemical and/or mechanical polishing.

Surface Coatings

Paints and wear- and oxidation-resistant coatings often have to be stripped for depot maintenance and then recoated. The cost for stripping frequently is a multiple of the cost of application. "Paint for Life" is an ideal goal. Initial cost of the material should not be the only consideration. However, localized repairs are desirable, such that the coating only forms on a scratch, for example. Electrical fields or chemical reactions with the bare substrate could be used to cause localization. Very high-temperature materials may need a transient protective coating to be formed during heat-up or cool-down. For example, the oxidation of carbon/carbon composites is poor at relatively low temperatures. Thus, a carbon/carbon composite turbine blade or combustor might provide longer lifetime if a small amount of a boron-containing fuel was used during engine startup and shutdown.

Passive Self Healing

The recovery of load-bearing capability after failure would be a major step forward in the development of man-made materials. Biological systems show the ability to repair, albeit slowly. In a sense, metals that exhibit plastic deformation exhibit self-healing. Atomic bonds are

broken and remade as a dislocation moves through a metal. Very fine-grained nanostructures may also allow deformation to occur, but by a different mechanism. The two required characteristics are the reformation of bonds, and the ability to accommodate large strains to relieve high stresses. Recovery of load-bearing capability has been demonstrated with graphite. The possibility exists for the development of carbon-fiber or other composites that can quickly recover the ability to carry loads.

7.4 Summary

- Any significant performance gains in our future systems, such as hypersonic vehicles, will depend on structural materials.
- Computational capability will allow rapid scanning of unstudied, complex systems for discovery of new and desirable chemical compositions. Systems containing low-density elements are likely selections. Understanding from atomic-to-structural scales will result in higher strength and new ductile materials. Improvements in mechanical properties can be expected to double present strengths.
- Multifunctional structures are a trend. Integration of sensors and thermal and electrical conductors with load-bearing structures will make future airframes look more like a giant semiconductor chip. Gradients in materials composition, rather than discontinuous jumps, are more likely to minimize interfacial stresses and failures.
- Free-form manufacturing may become the norm. Replacement of worn parts can be done by tomographic scanning, modification of input for wear, and free-form manufacturing.
- Processing and fabrication processes that minimize “touch” labor will increase in importance. Software for easy application of this technology will speed its introduction and growth. The use of specific materials that simplify processing will also increase in importance.
- Self-healing materials and films will be developed.
- Finally, designers of structures should also consider processing, fabrication, joining and assembly, inspection, repair, and disposal to reduce life-cycle costs.

8.0 Engine Materials

Research and development of materials suitable for advanced engines, including turbine engines and other propulsion systems such as ramjets and scramjets, has over the past 50 years proceeded at a prolific rate. The overall aims of these R&D efforts have been directed into thrust increases coupled with weight reductions, leading to increased engine performance as well as improved specific fuel consumption. The origin of these various efforts has been based largely in the programs undertaken by the engine producers, coupled with programs run by DoD laboratories and ARPA. Universities and national laboratories have been involved in much of the basic research areas (i.e. 6.1 programs) and to a lesser degree in exploratory development (6.2 programs). Much of the progress has been initiated by visionaries in the industrial sector, where the business of engine materials development is well known and a key issue, but often as a result of creative synergistic interactions with scientists and engineers at government and academic institutions. An important issue, to which reference is made in other sections of this report, is that future advances in engine materials will be severely hampered by the fact that investment by the engine producing industries and risk-oriented agencies in these innovative, visionary programs has decreased precipitously. Decreased funding means that there are fewer technologists, with the essential experience, working in or with these industries, and the danger is that we will fall below a critical mass required to permit creative synergism between industry and government to occur.

In this report, materials research and development over two time scales is addressed, one being 10-15 years and the second being 20 years and beyond. In terms of the first, these types of research projects are those involved in 6.2 programs, whereas for the longer time scale, these projects are best described as being of the 6.1 variety. For turbine engine components, the Integrated High Performance Turbine Engine Technology (IHPTET) Materials Program initiated in 1988 includes much of the relevant projects for engine materials. Materials for other propulsion systems have been researched in programs such as the National Aerospace Plane (NASP), and Hypersonics Technology (HYTECH). IHPTET is a three-phase program scheduled for completion within the 10 to 15 year timeframe. Carried into Phase III this is an extremely ambitious program which has precipitated remarkable creativity within the materials sector which is far from being realized. A number of materials being developed in this effort, both in Phase II and projected for Phase III, will require significant further optimization in the future. A number of Phase II technologies are in serious danger of not being developed to the level of production readiness, while some projected Phase III materials technologies will simply not be suitably developed to meet the Phase III demonstration milestones. Stated differently, even the materials technologies demonstrated via the IHPTET program will require 10 to 15 years to reach field deployment. Within the context of this study, some have suggested that even the technology revolution sought in IHPTET Phase III is merely "near term," thus an even more distant perspective must be developed. For this, there are some exciting possibilities which are described below. However, it should be remembered that step-function progress, in contrast to continuing evolutionary improvements, in materials technology requires that a significant cadre of technologists be focused in these new areas. Hence, attaining progress requires new and effective teaming arrangements between universities, government, and industries.

8.1 New Engine Materials: Why are They Important to the Air Force?

The importance of new engine materials to the Air Force involves increased improvements in engine performance with the added advantages of affordability and environmental friendliness. Clearly, some of these factors are of a strategic nature, some impinge on environmental issues, and others clearly address the issue of cost. In the first of these performance, a goal of the IHPTET program is to reduce engine weight by 50 percent and increase thrust to weight by 100 percent. To illustrate the kinds of weight savings that can be achieved with new and improved materials and processes, and the implication of such weight savings, we refer to the estimates made for the lifetime of the F-22 fighter, where each pound of weight saved in an engine results in a saving of 8.7 million gallons (73 million liters per kilogram saved) of jet fuel. At today's prices, that saves \$4.8M in fuel. Estimates of the weight of a compressor bladed ring made from existing superalloy materials is about 25 kg (55 pounds), whereas the same component fabricated from titanium metal matrix composites (Ti-MMCs) would weigh 4.5 kg (10 pounds), a significant savings. For these same materials, the combined weight of the third and fourth rotors, with attendant spacer, is reduced from 69 kg (150 pounds) to 15.5 kg (34 pounds). General Electric's substitution of g-TiAl as the material for the low-pressure turbine (LPT) rotor in a CF6-80C engine results in a reduction of approximately 136 kg (300 pounds). Multiplying these weight savings by the saving in jet fuel used, and even structure redesign, implies a very marked reduction in operational cost to the Air Force. To the warfighter, these gains in engine performance can also be translated into capabilities: For fighters—sustained supersonic operation, 45 percent reduction in take-off gross weight (TOGW), smaller turning radius and increases in range and payload; For transports—increased range and payload, with longer life and reduced maintenance; For expendable engines/missiles—150 percent range increase for strategic subsonic propfan and 75 percent range increase for supersonic tactical turbojets. Over the long term—20 years or so—these benefits will multiply as new materials and designs enable propulsion systems with revolutionary improvements in cost, reliability, performance, and environmental considerations.

8.2 Basis for Improvements in Materials for Engines

The most significant factor upon which improvements in engine materials are based involves the thermodynamics of the combustion process. Figure 8.1 is a schematic diagram of a gas turbine engine, from which it can be seen that propulsion is derived from the combustion of a mixture of jet fuel and compressed air. In general, thermodynamics are optimized by increasing the pressure of the air and the temperature of the combustion process. Hence, as the compressor increases the pressure of the air such that the compressor discharge temperature (T_3) is increased, the temperature of combustion increases so that the high pressure turbine inlet temperature (T_{41}) is also increased, and the overall efficiency of the engine improves. The desire to increase these temperatures leads to the first requirement in terms of improved materials, which is for materials exhibiting enhanced elevated temperature properties, not only in terms of mechanical response but also in terms of resistance to corrosion and oxidation. Of course, a second requirement immediately follows, which is that these enhanced properties should be achieved without weight penalties. In fact, increased temperature capabilities and lower materials densities are often played off against one another in application in given components. An example of

how these temperatures, and T_{41} , have increased and are expected to increase with time is shown in Table 8.1.

Table 8.1. Engine operating parameters over the period 1970-1994, and projected to the year 2010. OPR is the overall pressure ratio, and T_3 and T_{41} have been defined in the text (see Figure 8.1). * data for advanced subsonic flight; § data for the high speed civil transport (HSCT). Data provided by Dr. Lyman Johnson, GE-AE.

Year	OPR	T_3 (°C)	T_{41} (°C)
1970	15:1	590	1345
1994	38:1	695	1425
2006§	25:1	620-705	1540-1650
2010*	75:1	815	1760

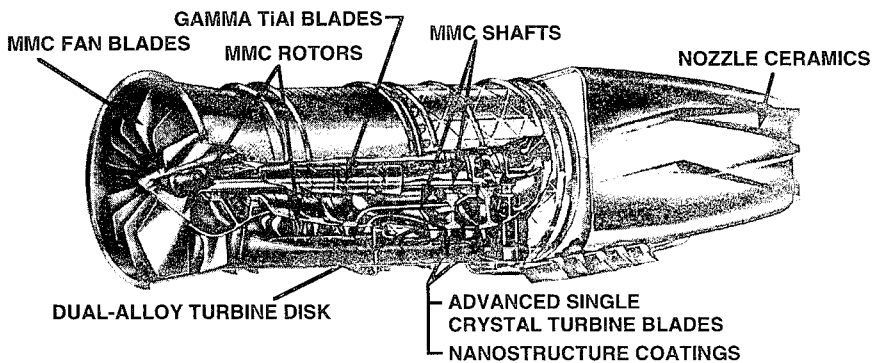


Figure 8.1 Schematic Cut-Away of a High Performance Gas Turbine Engine

In addition to the requirements of higher temperature capabilities to enhance the thermodynamic efficiency of the system, and lower densities to improve specific properties, other characteristics of engine materials need to be enhanced. For example, the durability of components must be improved, particularly as the temperature capability is increased. Also, resistance to environmental degradation is extremely important and the improved materials must be sufficiently damage-tolerant to meet design criteria. The specific stiffness must be enhanced; this is particularly an issue for fan blades and other large structures. The costs involved in processing

and production must be minimized so that components made from advanced materials are affordable. For example, component affordability may be improved by increasing yields through the use of process modeling, improved reliability through process controls, and improved cleanliness and near net shape processing.

Improvements in engines may be effected by use of materials which are enhanced as described in general terms above. However, often it is not an optimum situation when a new or improved material is substituted for an existing one in a given component. Rather, the design of the component should be re-examined in light of the improved properties of the material. Conversely, new designs are not appropriate if there are no materials which exhibit properties required of the given component. Hence, it is extremely important that an integrated approach evolves in which designers, materials engineers and production engineers develop new systems solutions. A combination of innovative design and materials enhancements represents a very powerful tool for optimization of turbine engines and all other types of propulsion systems. In terms of the materials limitations of today and the near future, it is also important to recognize that the same materials come in several forms, which leads to multiple service limitations. For example, nickel-based superalloy technology falls into several broad classes, such as single-crystal alloys for first-stage turbine blades and powder metallurgy wrought alloys which are used for turbine disks. The disks cannot be made today from single crystals, while the disk alloys would not serve in the first-stage turbine of modern engines. Temperature, stress and lifetime must be considered together in defining materials performance. For these reasons, one must speak not only in terms of alloys or materials, but also in terms of processes and components together with the alloys. Only then are technologies defined.

If R&D resources continue to be invested, dramatic improvements in propulsion materials will be achieved over the next 10 to 15 years. Materials for hypersonic propulsion systems will be developed under programs such as HYTECH and will include nickel-based superalloys, advanced refractory alloys, intermetallics, and coatings for thermal control and environmental resistance. These materials will be for non-manrated systems in early development but will eventually be ready for manrated applications as the reliability of the materials is increased.

Significant improvement in turbine engine performance will be realized over the next 10 to 15 years if materials issues in the following critical technology areas are addressed. These areas may be viewed as seven core technology areas for turbine engine structural materials. The materials capability in several of these areas pace all performance measures of engines. Revolutionary advances are being sought in some of these under the IHPTET Materials Program. The critical components are:

- Light weight fan blades
- T₃ compressor disks
- Compressor blades
- High-pressure turbine (HPT) disks
- HPT airfoils
- Static components (cases, ducts, etc.)
- Combustor and exhaust nozzles

There are a number of candidate materials systems which are currently under development, and, if successful, may be applied in engine applications over the next 10 to 15 years. These are described briefly below.

Light Weight Fan Blades

Of the components listed above, fan blades are operated at the lowest temperatures. However, these items are large, and hence considerable weight savings may be realized by use of low-density materials which exhibit appropriate mechanical properties, for example, a tensile strength of 560-630 MPa (80-90 ksi), which precludes many light weight materials. Considerable interchange between designers and materials engineers has taken place regarding this component, and innovative designs including hollow blades has resulted. For these components, a high specific stiffness is required, and so materials of choice have centered around the exploitation of organic matrix composites (OMC), such as graphite-reinforced resins, and titanium alloys.

In the first of these, OMCs, there are major advantages in terms of weight and durability. For example, the specific strength and stiffness are better than twice those of metallic structures, and the fatigue limits are equally superior. Although these types of materials find application as fan blades at present, there is a need for improvement in capability. For example, for advanced turbine applications there is a need to increase fan temperatures up to 482°C (900°F). This requirement is far beyond OMCs at present, and an ambitious goal which would still offer considerable advantage would be 427°C (800°F). Manufacturing methods under development include improved woven preforms, resin transfer molding, and automated tow/fiber placement. Emerging systems include efforts aimed at development of toughened epoxies, thermoplastics and high temperature matrix resins. Finally, repair of these types of materials is a potential problem, and effort has been placed in this area, such that efficient repair methods are emerging. In general, OMCs are not considered to be suitable for large high-speed fans.

In terms of the upper temperature range for fan blade applications, namely 482°C (900°F), the material of choice is titanium, and in order to reduce weight, a design involving a hollow blade is used. The aim is to develop materials for large high-speed solid fan blades, since the hollow blade design involves a substantial increase in cost. In terms of the optimum design—a solid blade—materials are required which not only meet the strength requirement of 560-630 MPa (80-90 ksi) but also have a maximum density of 3.3 gm/cm³ (0.12 lb/in³). This is a very difficult set of requirements. This area of component development involves materials research over a period of time greater than that considered here, investigating materials concepts well beyond all those conceived today.

T₃ Compressor Disks and Compressor Blades

The need is for materials with elevated temperature capabilities which will permit the compressor discharge temperature (T₃) to increase by up to 204°C (400°F), a goal of phase III of the IHPTET program. This will require increases in the performance of compressor disk materials by 66°C (150°F), i.e. up to operating temperatures between 871°C (1600°F). Materials currently under development with reasonable chances for successful application as disks are titanium-based MMCs and for blades alloys based on the intermetallic compound gamma titanium aluminide (γ-TiAl). The most structurally efficient approach being researched is a

combined blade and disk, either in the form of a bling or an integrally bladed rotor (IBR). The first of these involve a series of titanium alloys as the matrix, including Ti-64, Ti-1100, Ti-6242S, alloy C, and the intermetallic compound known as orthorhombic Ti (Ti_2AlNb); these are generally reinforced by fibers of SiC. An example of properties obtained for such systems would be for Ti-6242S reinforced with SiC fibers (150 μ m diameter): room temperature ultimate tensile strength (longitudinal) of 1.9 GPa (276 ksi) and a Young's modulus of 229.6 GPa (32.8 msi). The best promise is afforded by orthorhombic Ti-MMC, where strength levels are sustained to higher temperatures than with conventional titanium alloy matrices. These Ti-MMCs, if used in compressor rotor applications, will require significant additional development.

In terms of alloys based on the intermetallic γ -TiAl for blade and rotor applications, while there has been considerable development to date, not even static components are in service to date, nor will they be for at least three years, even in the commercial sector. Introduction of these alloys will be followed by at least 10 more years wherein today's gamma-alloy technology is fully transitioned from the laboratory to full-scale production in many components. The attractive features of these gamma alloys include a relatively low density (about half the density of nickel), a fairly flat modulus curve over a wide temperature range, outstanding specific stiffness, and useful mechanical properties up to approximately 750°C (1380°F). In the near term these attributes are being sought for static components, such as ducts and nozzles. However, none of these planned introductions is likely to be for compressor disks, or even blades until the latest stages of this period. Risks are quite high for such components, hence the inertia to overcome is great. For the longer-term, higher-risk components such as rotors and cases, there is still a need for R&D over the next 10 to 15 years to advance gamma-alloy technology. In this sense, the turbine-engine business is at the dawn of the next 15 years. During this period dramatic reductions in engine weight will be realized as designers have opportunities and learn how to introduce gamma alloys in engines.

HPT Disks

In principle, as the temperature of the engine is increased, the temperature that HPTs experience also increases. There are schemes which may be employed to meet that requirement, and some of these are discussed in the section dealing with the long-range plans. One solution is to employ materials with improved elevated-temperature capabilities. For example, HPT disks (816°C, 1500°F) are required to exhibit good creep resistance at the rim of the disk and optimum resistance to fatigue in the vicinity of the bore. A potential solution to this problem is to employ a dual-alloy concept, as adopted by the IHPTET program, in which different alloys are used for the rim and the bore, where these have been optimized for the two types of physical requirements and are joined metallurgically. In this way, it has been possible to provide a dual-property disk. Such dual-alloy technologies have been in exploration since the early 1980s, but may become a reality through IHPTET and programs which transition IHPTET technologies to flying aircraft.

HPT Airfoils

Single-crystal nickel-based superalloy HPT blades are the crowning achievement of more than 70 years of superalloy development in the gas turbine era. For component application at the present, there is no competition for a coated high-performance, single-crystal, nickel-based

superalloy HPT blade, and advanced processing methods will continue to improve the properties of these materials. An additional increment in improved performance with nickel-based superalloys will be achieved through the use of thin-wall airfoils produced by deposition techniques.

As part of the ongoing search for new turbine materials, there has been a considerable amount of development on the production and property enhancement of single crystals of the intermetallic compound NiAl. This material has a number of intrinsic advantages over superalloys. First, it is 30 percent less dense, giving a reduction in rotor weight of 30 percent. A 200 percent higher thermal conductivity implies a reduction in airfoil temperature of 38°C (100°F). Both of these factors will lead to an increased thrust/weight ratio and lower specific fuel consumption. A potential problem with these materials involves very reduced tensile ductilities; for NiAl alloyed for high strength, the ductile-to-brittle transition temperature rises from approximately 320°C for the binary compound to greater than 760°C for alloyed versions. Issues to be resolved with this type of material are alloying studies for higher levels of fracture toughness, process development for reduced sizes of defects, establishment of damage-tolerance/life-prediction methodologies, and the development of innovative design concepts to compensate for low tensile ductilities.

Static Components

Two classes of materials are envisaged for these applications, namely, for low-temperature environments the use of OMCs, and for elevated temperature applications orthorhombic Ti and g-TiAl. In the first of these, graphite-reinforced epoxies and high-temperature resin matrices are being developed for the following applications:

- Fan case: 150°C - 260°C (300°F - 500°F)
- Fan duct: 300°C (550°F)
- Intermediate case frames: 300°C (550°F)
- Inlet case frames: 150°C (300°F)

The potential benefit from the use of OMCs in these applications involves a weight savings of approximately 30 percent.

For applications such as cases and ducts, which experience temperatures up to 760°C (1400 F), γ -TiAl is being developed. This intermetallic compound has been described above but in summary it is a high modulus material which has approximately 50 percent the density of nickel and 80 percent the density of titanium. It is castable, and it can be machined and welded, even though it is more brittle than conventional materials. Development programs are in place to provide solutions to the problem areas.

Combustor and Exhaust Nozzles

Ceramic matrix composites (CMCs) are being developed for application in these components. There are three driving forces for their use: 1) increased thrust/weight ratios through elevated temperature combustion, 2) lower emissions from higher temperatures in the combustor, and 3) achievement of reduced signature levels in advanced fighter engines. The ability, in

principle, to operate the combustor at significantly higher temperatures through the use of CMCs does offer the advantage of lowering the emission (NO_x) levels dramatically, and such environmental concerns are becoming increasingly important. Intrinsically, the use of ceramic materials for these very high temperature applications, typically in the range 1200°C - 1400°C (2200°F - 2600°F), is attractive because of the well-known properties of such materials. However, SiC-matrix materials reinforced by nicalon fibers are limited to approximately 1100°C (2010°F) and oxide-based systems potentially limited to 1350°C (2460°F), are only in early exploration; as can be seen, they barely make the cutting edge for these applications. Other properties, such as toughness and ductility, also raise obstacles to application, although the use of fibers as the reinforcing medium has tempered the toughness problem. Properties such as thermal fatigue and corrosion resistance are relatively unexplored in the relevant component geometries.

While there are still many development challenges, CMCs are slated for application as compressor shrouds, combustor liners in the high-speed civil transport (HSCT), divergent seals, and spherical convergent flap nozzles (SCFN), and following considerably further development (see below) as airfoils. CMCs will be used extensively in expendable engines, including rotating ports, which will provide invaluable experience for future use.

8.3 Concepts for Improved Materials Beyond the Next 20 Years

In discussing research concepts for materials to be developed over the next 20 years and beyond, two aspects are considered. The first of these involves a discussion of how the various candidate materials topics are developed, noting that recent changes in research infrastructure presents challenges which must be faced. The second aspect considers some examples of exciting, innovative materials technologies and systems.

As has been pointed out above, the period 10 to 15 years ahead in terms of materials development realistically refers to materials which are either transitioning from 6.1 funding to 6.2, or those already under exploratory development. When considering a longer period, such as 20 years and beyond, it is important that research concepts chosen for study are those which are highly creative and most definitely appropriate for 6.1 funding. Traditionally, the engine producers have played a major role in selection of long-term research projects. Thus, with significant investment in their own industrial R&D laboratories, and largely under internal R&D funding, technologists have had the resources to conduct research which, because of their familiarity with the business of producing engines, has been of a nature that would have a high probability of success in terms of return on investment. Typically, the subject of emerging technology studies would be chosen on the basis of interactions between these technologists and the materials community as a whole. These efforts were coupled with government funding, and technology transfer occurred with scientists, for example, in the Air Force. Upon developing directions based on an integration of these research concepts, R&D programs were established by the government in which the various industries competed and participated. In this way, a significant input into federally funded programs of research originated at the engine companies, and hence relevance was assured.

Two very important changes have taken place in the recent past. First, the investment by the engine companies in research has dropped precipitously, and very little funding of what might be termed technology invention now occurs. The result is that work which might lead to

new ideas is not being done, but rather the engine companies appear to be pinning their hopes on the concept of continuous evolutionary improvement of existing products.

Second, a decade of experience has been built in the Air Force laboratories which are well postured for exploring and advancing the projected revolutionary technologies and research. At the same time, the gas turbine industry has focused most of its research investment on the evolution of commercial products. The result, if this trend continues, is an emerging mismatch which will adversely affect technology readiness for the Air Force in the long term. Natural barriers will rise between the three origins of advanced technology—universities, government laboratories, and industry—which have traditionally supplied technology superiority through synergy, not independence. A simple solution involves two steps, one being an increased investment by the engine companies in long-term research, perhaps an unlikely eventuality at present, and the other a closer alignment of the defense customer's expectations with the business realities. The recommendation, then, is that the Air Force must continue to provide leadership in long-range research needed for future engine materials if military capabilities are to be advanced, and that such research must be conducted in partnership with all levels of the engine industry. The industry should be given direct support for, as well as incentives to invest in, materials research. Air Force laboratory personnel should continue to realistically couple the research required to meet military needs with the marketplace realities of the engine industry. This includes prime contractors and suppliers, which are performing less of the research every year, but all of the transition. Furthermore, the Air Force materials scientists and engineers must continue to be responsible for establishing effective teaming arrangements between themselves, those in the engine business, and qualified personnel from universities and government laboratories.

Materials Technology and Systems

In considering new research concepts for materials in engines to be developed beyond the 20 year period, it is possible to consider these systems in three different categories:

- Research on existing materials which have remarkable properties in one sense, but other undesirable properties which have limited their application. Research is aimed at applying innovative concepts, including processing, compositional and microstructural modifications, to provide solutions to these limitations.
- Development and synthesis of new materials making use of innovative schemes for materials processing. This represents a very exciting possibility for advances in the engine business, with the possibility of truly revolutionary advances.
- Development of new systems applications, where improved or alternative materials will be used, possibly in conjunction with changes in design, which will lead to marked improvements in performance.

Examples of these three aspects are given below.

Existing but Limited Materials

- *Oxidation-resistant refractory alloys*: Alloys based on high temperature refractory alloys exhibit high strength, good ductility and toughness. Metallurgical techniques can be used to develop reasonable creep resistance. The show-stopper tends

to be a poor resistance to environmental degradation, such as oxidation. Attempts to make these alloys more oxidation resistant in the past have generally resulted in marked reductions in ductility; indeed, the alloys are rendered unsuitable for application. Innovative approaches to the oxidation problem have demonstrated that it may be possible to solve this problem, while maintaining an attractive balance of properties. Application of novel processing routes may well not only render these alloys oxidation resistant, but also provide useful creep and fatigue resistance. An example of the improved resistance to environmental degradation is given in Figure 8.2, and the improved stress rupture properties are indicated in Figure 8.3. A successful outcome in this research effort would be a 200°C increase for HPT blades.

- *Exotic materials:* There are a number of so-called exotic metals and alloys which exhibit attractive properties but have not found application because of either expense or other factors such as a tendency for toxicity. An example of this class of materials is beryllium. This metal has a very low density and a high value of stiffness. These properties when combined with attractive mechanical properties cause the metal to be a prime candidate for turbine engine application. However, beryllium has been traditionally moderately expensive, and the oxide, when finely divided and present in relatively large concentrations, can cause berylliosis in susceptible persons. For these reasons, there has been a reluctance to apply this metal in components. However, recent research has resulted in the development of investment casting techniques in which near-net shape processing of components is possible. This processing results in the material processing costs being significantly reduced, and some alloys processed in this manner have exhibited

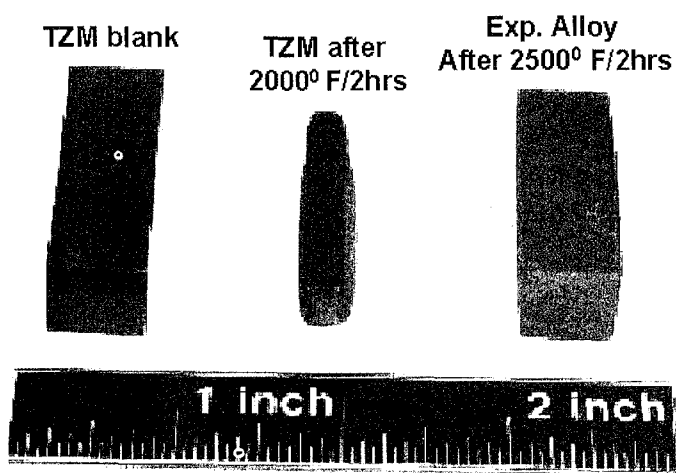


Figure 8.2. Comparison of performance of TZM Molybdenum with a new experimental Mo alloy after the given exposures to oxidizing environments. (Note: the resistance to dimensional change exhibited by the experimental alloy demonstrates dramatically improved performance)

Stress/Rupture of Molybdenum Alloys vs PWA 1480

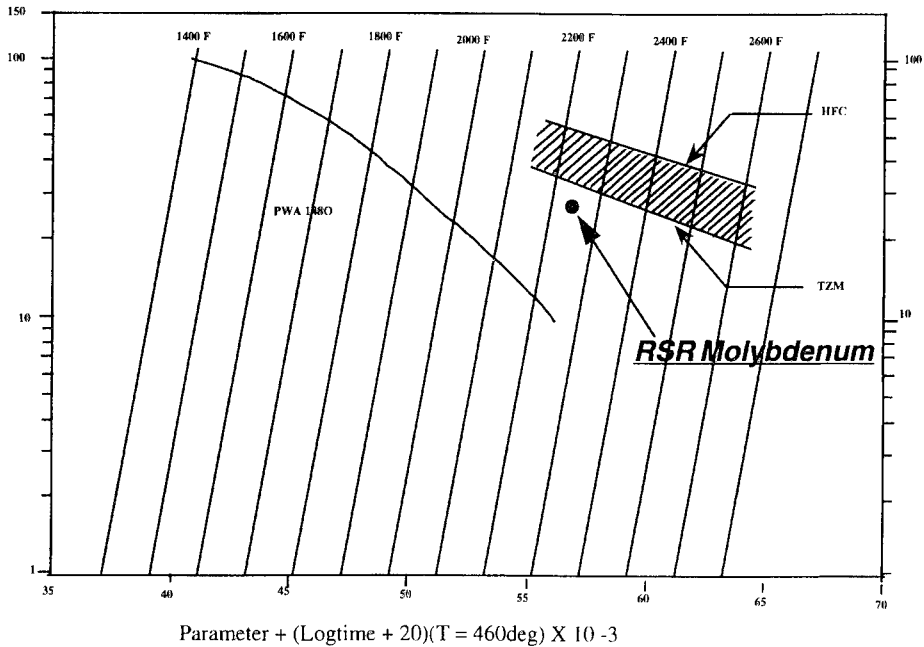


Figure 8.3. Comparison of the stress/rupture properties of an experimental Mo alloy (denoted RSR Molybdenum) with those of existing Mo alloys and also a high performance Ni-base superalloy single crystal (PWA 1480)

useful combinations of properties, an example being Be-31Al-2Si-2Ag. The toxicity of BeO has been carefully studied, and many of the causes for concern have been shown to be inappropriate. Hence, there is a possibility that materials such as beryllium will find application in the future. This metal and its alloys are candidates for fan blade (cores) because of its high strength, very high stiffness, and ease of processing, permitting use of inexpensive solid fan blades. Such possible long term shifts in the historical view of materials can open entirely new horizons for component design and higher-performance engines.

- *Ceramic composites/oxide fibers:* There has long been a desire to include more ceramic-based materials in gas turbine engines, since these materials are usually of moderate density and permit higher operating temperatures. As explained above, any increase in temperature translates into increased efficiency, either applied as increased power or reduced specific fuel consumption. And, as noted, an additional advantage of operating combustors at higher temperatures involves a marked reduction in emissions, particularly nitrous oxides. Application in combustors is projected in the 10 to 15 year timeframe, but if certain property limitations of these types of materials may be overcome through innovative research and development, then more general application in critical components in the engine may

be realized in the longer term. For example, application as advanced airfoils, permitting virtually uncooled turbines, may be possible. This eventuality requires significant improvements in the properties of fibers and coatings to enhance compatibility and interface properties. In the long range, fiber manufacturing is envisioned to be so well understood and routine that fibers may be made to order, tailored to specific component or system needs. Such fibers may be produced in situ as composites are fabricated and may have locally tailored properties.

Innovative Synthesis of New Materials

Beyond 20 years, realized visions in synthesis and characterization will bring entirely new opportunities for materials. R&D will lead to the design and synthesis of high-temperature engine materials that will be tailored for specific applications/components from predictions based on computational methods. The ability to understand, control, and design materials will experience a revolution brought on by evolving computational, processing, and investigative tools. These new materials, which will tend to have microstructures which are designed and controlled beginning at the nanometer scale, may be selectively synthesized atom-by-atom as a result of an evolving revolutionary process method, and will exhibit heretofore unimagined levels of defect control. Such synthesis capability leads to a revolutionary view of materials. For example, today's engine materials are commonly viewed as a load-carrying monolithic structure and a coating added to engineer surface properties. In the future, such distinctions between the material and coating will become irrelevant since the materials will be tailored through nanoscale synthesis methods for specific components. The materials will be composites engineered from the nano- to macroscopic length scales. Structural and engine components will see the revolution in design and manufacturing that electronic devices have experienced for more than a decade. Such methods open the possibility of breaking down age-old design philosophies, such as no primary reliance on a coating, thereby opening the door to entirely new applications for materials. The essential computational tools are now in the beginning stages of evolution and, to realize our futuristic visions, materials characterization methods will need suitable advances. Just a decade ago, simple analysis of the chemistry and crystal structure of the constituent phases in an engineering material required several person-years of effort. Today, improved characterization techniques and computer control permit such analyses in a matter of several weeks. Such growth brought the maturity of the discipline of materials science as opposed to the historical fields of metallurgy and chemistry. In 20 years time and beyond, still further improvements in characterization tools, coupled with integration of such tools with computational materials science methods, will bring revolutions in many materials. Such techniques offer the first real hope for shortening the development cycle, so often discussed but never realized.

- *Laminated materials*: There is an increasing interest in laminated materials. These range in scale from about 1 mm down to about 1 nm. Consideration of these materials for engines is divided here into two scales, one appropriate for metallic structures with interlayer thicknesses ranging from ~ 1 mm down to ~ 100 nm, and the other for ceramic-based materials with interlayer thicknesses on the nanometer scale. Schematic representations of the way in which these materials function are shown in Figure 8.4. In the case of the former, referred to here as laminated

materials (compared with nanoscale materials below), recent experiments involving layered composites of alternating layers of brittle high-temperature intermetallic compounds and tough metallic refractories have shown some exciting elementary mechanical properties. Equally or perhaps more importantly, the process methods envisaged for fabricating such nanometer multilayers may lead to revolutionary concepts for processing components and entirely new classes of alloys. Research is currently focused largely in the areas of innovating synthesis of laminates, however, the expectation is that improved properties such as non-fatiguing alloys, fracture-tough intermetallics and unprecedented levels of creep resistance will be realized. At first, it is envisaged that laminated composites would be used in critical regions of components, largely as outer structures on a substrate of an existing advanced material, for example metal-toughened intermetallic composite airfoil skins. Longer-range concepts include possible substitution of casting by use of deposition techniques in the production of complete components, such as airfoils. An example of the microstructure of an intermetallic/metallic multilayer is shown in Figure 8.5, and a schematic representation of the possible application of these materials as coatings is shown in Figure 8.6. Eliminating the necessity of foundry techniques would of course imply that casting defects, such as chemical segregation (micro- and macro-), and microstructural variations, would be eliminated. Materials could be fabricated having nearly complete freedom in combining elements rather than being constrained by natural limitations of current processes, leading to completely unknown new materials.

- *Nanoscale materials:* These types of materials will have broad applicability; initially in thin films such as coatings, and ultimately in entire engine components.

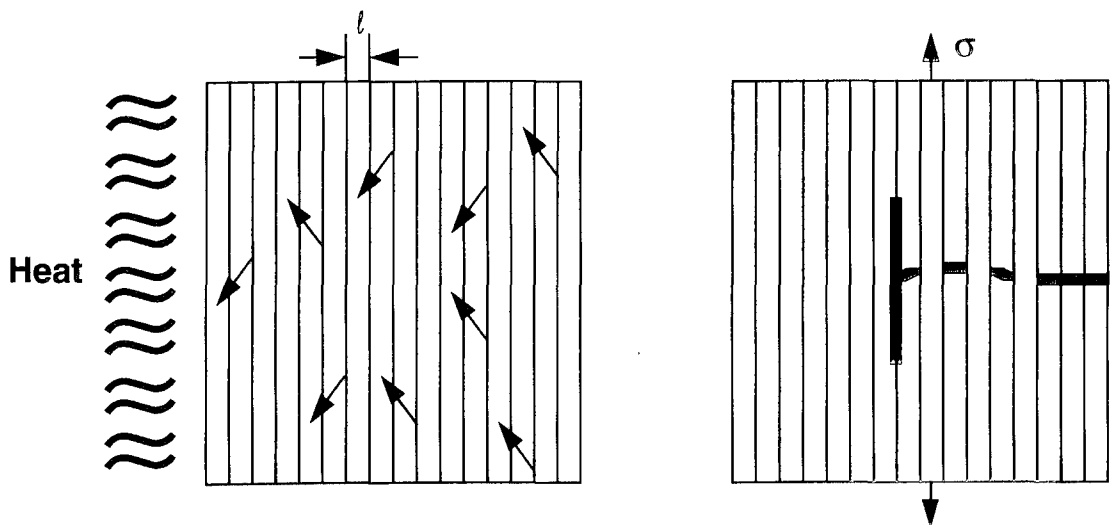


Figure 8.4. Schematic diagrams to depict a possible mechanism of the function of a nano-layered thermal barrier coating (left), and crack deflection in a microlaminated sample(right)

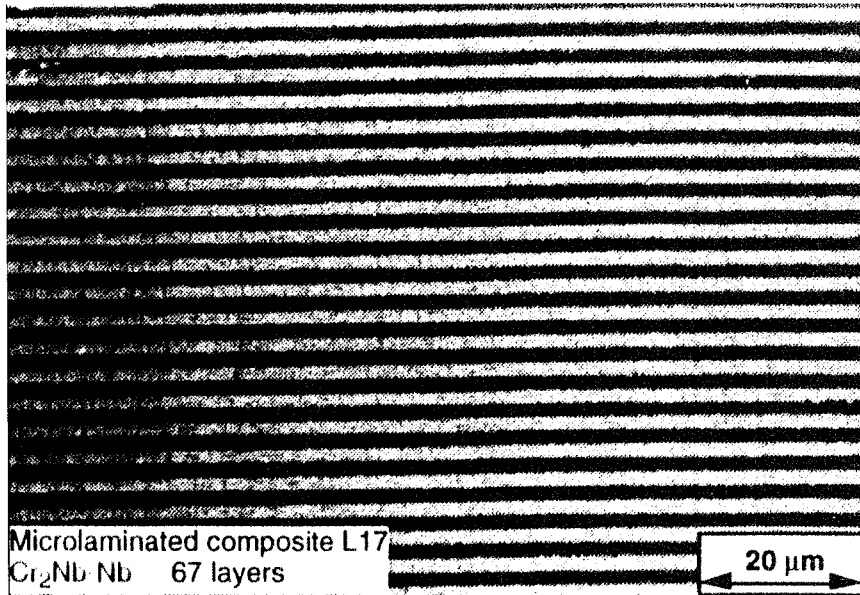


Figure 8.5. An electron micrograph of a microlaminated micro-composite consisting of 67 layers of $\text{Cr}_2\text{Nb}/\text{Nb}$

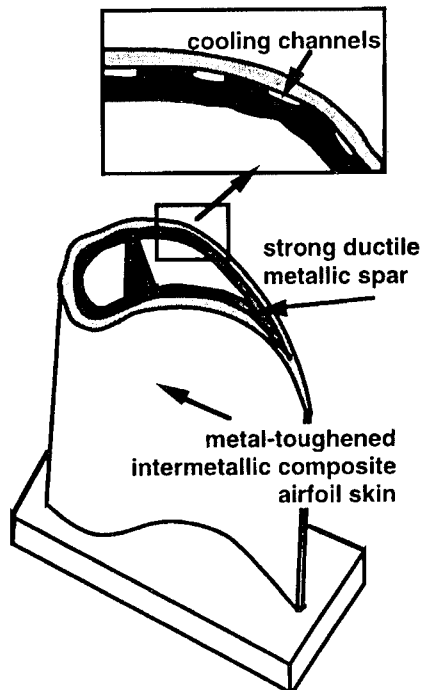


Figure 8.6. Schematic representation of the use of laminated micro-composites in turbine blade applications

They are now beginning to find application as thermal barrier coatings on nickel-based superalloy turbine blades. A comparison in the variation in thermal conductivity with temperature for monolayer TBC and nanolayered TBCs is shown in Figure 8.7. Quite remarkable enhancements in temperatures may be realized, for example increases of $\sim 260^\circ\text{C}$ for HPT blades are expected for a fully developed system. More research is required in order to understand the mechanism of the reduced thermal conductivity of these nanolayered materials, despite the depiction of a possible mechanism shown in Figure 8.4. Such a detailed mechanistic understanding is required so that full exploitation of these types of materials may be effected. In other applications, nanoscale ceramic composites may be synthesized which exhibit very much enhanced erosion and wear properties, and these materials would find application as coatings. Combined with new process methods for base metal synthesis and multilayer technology, complete control of material composition and structure will be possible such that materials will be tuned to their specific function from sustaining load to tunable outer layers for signature control in a continuous component.

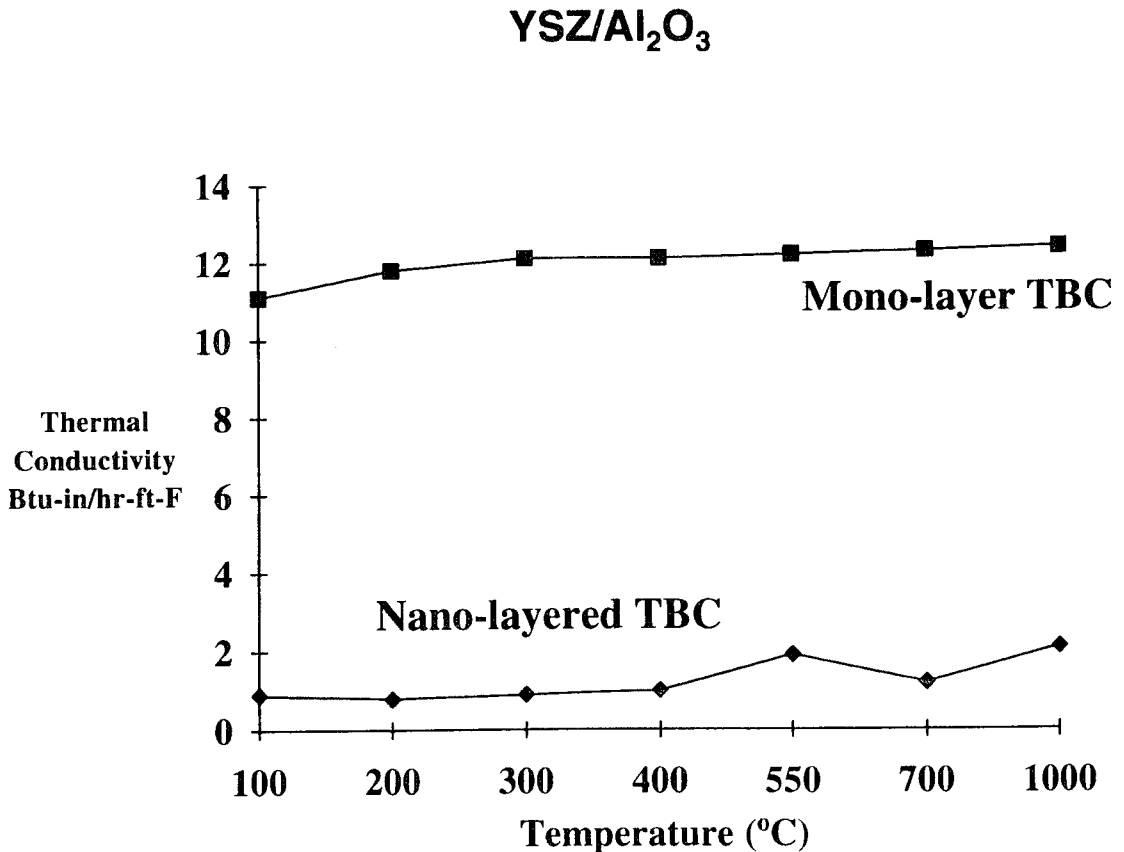


Figure 8.7 Comparison of the thermal conductivity as a function of temperature for mono-layered thermal barrier coatings and multilayered materials

- *Amorphous metallic alloys:* Amorphous metallic materials have been developed with very attractive properties, including high strength (1.8 - 2.5 GPa), low coefficient of thermal expansion (CTE), reasonably low density $\sim 4.5 \text{ g-cm}^{-3}$ (for materials based on Ti-Zr-Cu-Ni-Be), and excellent resistance to corrosion. Interestingly, these amorphous materials may be formed in bulk quantities using reasonable rates of cooling, and because they solidify with essentially no shrinkage, they exhibit good net shape processing capabilities. They are stable over wide ranges of composition, and an obvious application involves the use of the material as a brazing alloy. More interestingly, because the CTE values of these amorphous metals are similar to those of ceramics, there is an implication of good compatibility with ceramic reinforcements. Therefore, further research is required to exploit this compatibility for application as matrix materials in novel ceramics.
- *Novel ceramic processing:* Structural ceramic materials offer major advantages for gas turbine and other propulsion systems. Often application is limited not only by certain properties but also by complicated processing routes, and therefore costs. There is a need for the development of innovative means of synthesizing and processing existing and novel ceramics, particularly methods involving near net shape capabilities. A continuing effort has been directed at ceramic processing from polymer and, more recently, metal precursors. Thus, in the case of polymer precursors sol gel processing is an example, and in the case of solid metal precursors, this technique has resulted in the production of oxide-based high-temperature superconductors. Other innovative means of processing ceramics involve displacement reactions, where ceramic/metallic composites may be produced in which the two phases are intimately mixed and continuous throughout the microstructure. Major enhancements in our ceramic materials synthesis and processing are a critical necessity for propulsion applications.

8.4 Materials in New Systems Applications

- *Magnetic bearings:* High temperature capabilities of new magnetic materials give rise to rather radical implications for design of disk systems (compressor and turbine). For example, in high-g turns, there is a tendency for components to impact one another. At these temperatures, there is a possibility of friction welding to occur, with obvious, disastrous consequences for component degradation. The application of magnetic bearings would not only minimize rotor axial loading, but also provide an opportunity to exploit the possibility of dynamic positioning of disks during operation. For example, it would then be possible to avoid bumping of seals, and also to provide dynamic balancing of disks during blade-out.
- *Alternative fuels:* Emphasis in the short to middle term is on the concept of single-liquid fuels to be used simultaneously for fuel and lubrication. The benefits of single fuels include significant weight reduction in engines by obviating the relatively heavy machinery for cooling and recirculating lubricants (greater than 100 pounds), elimination of the problem of thermal breakdown of the lubricant, avoidance of costs associated with disposal of spent lubricants, and simplicity in terms of the logistics of handling only a single fluid. Candidate approaches for single

fluids are conventional fuels, which would need additives for elasto-hydrodynamic lubrication, endothermic fuels (see fuels section), and cracking of high molecular weight hydrocarbons. In addition to these alternative fuels, clean and abundant fuels include hydrogen and atomic energy. In the case of the former, environmental problems associated with conventional fuels do not exist. Advantages in terms of being able to apply materials, which would normally be limited by oxidation resistance, would be offset by the possible problems involving hydrogen embrittlement. The use of aircraft nuclear power is a long-term goal, but apart from the emotional issues remains a very strong candidate.

- *Hypersonic propulsion systems:* Far-term development of hypersonic vehicles will lead to routine access to space using SSTO vehicles. The vehicles will most likely be powered by air-breathing propulsion for most of the flight and a rocket for the space portion. An efficient, lightweight air-breathing propulsion system will require advanced new materials, such as beryllium composites or very high-temperature fiber-reinforced ceramics. These systems will also be the users of materials technologies just now entering research, such as nanostructures, functionally graded materials, high-temperature electronics, and multilayer functional coatings.

9.0 Nonlinear Optical and Electronic Materials

Electronic and optical technologies provide critical building blocks for all advanced weapon systems. They are required for information gathering, transmission, processing, storage and display, for the control of weapons systems, and for energy generation and direction concepts. Currently, the electronics and photonics industries are built on only a handful of materials, principally semiconductors, such as silicon and gallium arsenide, and a few solid-state inorganic compounds. We expect these materials to continue playing a major role in the industry. However, for higher performance systems, these materials are intrinsically limited, and new materials must be found and developed. In the future, a much wider array of materials, from novel multilayered semiconductors to new polymeric materials, will be available for advanced optical and electronic applications. These new materials will be designed and processed at the atomic scale to provide optimized electrical and optical properties to meet specific Air Force requirements. As our capability to custom design and grow new materials expands, electronics foundries will change to a flexible manufacturing format where the same growth and processing equipment will be used to create a wide variety of optical and electronic devices on demand.

These improved materials will make possible sensors with high sensitivity across the entire electromagnetic spectrum, data transmission links with greater than 200 gigabits/second, parallel processing of data at breathtaking speeds, three dimensional data storage with almost instantaneous access, and holographic cockpit displays. They will make possible the next generation of control systems such as the mounting of sensors and processors directly on aircraft engines. These materials will lead to new weapon concepts, such as directed energy weapons, as well as to the systems which counter them.

9.1 Electronic Materials

We categorize electronic materials as active or passive. Those considered in the following discussion have high potential for future payoff to the Air Force. In most cases evolutionary development is required to meet this potential. In some cases there are revolutionary possibilities as well.

Passive Materials

High Performance. Radome materials, which will ensure that the USAF can establish a position of air superiority and provide theater defense from missiles and high-performance hypersonic aircraft, must be developed by the DoD. This technology has little commercial use. Because of the extreme requirements on these materials, it will be necessary to establish and maintain a fundamental research base in materials development and processing in this area. A consistent, long-term commitment to develop high-temperature radome materials will provide materials of the future for hypersonic vehicles.

The radome is a critical component in numerous weapon delivery systems and often is the component limiting the performance of supersonic and hypersonic vehicles. There have been several surges in funding during the last few decades to develop suitable radome materials, but these efforts have often been abandoned due to the technical challenges of the problem, shifts in the political climate surrounding the systems, and the transfer of the technology responsibility from one DoD component to another. The area in which most of the progress has been made is

in the development of millimeter-wave systems centered around 35 GHz. However, as weapon systems are miniaturized and the need for system resolution increases, the need for radomes operating at around 94 GHz will become significant. Additional target accuracy can be attained through the use of a multispectral targeting system. Such a system could employ both RF and optical tracking (IR or visible), along with ground/air-platform guidance.

The materials requirements on a hypersonic radome are extreme, with temperatures ramping up to 1000°C within a few seconds and the threat of high-speed rain erosion. In addition, the sensor system must be capable of seeing through the radome throughout the mission. This necessitates that the dielectric constant and attenuation (loss tangent) of the radome material to be relatively constant over a broad temperature range. Otherwise a radome must be designed that can be cooled. Previous efforts have met with some success in developing radome materials and concepts which meet the above requirements at 35 GHz. The challenge is to move to shorter wavelengths. In all cases, materials processing has been a major stumbling block in successfully developing hypersonic radomes.

In the area of multispectral radome materials, polycrystalline CVD diamond appears to be a viable material for the future. In some respects diamond is the miracle material of the future, but there are some significant hurdles to overcome, especially when it comes to processing.

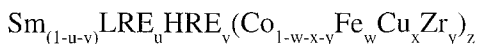
Advanced Tailored Dielectrics. Dielectrics often limit the achievable performance of electronic systems. A whole host of applications require the use of tailored dielectric materials, including permittivity (ϵ) and permeability (μ). Examples range from low-observable coatings to antenna systems. Regardless of the application, advances in materials technology are necessary to manufacture materials with tailored dielectric properties. Often the dielectric properties required are extreme and not achievable using current technology. For an example in the area of antenna miniaturization, an antenna element can be buried in high-dielectric-constant material, effectively reducing the physical size of the antenna while still allowing low-frequency operation. In some cases dielectric constants well over 1000 are desired without any associated loss due to absorption. One approach to achieving this type of dielectric behavior is to use dielectric mixtures. The processing of such materials is often difficult and not easily repeated. In addition, current tailored dielectrics are often not very robust. Future supersonic platforms will require advanced tailored dielectric materials capable of withstanding the rigors of supersonic flight without a loss or change in the dielectric properties of the materials.

Organic Conductors. Electrically conductive polymers first aroused interest about 20 years ago. The major materials explored to date are polyacetylene, polypyrrole, polyaniline, and polythiophene, although many others have been reported. In spite of all the investment in polyacetylene, it remains an intractable and environmentally unstable material. It will not likely see any technological uses. Polypyrrole is commercially available, but is not a well defined material. More importantly, it is not processable and suffers from long term stability problems. It has, however, been incorporated into some electromagnetic interference (EMI) shielding applications. Polyaniline is being commercialized by the civilian sector, but suffers from moisture instability and often the conductivity levels vary by orders of magnitude depending upon the moisture content. These characteristics, and its inability to withstand harsh environments, make it unsuitable for pressing Air Force needs. Polythiophene is still a laboratory material, but it warrants serious consideration.

The applications of conductive polymers are myriad. Light-emitting diodes, photovoltaics, and corrosion inhibition based on conductive polymers have all been demonstrated. The Air Force has interests in all of these areas and should nurture their R&D. It especially needs conducting polymers as engineering materials for gap sealants, conductive matrix resins, and conductive wires. These are niche applications that are not likely to be addressed by non-DoD efforts. Industrial efforts are unlikely to address these critical needs. Air Force leadership in discovering and developing new, environmentally and thermally stable conductive polymers is needed.

Magnetic Materials. There are opportunities for impressive advances in airborne power applications for more-electric-system-concepts that depend on advances in magnetic materials. These include both near term and far term work on improving soft and hard magnetic materials for AF specific high strength/high temperature/low electrical loss applications, of which starter/generators and magnetic bearings are a subset. In the long term, there are real possibilities for nano-structure or meso-structure technologies to provide superior advanced magnetic materials. Laminated solids could replace the present physical stack of laminations, separated by a thin insulator, as core materials for generators and motors. Near term, diffusion-bonding techniques for metal-to-metal and ceramic-to-ceramic interfaces would improve the stiffness and strength of core materials.

Impressive evolutionary improvements seem possible. Examples are twice the mechanical strength and an order of magnitude lower electrical loss, 550°C operating temperatures for soft magnetic materials, and an increase in operating temperature for hard magnetic materials from 300°C to 450°C, with extended life at these temperatures and a factor of two increase in energy density. This is possible by optimizing known systems, the 50 percent Fe - 50 percent Co class of soft materials, and improving hard rare-earth/cobalt magnets of the 2:17 type of the form,



where LRE and HRE are light and heavy rare earths respectively, and the overall ratio of rare earth to the other metals is 2:17.

Breakthrough capabilities should also be pursued, since they can lead to even greater performance gains. For example, each enhancement factor of 3, 5, 10 or 15 in magnetic properties over the two baseline systems would be important as performance increases with the square of the attainable magnetic induction field. Raising the Curie temperature to 2000°C or 3000°C would be a boon to many new high-payoff applications.

Active Materials

Multilayered Semiconductors. In recent years major steps have been made toward a new approach—bandgap engineering—for designing and growing semiconductor structures with tailored electronic and optical properties. By controlling the composition and thickness of multiple semiconductor layers, the electronic band structure of this multilayered material can be tailored to achieve desired properties in a nearly continuous way. The development of highly controllable deposition systems for semiconductor thin films, such as molecular beam epitaxy

(MBE) and metalorganic chemical vapor deposition (CVD), has made it possible to grow ultrathin (10 - 100Å) epitaxial layers of various compositions on semiconductor substrates on an atomic layer-by-layer basis. Thus, the opportunity now exists to custom-design semiconductor structures with unique electronic and optical properties that are unattainable in single-layer materials.

So far, only a few of the many possible semiconductor alloys have been grown in multilayered structures. But even these few alloy combinations have provided many new electronic and optical capabilities such as solid-state lasers, high electron mobility transistors (HEMT) and quantum-well infrared photodetectors. The next advances will be to establish the specific epitaxial growth processes and conditions for new alloy compositions and layer combinations, and to move beyond multilayered structures with the same lattice constant as the growth substrate. These advances will greatly widen the array of materials choices available to future "bandgap engineers." For instance, patterned substrates would enhance the capability to grow high-quality lattice-mismatched or strained semiconductor layers. In addition to current planar epitaxial layers, growth techniques for controllably growing quantum wires and dots of semiconductor materials need to be developed. To take full advantage of bandgap engineering, quantum mechanical models for predicting the electronic and optical properties of new multidimensional structures are required, as well as growth-process modeling of epitaxial deposition systems. Some such models are already under development, but need to be broadened to cover many materials and designs within the same simulation, instead of the current practice of modeling one specific material or design. These models will greatly reduce the time it takes to develop an advanced electronic material for a given application.

In addition, development of new growth and production processes for present III-V based semiconductors, such as direct-write selective area epitaxy, will enable multifunctional devices on a single electronic chip. The integration of several electronic and optical functions into the same chip will provide faster devices, miniaturized systems, and more reliable systems. A great many electronic failures in military systems are due to the thermal environmental effects on the wire bonds used for connecting devices. New ways of producing devices which reduce the number of wire bonds will significantly improve reliability and lifetimes. Direct-write selective area epitaxy, a process for growing different semiconductor device structures on the same substrate, is one technique envisioned for bringing about multifunctionality. The use of textured substrates is another method which could provide the capability of growing more than one type of semiconductor heterostructure on the same substrate, possibly at the same time. These technologies would revolutionize the way electronic chips are fabricated by eliminating the need for lithography, thereby greatly reducing the number of device processing steps and their associated costs.

As an example of how the development of multilayered semiconductor structures could impact future Air Force capabilities, we consider infrared detector imaging arrays. Multilayered semiconductors would allow multispectral imaging using one focal plane array instead of separate arrays for each wavelength band. Multispectral imaging allows better discrimination between the background and target, providing the warfighter with a sharper image. Besides integration of multiple wavelength bands in one detector, first-level signal processing for this sensor could be integrated onto the same chip. By performing first-level integration on the same chip as the detector, the sensor becomes smarter and a layer of complexity is removed from the

device processing. These capabilities would provide the advantages of smaller, more compact sensors that are lighter, use less power and provide more information.

High-Temperature Wide-Bandgap Semiconductors. Silicon carbide (SiC) and the other wide-bandgap materials will be instrumental in developing device technologies for the next 30 to 50 years. These materials offer the potential for an enormous range of applications, many considered impossible for conventional semiconductors. Some applications where SiC-based devices will be applied include electronics for hostile environments—high temperature electromagnetic radiation, high-power solid-state uncooled radar, and high-power switching and blue laser-based communications systems. In addition, wide-bandgap semiconductors capable of emitting and receiving signals in the blue and ultraviolet portion of the electromagnetic spectrum will receive increasing attention for optical computing applications, where these short wavelengths will provide much wider information bandwidths. Defense requirements for high-temperature, high-power-density electronics include power components, engine sensors, distributed processing for the More-Electric Aircraft (MEA) initiative, and uncooled microwave components for radar and communications. To meet these requirements, and increase reliability and affordability, breakthroughs in materials processing will be required.

SiC single-crystal material of adequate quality and size for demonstrating general electronic applications has only become available within the last few years. Wafers are available which are small and loaded with defects and impurities when compared to silicon. Only the simplest devices have been demonstrated, and these were made small in area to avoid defects such as pinholes in the wafer. However, these devices have demonstrated the technical feasibility and tremendous potential for future applications. A lot of material and process development will precede the insertion of SiC-based electronics on critical aircraft systems. Routine use for these devices in electric vehicles, MEA, communications and power management systems can be expected within 20 years.

Thin-Film High-Temperature Superconductors. With the discovery of the superconducting copper oxide compounds (called the high-temperature superconductors), superconductivity is poised to make a greater impact on technology and society in the next century. Whether or not superconductors can have the same dramatic impact of semiconductors depends a great deal on further improvements in these materials. As the processing techniques for thin films continue to improve, it is anticipated that some of these materials will work their way into microwave communication systems, acting as filters and antennas. RF circuits made using superconducting thin films provide orders of magnitude performance improvements while also reducing size and weight. The Air Force is currently developing high-temperature superconductor switchable filterbanks which will provide new capabilities for aircraft to filter out extraneous radar signals that could confuse onboard radar warning receivers in the modern-day electronic warfare environment.

While some applications are nearing the demonstration phase, other applications for high-temperature superconductors are 20 years or more in the future. A technology for making reliable Josephson junction circuits needs to be developed for signal processing applications. Josephson junctions, fabricated by sandwiching a thin normal metal or insulating barrier between two superconducting layers, can be made to turn on and off rapidly with low power.

These junctions could replace the circuits now used in computers and significantly reduce the power used and theoretically increase the speed of computation by up to 50 times.

Development of high-temperature superconductor technology is also required to manufacture practical superconducting interference devices (SQUID) capable of detecting extremely small variations in magnetic fields too small to be sensed by conventional means. SQUIDs could be used to detect very small deep cracks and hidden, inaccessible corrosion in aircraft structures. The Air Force should play a leading role in developing this technology because of the importance of nondestructive evaluation/inspection (NDE/I) for aging aircraft. As one example, it is envisioned that hand-held scanners based upon high-temperature superconductor technology could be developed to reliably detect corrosion hidden inside wings, a significant problem for aging aircraft in the Air Force.

Finally, even greater technological change may result from basic research on superconductivity. Once the materials and mechanisms are understood, even higher transition temperatures may be reached. Even if room-temperature superconductivity is not possible, raising the transition temperature to temperatures attainable with technology used in household air conditioning is not an unreasonable goal. Additionally, molecular-based superconductors which are currently laboratory curiosities should be considered. Very little is understood about how to build such materials. This is a fertile area for increased, broad-based research, spanning theory, modeling and synthesis.

9.2 Optical Materials

Optical technology is the science of employing light (i.e., photons) to perform various functions. It has been responsible for many recent technological breakthroughs, such as the IR imaging technology demonstrated during Desert Storm and the fiber-optic communication system which now links our world. However, we now appear to be in a historically significant period of R&D for optics, from which a revolutionary optical technology with greatly expanded capability has begun to emerge. This technology is nonlinear optics, which includes *electro-optics* and *photonics*. It provides active building blocks to the system designer's armamentarium in the same manner that semiconductor devices provided the building blocks for the electronic revolution. Continued evolutionary improvements in linear optical materials are needed as well as revolutionary changes in nonlinear optical materials.

Linear Optical Materials

Multi-Spectral Windows and Domes. With the increasing reliance on optical sensors to perform numerous Air Force missions, it is becoming necessary to acquire imagery through several spectral windows. The common atmospheric transmission windows are the visible, near-infrared, mid-infrared, far-infrared and mm-wave. Each spectral window has its own benefits and shortcomings. For example, visible scenes offer the greatest resolution, but a visual scene can be easily obscured by darkness or bad weather. Thermal imaging can pierce the veil of darkness but has limited success in bad weather. Millimeter-wave imaging offers all-weather operation, but does not offer high resolution images. The availability of multiple imaging sensor systems provides the ability to operate under all conditions and provides additional dimensions for target identification.

It is expected that future electromagnetic countermeasures will extend throughout the usable spectrum, and multiple spectral windows will provide an element of redundancy necessary to increase the probability a weapon system can complete the mission.

It is advantageous for several reasons to combine several sensors into a single suite which looks through a single aperture. Unfortunately, there are only a few materials currently available for use across the spectrum, and all these materials have poor physical properties with regard to durability. New multispectral optical materials capable of operating under harsh environments are required. Diamond suits the needs for many of these applications, however it will have limited applicability in the mid-infrared. High quality, ultralow-loss remains a significant materials challenge. For this reason the Air Force must continue supporting the development of diamond coatings, windows and domes and must as well investigate the potential for new multispectral window materials.

Advanced Coatings. Optical coatings are used in every optical system deployed. As these systems become more complex, the demands on coating performance increase. Many coatings must withstand harsh conditions, such as dust and rain erosion as well as provide a high degree of optical performance over multiple spectral bands.

Specialized optical coatings must also provide protection of optical sensors against specific optical wavelengths employed as laser range-finders and designators. Several technologies have been developed to meet the demanding spectral characteristics, but in some applications their cost is prohibitive or performance is marginal. Future technologies, including structured polymer films and spray coatings offer the potential to enhance the performance in selective areas while reducing the cost of deployment.

High-Performance Dyes. The necessity to protect a pilot's eyes from laser range-finders and designators requires the use of laser eye protection incorporated into the helmet visor. The performance of available dye-based visors is far from ideal. The spectral requirements on dyes employed for vision protection are many and demanding. In addition to the spectral requirements, these dyes must exhibit environmental stability and be compatible with an appropriate fabrication process.

During the last decade, great strides have been made in the fundamental understanding and in the ability to calculate photochemical processes at the molecular level. With this new understanding as a backdrop, the potential exists for considerable improvements in the performance of laser protection dyes. The development of new, high-performance dyes will require the use of computational chemistry approaches coupled with an intensive synthetic program. The design of future high-performance dyes will be based on a solid understanding of the electronic structure of the materials and their interaction with various host materials.

Holographic Materials. Optical holography is a technique based on the interference of two optical beams to write intensity and phase information into a solid material. Holography applications range from spectral filtering to information storage. For example, holography is one technology employed for heads-up displays (HUD) in fighter cockpits. In the future, holography has the potential to impact a much wider range of applications, including ultrahigh-bandwidth communication systems, ultrahigh-speed and density data access for complex computational tasks (e.g. target recognition), and laser eye protection.

Existing static holographic recording materials are typically based on photochemistry and use the photographic process. Unfortunately, these materials are temperature and humidity sensitive, cannot be made very thick, and are quite costly to produce. All of these characteristics limit the applications which holography could make and impact. The future will require new materials which are more robust, offer higher information storage density, and are inexpensive to produce. One potential class of materials which may meet these requirements is photosensitive silica-based glasses. These relatives of glass-ceramics are demonstrably capable of very high density information storage, however, little is known about the thermodynamics and kinetics of these materials. Research on this class of materials is necessary for it to eventually meet the demanding requirements of future holographic applications.

Polymer dispersed liquid crystal (PDLC) is another class of holographic material under current study. It can function as a two-state hologram. This class of material can be switched from "clear" (that is, no hologram visible) to "on" (hologram visible) by applying an electric field across the thick film. Although early in the development, these materials offer the potential of switching holographic optical components (e.g. lenses and filters) for use in optical devices, as well as optical correlation systems (e.g. target recognition). Considerable research and development is still required for these materials to realize their potential, especially in the area of materials processing based on the thermodynamic phase stability and kinetics of these multicomponent polymer systems.

Integrated Optics. It is likely that the capability of photonic circuits will exponentially increase just as electronic circuits have over the last three decades. It is not unthinkable that photonics will pass through a similar process of miniaturization and increasing complexity over the next several decades. Optical materials technologies will be key in the development of photonic industries. One materials technology which will likely undergo an evolutionary development is that of integrated optics. In the same way that enhanced lithographic processes have made electronic integrated circuits increasingly more powerful, new processes to write precision optical pathways must be developed in order to realize the photonics revolution. Several technologies currently exist to generate optical pathways in integrated optical devices. They are relatively crude, and there is a lot of room for these technologies to be developed.

Other technologies may also play a significant role in the future of integrated optical components, such as holographic interconnects. Holography offers the potential of opening up the third dimension and opening up the possibility for ultradense photonic circuits. It is difficult to predict where this technology will lead. The promise of optical processing at immense bandwidths dictates the need for research in this technical area.

Nonlinear Optical Materials

The advantages of nonlinear optics (NLO) over electronics for information manipulation include immunity from electromagnetic interference, elimination of electrical short circuits and ground loops, safety in combustible environments, low-loss transmission, large bandwidth, security from tapping, possibility of 3-D integration of devices, small size and light weight, and inherent paralleled processing of data for orders of magnitude increase in computing power. In addition, NLO can significantly improve the performance and character of laser sources

providing new capabilities such as 1) wavelength conversion offering new discrete wavelength lines and wavelength tunability over a much broader spectral range than is possible with chemical lasers, 2) amplification, 3) Q-switches for pulsed lasers, and 4) optical phase conjugation for more ideal beam profiles and the coupling of laser beams. On the distant horizon, all optical data processing promises orders of magnitude increases in computing power.

Nonlinear optical responses are divided into second-order and third-order effects. In simple terms, a second-order material can be used for generating new laser wavelengths, for the photorefractive effect yielding improved laser beam profiles and distortion correction, and for electro-optic effects for controlling light by electric fields from electronics. A third-order material can be used to control light by light for intrinsic limiters for laser-hardened optics and for all-optical computing concepts.

The material properties for NLO materials are extremely demanding. The desirable properties include very large nonlinear optical responses, low power thresholds, fast switching speeds, high optical damage thresholds, low optical loss, thermal stability, temporal stability, and processability into optical quality films, fibers, and circuit components. We consider second-order materials, both inorganic and organic, and third-order organic materials. We note in passing that new phenomena are being discovered or realized in this area, so some of the boundaries are not even known. For example, it was demonstrated about three years ago that considerably larger effective third-order responses can be created through cascading, a phenomenon based on utilizing second-order material to introduce large nonlinear phase shifts obtained from phase-mismatched second-harmonic generation. For another example, only five years ago two-photon upconversion driven lasing was considered an impossibility. It has now been demonstrated by two independent laboratories. The field is obviously quite fertile.

Second-Order Materials. Second-order materials are needed to improve the performance and character of laser sources. These sources are basic to an incredible breadth of applications including IR countermeasures, remote sensing of chemicals, wind shear detection, medical diagnosis and treatment, materials processing, scientific instruments, optical communications, low-light imaging, atmospheric aberration compensation for astronomy and satellite tracking, scene projectors for testing and entertainment, optical signal processing, data storage, underwater communications and imaging, and remote identification of biological materials. Several materials are needed to optimize performance in each spectral band, and considerable success has already been realized in this regard. Emphasis should be given to developing improved crystal growth and processing techniques which are applicable to many material compounds.

Second-order materials are needed for electro-optic devices for applications including optical interconnects (i.e., data links), communications (requiring switches, modulators, and directional couplers), multichip modules, phase shifters for phased-array radar, and new sensors such as electric-field sensors. Lithium niobate (LiNbO_3) is currently used but is severely limited in a number of respects. Device fabrication cost is high, the electro-optic coefficient is low, leading to centimeter-size devices, the material is not integratable with electronic substrates, and device operating voltages drift with time.

Other inorganic ferro-electric materials such as barium titanate and lithium tantalate appear promising. Barium titanate shows particular promise, having a threefold improvement in

figure-of-merit n^3r over LiNbO_3 , and having recently been deposited with extremely high optical quality as single-crystal thin films on silicon substrates. An additional material system, semiconductor multiple-quantum-well structures, has already been proven viable in S-SEED devices, although performance is limited in certain regards. Crystalline organics, a third system, offer by far the highest nonlinearities known, and processing techniques appear feasible for integrating these films with semiconductor substrates. The final group, electro-optic polymers, appear inherently inexpensive with regard to processing and deposition, fast due a small dielectric constant, and integratable with electronic substrates.

These material systems appear promising, but each is limited in some way. Therefore, these systems should be pursued in parallel programs, eventually choosing a winner for continued development. Special emphasis should initially be given to electro-optic polymers due to their promising properties. Other areas worth pursuing include resonant two-photon absorbing materials. Two-photon absorbing materials hold great promise for the distant horizon for NLO applications. Unlike single-crystalline materials, two-photon absorbing materials require neither phase matching nor electric field poling. These characteristics would simplify manufacturing processes and eliminate second-order temporal stability problems. Very little is known for structure-property relationships for two-photon absorption, so this horizon is broad indeed.

Third-Order Materials. Third-order materials offer the possibility of revolutionizing the device architectures and capabilities of photonic and opto-electronic components. With third-order materials, completely optical analogs to electronic components are possible, such as all-optical transistors. The ultrafast response times of third-order materials make switches based on four-wave mixing enticing. The pressing need is for third-order materials with nonlinear optical responses (lower thresholds) increased by orders of magnitude. For logic units, nonresonance NLO effects are important. If these materials were resonance-driven, they would absorb too much energy, causing thermal expansion and degradation. Not enough discrimination between resonance-enhanced and nonresonance responses has been given in the third-order NLO materials field. Resonant materials are useful for optical limiting and sensor protection. With third-order materials, the response can be completely passive (i.e., dependent only upon the material and not any external fields). The Air Force should continue and possibly lead efforts to discover and develop new third-order materials. This is a clear technological driver for future components, and industrial efforts have decreased recently due to short-term priorities.

9.3 Summary

Long term vision is needed, and the Air Force should play a leading role in developing molecular and polymeric materials for electronic and photonic applications. There is serious discussion of molecular electronics — designing and building electronic and photonic functions into molecular and nanoscale components. While this seems almost science fiction, it may be feasible. The problems and opportunities outlined above for NLO and electronic materials are necessary stepping stones to the dream of molecular electronics. Additional steps worth pursuing include polymer-based photovoltaics and polymer electrode materials. Polymer photovoltaics will be significantly less dense than their inorganic counterparts. Spin coating manufacturing could make such devices very expensive. There is little or no work in this field. Much effort is directed toward polymer electrolytes for batteries, but little or no effort is focused on

polymer electrodes. Conductive polymers have been demonstrated as polymer electrodes; concept demonstrations have been successful. In spite of initial and now abated excitement, it is astounding that there are no efforts to optimize chemical structure for these purposes. The Air Force stands to greatly benefit from such work. Multilayer, easy-to-form batteries would offer many design advantages for Air Force systems.

10.0 Next Generation Energetic Materials

10.1 Fundamental Points

Materials for Air Force applications in propellants, explosives, and pyrotechnics are critical core technologies having impact on a wide range of munitions including warhead lethality and the kinematic performance of missile systems.

New energetic propellants and explosives are vital enablers of the Air Force's mission. Both the uniqueness and the high performance characteristics required of military systems limit the applicability of commercial technology to the Air Force needs of tomorrow.

10.2 Current Situation and the Future

We will present here a brief summary of the state of the art in energetic materials technology, the issues, and recommendations. This section is followed by a more focused discussion of energetic materials required for the areas of propulsion and explosives. In the individual areas of explosives and propellants, we discuss new advanced materials and discuss concepts that are capable of generating revolutionary advances in warhead lethality, pyrotechnics, and our ability to propel missiles, boosters, and spacecraft.

The U.S. energetic materials area has been narrowly focused on insensitive energetic materials for application to tri-service insensitive munitions (IM) for the past 10 to 20 years. Insensitivity is a critical issue, and programs related to the IM objective must be continued. Our emphasis on IM as the single driving force has pushed us into very narrow development programs and has probably resulted in missing opportunities for improved systems. An expansion of the objectives of energetic material research to focus on performance is needed to recover lost opportunities in the areas of molecular synthesis, formulation chemistry, detonation, combustion chemistry, and combustion physics. Materials design, based in quantum chemistry and solid-state mechanics, is defining revolutionary first principle approaches to energetic materials and offers "leap ahead" as opposed to "catch up" approaches to meeting tomorrow's challenges.

While new materials have been created, few of these new materials have been implemented into a rocket propellant system. There have been no major advances in materials in the propellant industry in the last 40 years, performance has not improved significantly, and the industry is moribund. Meanwhile, the Russians have fielded new strategic missile systems having significantly improved performance (see the discussion on ADN). Another example is the case of U.S. air-to-air missiles having a shorter range and inferior capabilities as compared with the current Russian weapons. Our most advanced propellant materials programs today are the High Energy Density Materials (HEDM) and Integrated High Payoff Rocket Propulsion Technology (IHRPT) programs. The goals of the HEDM and IHRPT programs are shown in Figures 10.1 to 10.3.

Under IHRPT, rocket propulsion capabilities should double by 2010, and the factors of reliability, cost effectiveness, environmental compliance, operational efficiency, and safety are integral to the effort.

The explosives community has maintained a broader technological foundation through aggressive program coordination under Project Reliance and the DoD/ DOE Conventional

High Energy Density Matter

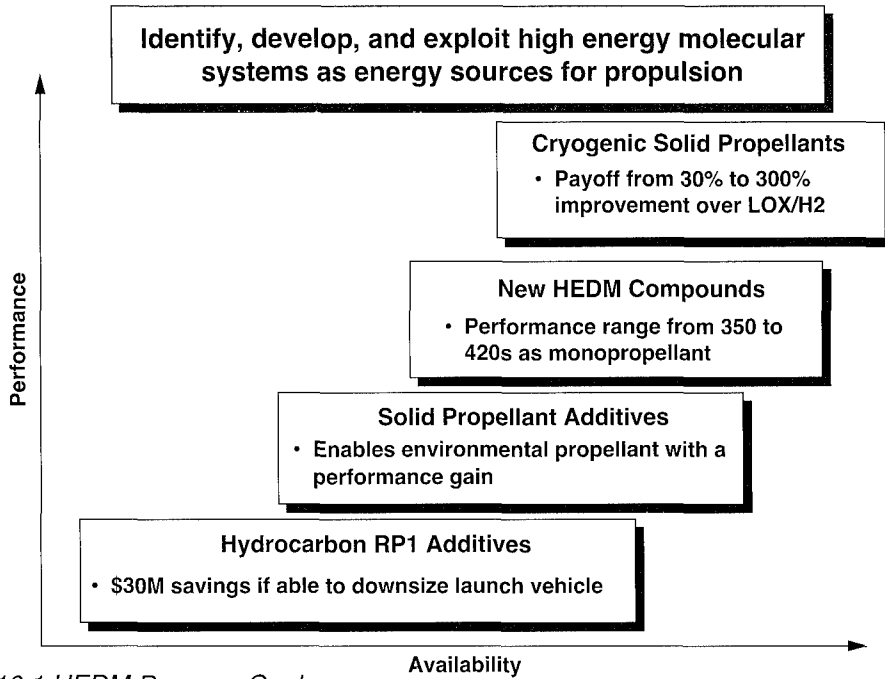
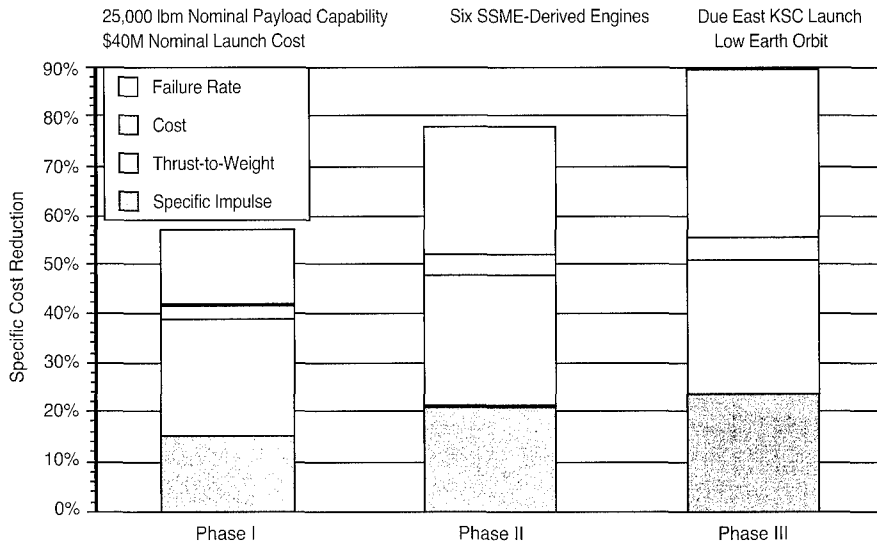


Figure 10.1 HEDM Program Goals

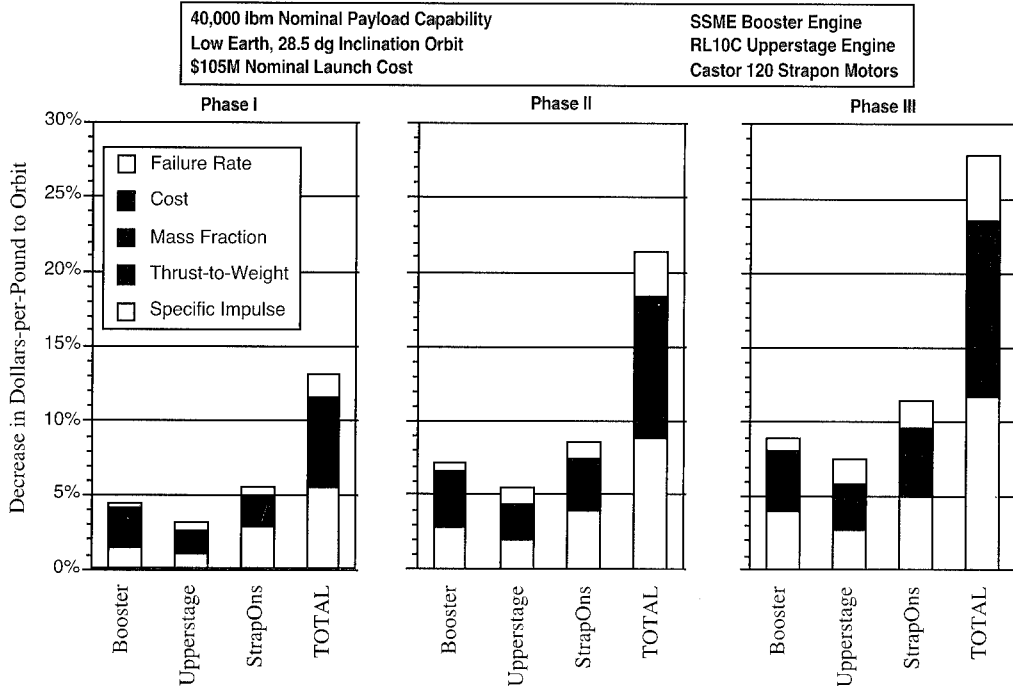
Fully Reusable Launch Vehicle Payoffs Based on IHRPT Goals Specific Cost Reduction



Tanck, P.A., "RLV Cost Payoffs," PLRKBBA, 30 May 95

Figure 10.2 IHRPT Goals for a Fully Reusable Launch Vehicle

**Expendable Vehicle Payoffs
Based on IHRPT Goals
Specific Cost Reduction**



Tanck, "Exp Veh Cost Payoffs," PL/RKBA, 30 May 95

Figure 10.3 IHRPT Goals for Expendable Launch Vehicles

Munitions MOU. However, even this technology base is being threatened by downsizing activities in both the DoD and DOE. New formulations have transitioned into weapons systems. Significant performance improvements have resulted from this work. LX-14, an explosive formulation developed at Lawrence Livermore National Laboratory containing HMX as the primary HEDM, has been transitioned into the warheads of the Hellfire and TOW-2 missiles. Recent examples of deployments include PBXN 9 as an interim IHE in the Hellfire and TOW upgrades, PBX 110 in the Standard Missile, and AF 108 in the joint service AMRAAM missile warhead. These examples are representative of formulation solutions to today's problems using yesterday's molecules. This is an area that can further profit from the introduction of the new energy storage concepts to improve performance.

These evolutionary advances in explosives are not capable of effectively attacking chemical and biological weapons (CBW). CBWs require specialized explosives and pyrotechnics, materials that are probably available, but not being exploited.

The USAF can achieve significant performance advantages in rocket propulsion, explosives, and pyrotechnics using new energetic materials and developing an understanding of their behavior and properties. Energetic materials are enabling technologies. New weapons based on advanced energetic materials would give the Air Force larger standoff distances, shorter

times to target, and higher destructive power in the near term. The safety of platforms depends on having a longer reach; we will have too few platforms in the future to risk losing them. Our adversaries are already projected to win short-range engagements due to improved propellant and explosive materials.

The neglect of developing new propellant systems contributes to the extremely high costs of getting payload to orbit. Simple improvements in the energy density of liquid fuels could enable the use of smaller launch vehicles for similar size payloads. This would have dramatic cost savings (estimated at greater than \$30M/launch for a change from Atlas 2 to Delta 2 and greater than \$130M for a change from Titan 4 to Atlas 2 AS). Similar improvements can be expected from the solid strap-on boosters.

A whole new generation of improved materials is available and materials are continuing to be invented for use in rocket propulsion and munition applications. These are fundamentally new ingredients for use in propellants and explosives. We are now entering into the fourth generation of conventional energetic materials, perhaps the next revolution in energetic materials.

One can define generations of energetic materials as:

- Generation 1—discovery
Gunpowder, fireworks, small arms
- Generation 2—formulation for safety
Commercial explosives (e.g. dynamite, TNT)
Gun propellant
High energy propellants (nitroglycerin)
- Generation 3—molecular synthesis for performance
HMX, RDX, aluminum, and ammonium perchlorate
State-of-the-art explosives
State-of-the-art high energy propellants
- Generation 4—combination of physics and chemistry to prepare alternative energy sources (the future)
ADN, CL-20, TNAZ, PGN, AMMO, BAMO, AlH_3 , and maybe other metal hydrides, focused energy, focused application materials, cryogenic materials

Each succeeding generation has significantly enhanced the capability of weapons either by improving performance or safety. The Russians fielded, 20 years ago, weapon systems based on at least one of the fourth-generation materials. First-principle-based design approaches promise to revolutionize many of our most fundamental concepts of energy storage in these systems. Metastable Interstitial Composite and Extended (MICE) solids are examples of these first principle design approaches.

The next 20 years will see significant improvements in conventional weaponry and a fundamental new understanding of energy storage. The new materials will give significant range enhancements along with improved safety. The new explosives can enable reducing the size of

warheads to either make smaller rockets or increase the range and/or velocity of existing rockets. The challenge is the identification of the process to ensure early exploitation of these materials to satisfy a wide range of Air Force mission needs.

10.3 Issues

We have recognized several issues that directly relate to the field of energetic materials:

Broad Based Issues

R&D technology base disappearing. The DoD needs to recognize and support the development of those technologies that will have a large impact on future weapon system capabilities.

No clear technology development requirements. The DoD has not provided the requirement or the financial means to maintain a strong technology base effort. The recently initiated IHPRPT program is the first example of a change in that attitude. Without strong leadership and clear directions to pursue technology development, the contractors and government laboratories fall into a mode of chasing near-term, system-oriented goals and having to start all over when that particular system is killed. Since we are falling behind other nations in capabilities in energetic materials, this is a problem.

Safety. Insensitivity of new propellant and explosive formulations has been of importance for the last decade. Significant progress has been made. IM is an enabling technology as it allows for more weapons to be carried or stored in closer confinement. This must remain an emphasis in any development/synthesis program. We need to emphasize finding ways to obtain higher performance while not sacrificing safety.

The bridge from laboratory development to use is fragile at best. There is no good mechanism to get from 6.1 to 6.4 and beyond. This results from a lack of application programs on standby which are ready to use the technology.

Specific Technology Issues

Is chlorine a real bugaboo or not? A decision needs to be made on what are the real environmental issues that have to be addressed. For example, is chlorine emitted by propellants a real issue? If it is, then we need a directed program to bring replacements forward quickly.

Rocket propulsion is not a mature area contrary to popular opinion. If a new system wants to buy its propulsion unit "off the shelf", it will be buying very old technology. It will not be taking advantage of the results currently available in research laboratories nor will it be taking advantage of the tremendous increases available from more research. The commercial sector will not be the leader in developing this technology. Energetic materials are not commercially developed other than in the mining industry. This area must be funded by the government and, due to the high-risk nature, it must be done with long-term programs.

The chicken or the egg problem. Few new materials are in current systems, because the system program offices don't demand them. Program managers don't allow new materials, because they don't have sufficient information about their properties, and no program office wants to be the first to take the risk of using a new material. Almost all development work on

propulsion in this country is dedicated to evolutionary improvements in existing systems, because of this chicken and egg problem. The developers don't want to use new materials because they are not readily available, not demonstrated, and are considered high risk. So in the face of these problems, no risks are taken.

Life cycle cost determined by more than just the initial material cost. The value of energetic materials is generally determined by the initial cost of the material. Explosives and propellants need to be judged on the total system cost and the value of the mission.

Multidisciplinary approach to problem. Energetic materials research is generally accomplished in a small group that is not in close communication with the potential developers and users of the technology. The developers and users need to communicate their needs to the researchers and researchers need to provide feedback on the possibilities of new materials.

10.4 Recommendations—Propellants

The USAF needs an aggressive program of research and development to create a new generation of boosters, interceptors, and spacecraft based on new ingredients and energy storage technologies. We have fallen behind our adversaries in this important area and our platforms are vulnerable to longer range, higher performance weapons from the FSU. New weapons based on higher energy propellants will enable the USAF to control their environment in a cost effective manner. The following items must be done:

- Fund the development of new energetic ingredients
- Fund the development of new rocket motors based on new oxidizers and binders
- Encourage unconventional approaches such as thermoplastic elastomers (TPE) and gel based polymer binder development
- Accelerate the use of energetic fuel additives to RP-1 liquid fuels
- Increase funding for basic research to solve the burn-rate problems of hybrid boosters
- Investigate the use of aluminum hydride in rocket systems
- Expand research into other advanced hybrid concepts and HEDM materials to give 350 to 420 second monopropellants
- Continue or expand research into cryogenic or other exotic propellants to seek a propulsion breakthrough

10.5 Recommendations—Explosives

- A window of opportunity exists for the USAF to bring to the field advanced weapons based on recently invented ingredients
 - Push forward the introduction of new oxidizers (CL-20) and energetic binders into a weapon system
 - Continue research on new methods of focusing and tuning the energy of explosives and developing new thermites

- Initiate weaponization investigations of tunable energy thermite systems
- Fund research into revolutionary concepts for new high explosives to fill the gap between conventional and nuclear weapons

10.6 Examples of the Contribution of New Materials

Solid Propellants

Calculations tell us that the use of an improved oxidizer (such as ADN) in a propellant system can give up to a 51 percent increase in range of a ground-to-air missile over a conventional AP/Al/binder system. Similar calculations tell us that the uses of ADN in inertial upper stage (IUS) orbit transfer from low earth orbit (LEO) to geosynchronous orbit (GSO) would provide a 8.9 percent increase in payload (452 pounds). Using ADN in the booster and IUS would give a 17.4 percent payload increase (886 pounds). Introduction of a more advanced system using aluminum hydride to replace aluminum and the use of ADN in the IUS would provide a 12.4 percent increase in the LEO to GSO transfer step (631 pound payload increase for a Titan IV). These are dramatic gains in performance, unmatched since the introduction of composite propellants in the 1950s. The dramatic payload gains can be traded off for a smaller launch vehicle, thus decreasing the size of the system and its cost. Significantly, ADN is environmentally benign if disposal is required; it photolytically degrades to nitrate and nitrous oxide, and is chlorine-free.

The use of an energetic binder can have a major impact on the solids loading of a propellant. The reduction in the solids loading is likely to greatly improve the safety of the overall system, possibly taking it from a sensitive 1.1 category propellant to an insensitive 1.3 system. For example, using a BAMO/AMMO binder to replace a convention binder with AP and Al as the other ingredients gives a reduction in solids from 90 percent in the conventional system to 80 percent in the advanced system while having the same energy density. A gap binder system may give similar results.

Liquid Propellants

Improvement in the specific impulse (I_{sp}) of RP1, a hydrocarbon fuel that is unchanged since the 1960s, can save up to \$30M per launch. This savings is in part due to the fact that a smaller, higher performance launch vehicle can be employed. Additives have already been identified to do this.

Hybrids

There are several ways HEDM materials may improve hybrids. First, an energetic material may be used to increase the burn rate or grain regression rate which is a major problem with current hybrids. A low rate requires extremely complicated grain designs in order to get adequate mass flow rates. Second, since the solid grain is essentially a rubber matrix as inert as a pencil eraser, it may be the ideal way to incorporate aluminum hydride, the new and very high-energy fuel that the Russians say they can use and one which the U.S. has failed to capitalize on.

10.7 Energetic Materials—Propellants

The current inventory of propellants and other energetic materials were identified 20 to 40 years ago as having the optimum fit to the cost/performance trade-offs of the time. We are currently flying or using systems that use storable propellants selected in the 1950s and 1960s to meet cold war performance, cost availability, toxicity, and environmental needs of the time. The result is old propellant systems that cost more and more as incremental patches are applied to bring out-of-date systems into compliance with current operational restraints. Our society, industrial base, and particularly environmental and health laws continue to evolve and redefine our operability restraints without a concomitant change in the energetic materials we employ.

Yet ingredients have been discovered and made available that are capable of providing revolutionary payoffs for the armed forces. Other new materials are under investigation. Thus, we can correct the situation by employing our best technology in a cost and time effective manner. High payoff items identified as opportunities in rocket propulsion are:

- Near term: Implement major improvements for solid motors by incorporating advances in binders and oxidizer (5 percent to 20 percent improvement in mass to orbit or a 5 percent to 15 percent increase in specific impulse) with a concomitant improvement in liquid systems. TPE's and gels will give environmental and processing advantages.
- Middle term: Develop advanced hybrid systems with improved performance (goal of 350 sec for a strap-on) new oxidizers, TPE binders, gel binders, new fuels like AlH_3 .
- Long term: Use cryogenic high energy density materials and materials like metallic hydrogen (specific impulse greater than 1500 sec (i.e. performance 4 times greater than LOX/H_2)) to revolutionize access to space.

Most of our solid propellant systems were developed in the late 1950s with some development continuing into the early 1970s. But no significant new energetic material has been introduced into the propellant area since then. However, many new materials and technologies are now available that we need to employ.

Solid/Gel Rocket Propellants

New propellants are required not only to increase the available energy of a propellant and raise the specific impulse (I_{sp}), but also to meet environmental and toxicity constraints and improved safety. Special requirements for handling and disposal significantly increase the cost of the overall system. New propulsion materials will significantly reduce overall weight and therefore the cost of propulsion systems. They also permit innovative manufacturing techniques which will yield revolutionary rocket engine designs. Finally a better understanding of the chemistry and material properties for propulsion systems will lead to solutions to problems that continue to plague the propulsion industry today.

Solid propellants are used in all application areas of rockets employed by the Air Force, including tactical, strategic, and space boost. Specific examples are:

Solid or composite propellants. A revolution is underway in the types of oxidizers and binders available for use in solid propellants. The combination of the new energetic binders with new oxidizers offers system benefits (I_{sp} , safety, energy density) exceeding anything fielded today. The new materials for propulsion must be viewed from a system view, that is, the effect of the combination of an energetic binder and oxidizer on performance rather than the effect of each individual component. The combination of the energetic binder and new oxidizer can reduce the solids loading in a propellant significantly. In one example, the reduction went from 91 percent to 82 percent while maintaining the same energy density. These changes increase the safety of the system while enhancing performance.

In the oxidizer arena, ADN is the most promising near-term material. The FSU demonstrated ADN-based ICBM boosters in the early 1980s. ADN offers payload increases ranging from 1.5 percent to 19.7 percent, depending on the application. An excellent example of the effect of using advanced oxidizers is in the earth to GSO application. Only the propellant sample in the IUS was changed, the basic booster was untouched. Calculations done at United Technologies show that using an ADN based propellant system gives an increase of 17.4 percent in the payload delivered to GSO. This is a quantum leap in performance. Higher levels of performance can be achieved by improving the energy density of the liquid booster portion of the system.

For tactical systems the I_{sp} can be improved by 5 percent by use of new oxidizers—CL-20, ADN, and others are candidates. The IHPRPT tactical propulsion goals are a good measure of what is desired. IHPRPT has improvements planned over the next 15 years that can only be achieved using advanced materials. Higher levels of performance improvement are possible and should be pursued.

CL-20 looks good for tactical applications both as a propellant application and as an explosive. CL-20 is the closest to scale up of all the potential materials. TNAZ has promise, and HNF is being explored as a possibility in the U.S. and abroad. CL-20, especially in concert with an energetic binder, can be used to give smokeless or minimum-smoke propellants with improved range over current propellants.

Ammonium nitrate (AN) has reappeared as a potential bright spot for low-cost, chlorine-free, smokeless propellants. A method for stabilizing the phase transitions of AN has been patented by the Thiokol Corporation that should overcome many of the problems (low burn rate, phase changes) associated with AN. Thiokol calls this new material phase stabilized ammonium nitrate (PSAN). PSAN can be used in propellant applications as the oxidizer for smokeless formulations. However, the use of PSAN to achieve a chlorine free exhaust carries with it a decrease in energy from the standard ammonium perchlorate propellants.

The new energetic binders allow for energy partitioning in tactical propellants. This means that instead of having all the energy in the oxidizer, the binder system contributes part of the load. The consequence of this is that the energy and oxidizing power of the system is better distributed leading to a better burn in a usually less sensitive system. The recently invented materials include PGN, AMMO, and BAMO.

Because these energetic binders are TPE, they are capable of benign removal from the system, enabling the whole propellant charge to be recycled. This use of energetic TPEs will minimize waste and allow recycling of the propellant charge. Overall we will have improved safety in a better performing, more energetic propellant system.

ADN or CL-20, in combination with an energetic binder system, could start appearing in systems within the next ten years and could be in widespread use in 20 years, having a major impact on Air Force operations.

The forecast is that we could have these energetic materials employed in a tactical system within the next ten years if development is encouraged. A great deal of development needs to be done, yet the potential is there and enough basic research is in the bank to enable a rapid development of the energetic TPEs, a system with the potential for major impact.

Solution propellants. A very recent development is the solution propellant. The advantages of this system are that it is an environmentally clean formulation including no chlorine and has potential for very high process efficiency. These solution propellants are water soluble, so disposal is accomplished by simply washing out the motor with water. They are processed by pouring the liquid or slurry materials into the case and then allowing them to solidify. The development work on this is ongoing at Phillips Laboratory (Propulsion Directorate) and at the Aerojet Corporation.

This technology is a medium-term possibility for system application.

Conventional Liquid Propellants

The Air Force uses storable liquid fuels and oxidizers in some launch systems. Liquid propellants have performance, restart, and throttling advantages over solid propellants and will continue to be attractive for use in future systems. Improvements must be made to reduce the hazards of handling and storage of the materials while maintaining or increasing performance.

Nitrate-based oxidizers (nitrogen tetroxide and IRFNA) and hydrazine-based fuels (A-50, MMH, and UDMH) have good performance and ignitability, but are also very corrosive, volatile, and toxic. These factors drive up the cost of manufacture transport, handling, vehicle design, pad operations, launch safety, launch window, and pad cleanup. The environmental factors alone are becoming a major driver in the need to replace older oxidizers and fuels. Reducing these hazards is required.

Liquid propellant fuels can be improved by an investigation into the use of non-volatile or non-toxic oxidizers and the use of new high energy hydrocarbon fuels. There are current investigations ongoing at Phillips Laboratory (Propulsion Directorate, Edwards AFB) and at the Office of Naval Research (ONR) on new oxidizers and fuels for rockets. Additionally, Wright Laboratory (Propulsion Directorate) is working on endothermic fuels that should be applicable to rocket propulsion. A significant potential is available for crossover between the two programs.

The emphasis at Phillips Laboratory on the creation of strained hydrocarbons that can give improvements of several percent of I_{sp} in the near term. Even small gains of a few percent

are enough to save many millions of dollars per launch (estimated at \$30M per launch). The materials under investigation as fuel additives include commercial replacements for RP1 such as decane, hexane, and cyclododecane, plus higher-performance synthetic materials such as spirocyclopropanes, triangulanes, cubane, and quadricyclane.

Oxidizers are a more difficult problem, however, viable alternatives are becoming available. ADN is an environmentally benign, high performance oxidizer that can be put into liquid form and used as a monopropellant system (ADN + ammonia, hydrazinium dinitramide + hydrazine, or hydroxylammonium dinitramide + hydroxylamine). Hydrazinium nitroformate (HNF) is a candidate oxidizer, but its toxicity has not yet been determined.

One promising way to improve system performance is the development of monopropellants with significant I_{sp} . A system of dinitramide salts with ammonia, hydrazine or hydroxylamine as the counter ion has been proposed as well as HNF.

There is a significant opportunity to develop new materials for liquid-fuel rocket propulsion having a major impact in the next ten years.

Advanced Fuels for Solids and Liquid Rockets

A major improvement in performance can be achieved by the development of new fuels in rocket propellants. An example of this is the claim by the FSU that they have been able to use

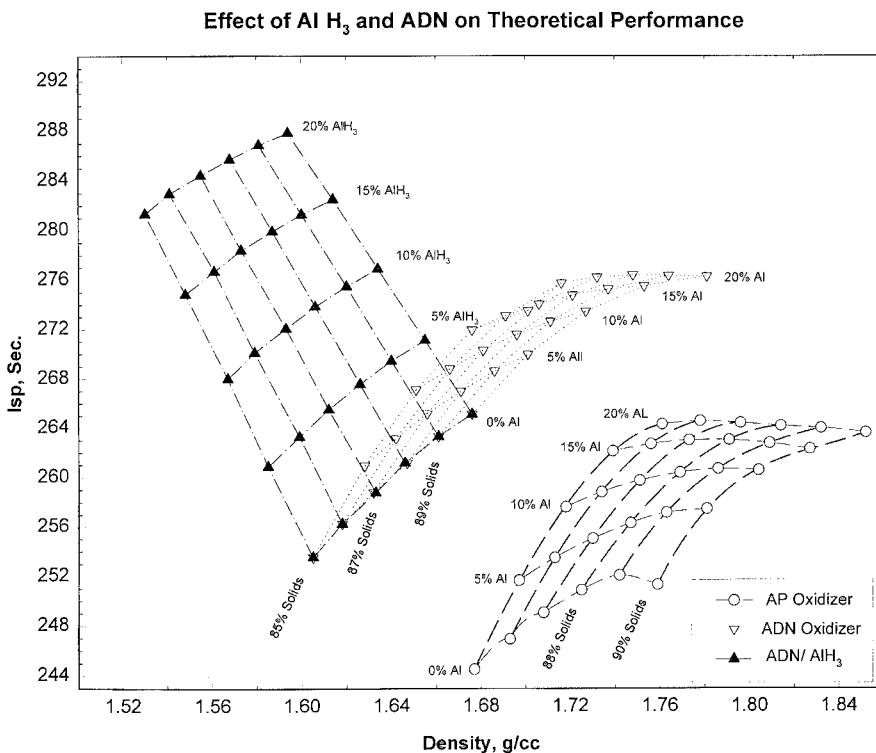


Figure 10.4 Propellants Based on Aluminum Hydride, ADN, and AP

AlH_3 successfully in solid rocket propellants as a replacement for aluminum metal. A major research program in the U.S. in the 1960s failed to accomplish this, but the Russians claim to have a fielded system with ADN as the oxidizer. This combination of AlH_3 and ADN could give as much as a 25 percent improvement in specific impulse in the rocket system. Figure 10.4 below shows a graph of specific impulse versus density comparing an AP-based oxidizer systems with an ADN based oxidizer system and of the combination of ADN with AlH_3 in a propellant formulation. A drawback of the AlH_3 system can be seen in the reduction in density of the overall formulation.

A number of other metal hydrides or other metal fuels can be considered for this application. At a minimum, we need to determine if the FSU statements on AlH_3 are factually correct and determine how they employed AlH_3 . Alternatively, we need to initiate a program to study the potential use of AlH_3 as a fuel for solid rocket motors. Interestingly, the best place to employ fuels such as AlH_3 is in hybrid type motors. Here, the fuel is surrounded by only an inert polymer matrix so the concerns about the fuel reacting with oxidizer or other substrates is eliminated. This may be the nearest term use for such exotic materials. This insertion of metals (or the use of otherwise pyrophoric organometallics) into an inert matrix opens up a world of possibilities. Finally, studies are underway to determine if atomic species can be distributed in the matrix. This approach will dramatically increase the energy density if successful.

Strained or high-energy hydrocarbon compounds should be investigated in further depth to determine their utility as fuel additives in hybrids and in liquid fuels. Both hybrids and liquid-fueled rockets need fuel additives to improve the energy content and the combustion efficiency and have great opportunities for early use. One can consider the use of Diels-Alder type materials that decompose to give easily combustible compounds. This approach would be akin to the Russian approach where they first determined the combustion requirements then designed and synthesized hydrocarbon structures to meet their needs. This resulted in improved combustion and engine performance. We could learn from this approach instead of relying on RP1, a fuel developed in the 1950s.

A more dramatic improvement might come from developing methods to decompose the hydrocarbons and generate hydrogen or atomic hydrogen. Molecular or atomic hydrogen have been shown to improve the combustion efficiency in endothermic fuels and should have the same effect in rocket motors.

Hybrid Motors. Hybrid motors have been proposed as a replacement for solid fueled boosters in space launch applications. This is a technology that could have an impact beyond space launch as a way to propel a rocket. Realization of the potential of hybrid systems requires both developmental and fundamental research.

We show in Figure 10.5 the basic hybrid rocket motor design. In a hybrid, a solid fuel core is used with a separate liquid oxidizer tank. The fuels currently used are conventional, readily available hydrocarbon binder systems.

The major problem in hybrids is that the burn rate is approximately an order of magnitude too slow to make the technology viable for use in a standard grain design. Engineering

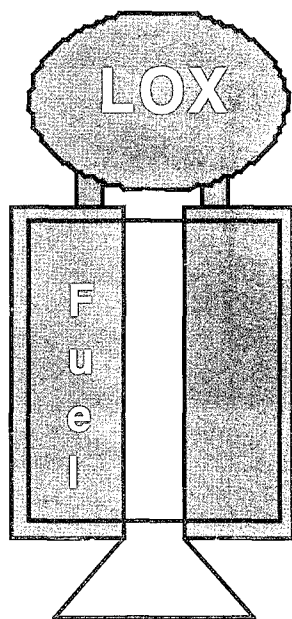


Figure 10.5 Basic Hybrid Rocket Motor Design

solutions require high surface area designs that drastically reduce density thus decreasing performance. Fundamental solutions to burn rate problems can only come about by improving the chemistry. There is no investment in this area, even though the payoff is extremely high.

This technology would profit from the introduction of metal hydrides such as AlH_3 into the matrix to improve the energy density and potentially the combustion rate. Other fuel additives and energetic hydrocarbons can also be profitably incorporated. A higher risk approach would be to introduce atoms or organometallics into the matrix to increase energy density. These new methods represent high risk methods until proven. Proving such approaches and removing the risk requires investment in exploratory research.

In addition to performance improvements, hybrids offer a means to reduce launch support costs. Since the current solid strap-on boosters have to be in place long before the actual launch, special safety practices must be followed on the launch pad. However, the hybrid grain is as inert as an automobile tire and no special safety practices are necessary. This technology has the potential to replace composite propellants and provide safe, inexpensive heavy lift capability within approximately ten years once the fundamental problems are solved.

Monopropellants. Monopropellants find use in applications such as maneuvering thrusters. The major threat here is the toxicity of the propellants and their limited energy density. Several advanced systems are possible based on the new energetic materials (ADN in ammonia is an example), but this area is not generally given much priority.

Exceptionally Energetic Ingredients and Cryogenic Propellants. The proposed goal of a new cryogenic propellant is to increase the specific impulse by 30 percent to 300 percent over LOX/H_2 . Most of this effort is ongoing at Phillips Laboratory and through AFOSR. This program is for identification and synthesis of novel cryogenic solids. Both agencies are funding a heavy computational effort to predict species for use in propellant systems.

There are two goals for this program. The near-term goal is to prepare molecules (e.g. solid ethylene) that can react with LOX to give I_{sp} of greater than 350 sec. The long term goal is the preparation of cryogenic solids containing atoms and other highly energetic materials with the ultimate goal of preparing metallic hydrogen. The long term goal is for improvement of specific impulse by 30 percent to 400 percent over LOX/H_2 .

The development program has started to show success. A cryogenic motor has been fired at Edwards AFB, using frozen ethylene as the fuel in a prototype hybrid setup. This demonstrates that frozen cryogenic materials can be successfully employed, an important first step. Ultimately, this should lead to using cryogenic solids containing additives in hydrogen or solid oxygen. This is a new type of rocket motor.

The next goal is to demonstrate that cryogenic matrices containing fuel additives and other energy dense ingredients can be burned in the motor. Ultimately, they will employ atomic species in a hydrogen matrix as the fuel to be burned. One potential system, is a H_2 matrix spiked with B_2 to yield a monopropellant having I_{sp} greater than 600 sec. The calculated additive effects of this combination are shown in Figure 10.6 below. There are other similar metal additives to hydrogen that can potentially significantly increase the I_{sp} , but we will not discuss them further.

B₂ Additive Effects on I_{sp}

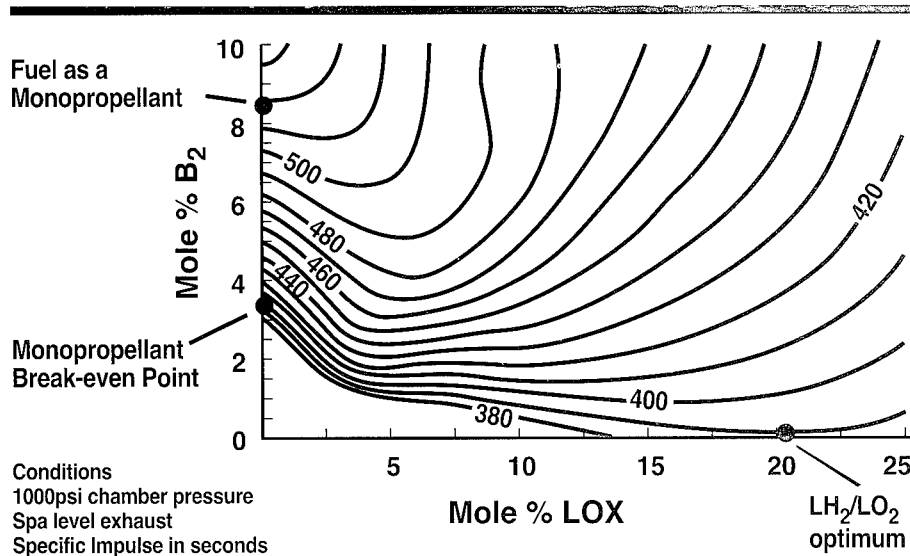


Figure 10.6 Effects of Metal Additives on Specific Impulse

At the highest level, it may be possible to prepare metallic hydrogen. Metallic hydrogen has a calculated I_{sp} of approximately 1600 sec, approximately four times today's systems. This is calculated to be the upper end that is possible for conventional propellant materials.

The cryogenic aspects of this program are clearly a long term, high risk effort, operating on a 30 to 50 year time frame for implementation, unless a dramatic breakthrough takes place. This program is the Air Force's best chance for revolutionary gains in performance, but it carries a very high risk.

10.8 Energetic Materials—Explosives

New higher energy explosives are available, but only minimal usage has been made of these materials. These energetic materials all have the ability to dramatically increase the explosive potential of warheads and bombs, thus increasing the killing potential. These new materials can be especially effective in directed energy explosive warheads proposed for use in the next generation of air-to-air missiles. We foresee in the long term explosive concepts being developed to allow for tuneability of explosive charges, a way to vary the energy output to match the mission requirements. We also need to rethink the design requirements for explosives to match the new needs of moving metal and momentum transfer in smaller warheads. Advanced thermites are available that provide the ability to attack chemical and biological warfare sites with improved probability of destroying the target without release of the agents.

More esoteric concepts can be employed in the long-term. These include using such theoretically possible molecules as polymeric nitrogen or fuels such as metal hydrides to the cryogenic explosives. High-payoff items identified as opportunities are:

- Near term: Achieve major improvements in the capability and reductions in the size of specialized warheads by implementing new materials such as CL-20. New explosives are exceedingly valuable for reducing the size of precision weapons.
- Middle term: Develop technologies to allow tuning of explosive charges (energies between conventional and thermonuclear) implement advanced thermites, nanoformulated explosives to improve yield and control.
- Long term: Pursue more esoteric concepts including using theoretically possible molecules such as polymeric nitrogen (three times the energy density of HMX), such fuels as metal hydrides, or cryogenic explosives.

Advanced Conventional Explosives

A prime contender for near-term application is CL-20, first invented at the Naval Air Warfare Center at China Lake. The U.S. appears to have a significant lead in the synthesis and availability of CL-20. The table below compares the properties of CL-20 with current state-of-the-art compounds HMX and RDX. In all categories of merit CL-20 vastly outperforms current materials. As such CL-20 development should be accelerated for applications where performance is of primary importance.

Table 10.1 Current State of the Art Explosive Compounds

Explosive Ingredient	Density (gm/cc)	ΔH_f (cal/gm)	Detonation Velocity (km/sec)	Detonation Pressure (kbar)
RDX	1.82	66	8.85	338
HMX	1.90	60	9.11	390
CL-20	2.04	203	9.66	454

The properties of CL-20 are such that warheads for penetrators can be half the size of the current generation. This means smaller or faster or longer range missiles and improved capability.

In addition to CL-20, there are several other compounds that are already available or are in the process of being developed. These include TNAZ, TEX, cyclodextrine nitrate, and HTREL, plus new oxidizers such as ADN that are currently available, and the developing area of high nitrogen compounds that have great potential for providing an enhancement over CL-20. Most of these compounds were developed under ONR sponsorship and AFOSR has almost no presence in the synthesis of new, conventional, basic energetic materials. In development efforts, the Air Force, Army, Navy, and DOE are well coordinated and integrated at the 6.2/6.3 level of exploration.

The currently available materials—CL-20, ADN, and TNAZ—could all be brought to field use within ten years, providing a dramatic impact.

Exotic Explosives

At the upper level of possible performance is the new HEDM type extended solid materials. These are proposed materials with a performance of three to five times that of HMX. Should these materials work out they would fill a performance gap above the current conventional materials. Currently proposed materials include compounds such as solid N_2 and other cryogenic explosives. These compounds are referred to as extended solids and are proposed to be prepared by high pressure synthesis possibly involving photochemical processing. New high energy fuels can be prepared using this methodology, including new isomers of BH_3 . New fuels can have great impact on the energy density of new fuels, explosives and propellants.

While this research is of high technical risk, the potential payoff is revolutionary and worth investment.

Pyrotechnics

Sophisticated sensor devices have made all areas of the electromagnetic spectrum accessible on the battlefield. Infrared (IR) sensors in particular are critical today. Simple pyrotechnic devices (such as IR flares) have been used for 30 to 40 years used to defeat IR seeker heads in air to air missiles, but seekers are so sophisticated that they can tell the color difference between standard flares and an aircraft, and whether the flare is moving or not (kinematic differences).

The USAF also finds uses for pyrotechnics in other roles. A recent requirement for pyrotechnics is battlefield illumination, particularly in conjunction with night vision goggles in special operations. In the night vision applications the flare emits in a narrow band to allow detection by frequency-specific goggles. Finally, pyrotechnics are excellent compact, very high heat sources that can be used for the destruction of CBW materials.

Pyrotechnics have had steady advances. There are ongoing programs to combine IR frequency selectivity, kinematics, UV opacity and RF properties in one aircraft flare. However, progress is slow as this is not a high priority. Be that as it may, a cheap flare can defeat an expensive missile and save an extremely expensive plane.

The most exciting progress is in development of very high heat source materials called metastable interstitial composites (MIC). The progress has been dramatic in the last two years. The nanomaterials developed having intimate mixtures of an oxidizer and fuel have dramatically increased the heating capability of devices built from these materials. Extreme temperatures with high energy density can be reached in very short times giving us a capability that lies between conventional weapons and thermonuclear devices. This is an area that needs exploitation and can be used to meet the requirements of several specific applications such as the destruction of CBW weapons. Using advanced pyrotechnic devices, the biological agents are capable of being destroyed in place while minimizing the potential exposure to other areas. Chemical agents can be handled in a similar manner.

These materials should be in the field in less than ten years. There is a need to speed their introduction into the inventory.

Story of the Synthesis of ADN and the Lessons Learned

In our panel deliberations, it was our opinion that the story of the discovery of ADN, its potential impact, and the inhibitors to introduction was worthy of inclusion into this report. ADN is an oxidizer, the oxygen source in solid propellants and other munition applications. ADN is recognized as having potential as a revolutionary replacement for ammonium perchlorate in missile systems. ADN is calculated to give higher I_{sp} propellants (5 percent to 20 percent depending on the application) and is environmentally benign.

In the early 1980s, the ONR initiated a search for improved energetic materials. This effort was a long-term research program into new materials, the kind that is effective but hard to maintain. This program led studies on the development of cubane-based explosives, fuels, and oxidizers. While in the process of developing an improved route to dinitramines for application on cubanes, Dr. Jeffrey Bottaro of SRI conceived of and synthesized the dinitramide molecule, the parent of ADN, in late 1989. SRI filed for patents on the composition of matter of the dinitramides in the U.S. and abroad, and these patents have been granted.

Following the publication of the patents in 1991, rumors began circulating that the USSR had employed ADN in some of their systems. These rumors were confirmed when Z. Pak of the LNPO Soyuz presented a paper at the AIAA meeting in 1993 describing some of their work. Later, the development work in the FSU was described in a newspaper article published in 1995.

The situation as we currently believe to be true is that the USSR ran an equivalent of the Manhattan Project to develop ADN for missile applications. The program was very heavily classified and compartmentalized. The Soviet ADN effort was apparently not detected by the U.S. intelligence community. The original inventors were awarded the Lenin Prize in 1976. This program moved ADN from the laboratory to production in seven years, an extremely rapid pace for the introduction of an energetic material.

The USSR operated at least one full-scale plant for the production of ADN for as long as 10 years through 1990. This plant had a capacity of 700 metric tons of ADN per year. This production is believed to have gone into the following families of missiles:

- SS-24 (second generation, first and third stages)
- Topol-M (second generation, second and third stages)
- SS-20-N

The Russians also claim to have used AlH_3 in their missile systems and are rumored to have an ADN/ AlH_3 system in operation.

The Russian facility for the production of ADN is mothballed. At least two U.S. groups are trying to buy the ADN technology from the Russians, but have not yet succeeded. Additionally, no one has yet evaluated a propellant sample of the Russian ADN-based propellant.

Several conjectures have been offered as to why the Russians put so much effort into ADN:

- Defeat of U.S. space-based early warning systems—no hydrogen chloride spectra to detect
- Lack of adequate ammonium perchlorate production
- Need for increased boost energy
- Method to violate missile treaties without detection—intermediate range missiles using ADN as the oxidizer would have ICBM-like range
- Fast burn first stage to decrease U.S. reaction time

Despite the evidence that the USSR had succeeded in implementing a revolutionary new ingredient into current systems, there has been minimal funding in the U.S. to verify the tremendous potential. ONR and BMDO have funded basic R&D on the synthesis, ONR has funded some initial propellant work, and Army Missile Command (MICOM) has funded some ADN work. Investigations are underway at Phillips Laboratory on using ADN in gel-type propellants.

The most important reason to present this lesson is that we have run into all the problems inherent in trying to bring a new material into the market. In the ADN case we have an ingredient with a demonstrated utility in the FSU plus a significant amount of calculational work done here in the U.S. Yet a sustained effort to apply the technology to a system in the U.S. does not exist.

Our experience with ADN would indicate that we have a very poor development history for new materials. Propellant developers are reluctant to investigate a new material unless it is available in large quantities, in the right particle size, and in abundant quantity at a very low price. New materials are never available in large quantities and are always expensive until economies of scale are introduced. If large, inexpensive samples of a new materials are not available, developers will do only minimal work on them. This is especially true for propellant makers who require large test samples. Unfortunately, it's hard to provide materials in quantity before they have been tested and determined to be of value.

New materials are inherently expensive to buy until they go into a system. There is no production capability to allow economies of scale to operate. The early high price tag inhibits timely evaluation and development. The problem will be even greater in the future because we have so few new systems coming along.

We also see that there is a need for a commitment by funding agencies to establish and maintain a research effort that will be adequate to provide the country a strong technology base. This requires developing materials and ingredients without necessarily having an immediate use for the materials, but rather the knowledge that having qualified materials on the shelf will result in the next system being developed using today's technology, not yesterday's.

11.0 Fuels and Lubricants

11.1 Fuels

Fuels, especially fuels for turbines, have two basic functions: a dense energy source and cooling. The energy density of hydrocarbon fuels combusted with air is unsurpassed. As a cooling fluid, state-of-the-art fuels (such as JP-8) have only limited capacity. Current and next generation turbine engines are exceeding the capacity of the fuel to handle the heat load. This is resulting in coking of the fuel and subsequent clogging of fuel passages and ignitors.

The need to use fuels as cooling agents is illustrated in Figure 11.1. This figure shows the aircraft heat loads with respect to time. As is clear, the fuel cooling requirements will rise dramatically when the F-22 comes into use, but even with today's current best fighters, the cooling requirements are exceeding the capacity of the fuel to provide adequate cooling.

Endothermic fuels are the enabling technology for turbines in the future. An endothermic fuel uses the engines waste heat to create a more energy-dense and better combusting fuel. Endothermic fuels are simply fuels that decompose under a thermal stress to absorb heat (provide a heat sink) and give off hydrogen and an olefin. The engine is cooled by heat absorption caused by a chemical process and more energy is available in the combustion process. Figure 11.2 shows the expected performance of the new endothermic fuels and other fuel advancements with respect to time. We are using JP-8 fuel in USAF aircraft today with a reasonable expectation of JP-8+100 being in use by the year 2000.

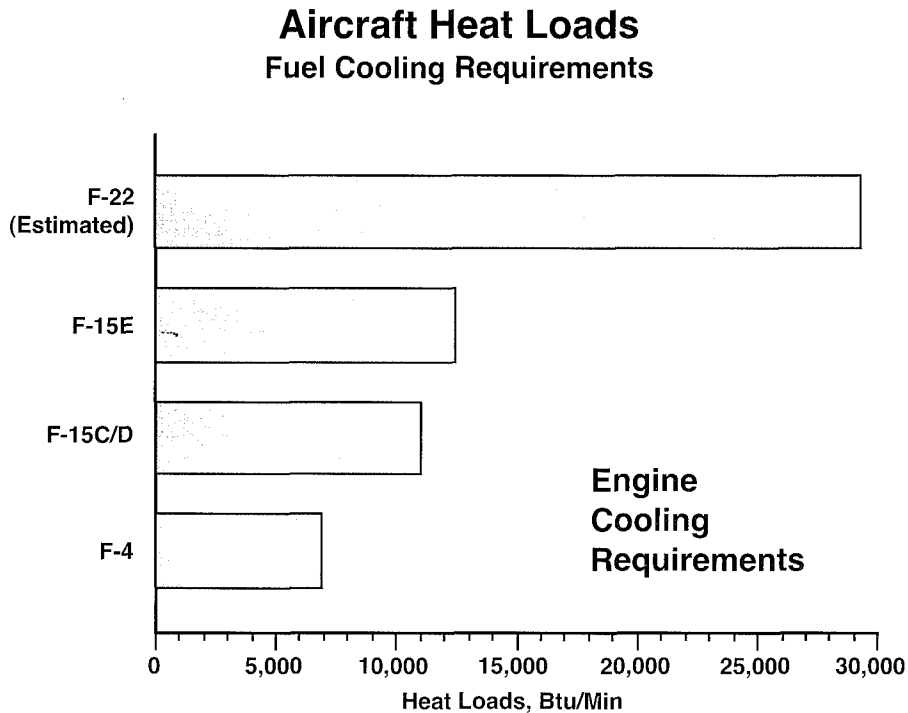


Figure 11.1 Aircraft Heat Loads and Fuel Cooling Requirements

High Heat Sink Fuels Technology Progress

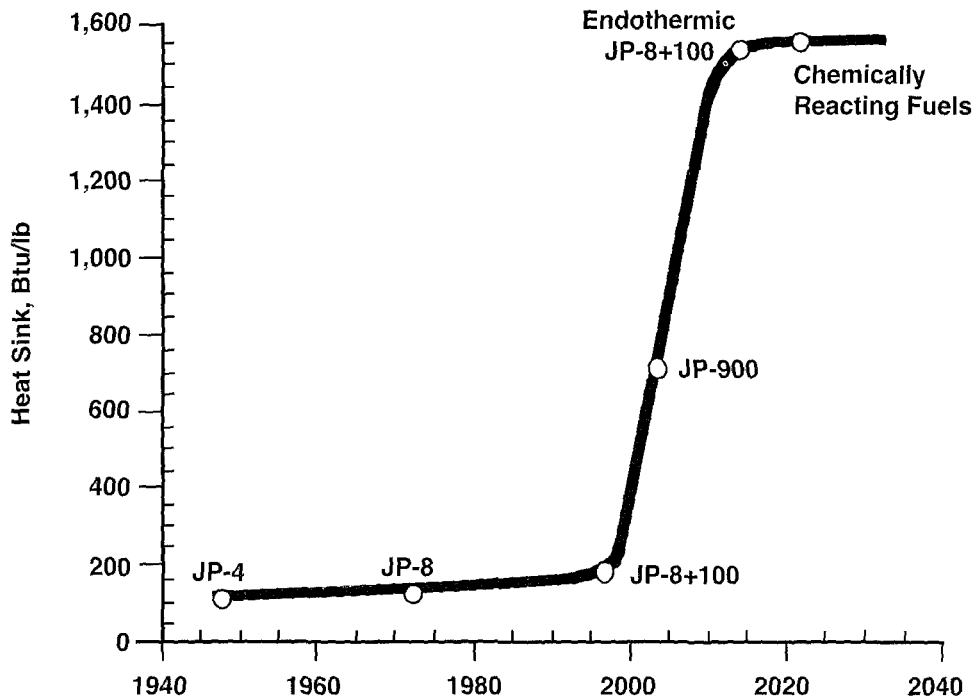


Figure 11.2 High Heat Sink Fuels and Expected Implementation Date

High-payoff items identified as opportunities are:

- Near term: Develop improved thermal stability fuels (achievable 1998-2003) and improved cleaning agents.
- Middle term: Develop endothermic fuels (2005).
- Long term: Develop chemically reacting fuels (2015).

11.2 Recommendations—Fuels

- A well directed program exists on new fuels. Continue the existing program.
- Implement improved thermal stability fuels at a faster rate along with fuel additives to improve engine performance.
- Continue with research on endothermic fuels and move forward the date of implementation into service.

11.3 Fuels—Expanded Descriptions

High Thermal Stability Fuels

The major short-term goal is the improvement in the thermal stability of the fuel. Engine temperatures degrade fuels, causing coking and subsequent engine failure. There is a program at Wright-Patterson AFB to increase the thermal stability of JP-8 by 100°F (JP-8+100) by 1995. Their next goal is to raise the thermal stability to 575°F (JP-900) by 2003 with a concomitant increase in the ability of the fuel to act as a heat sink by 500 percent.

Endothermic Fuels

The next stage of the program is to introduce endothermic fuels by 2005. The capability of the fuel to absorb heat should be 10 to 15 times that of JP-900. These fuels will have a higher energy density due to pumping of energy into the hydrocarbon fuel by the waste engine heat. Successful application of endothermic fuels should greatly reduce the cooling needs for advanced turbines and reduce their weight.

Combined Fuel Lubricant (Single Fluid)

An exciting concept is the total elimination of the lubricating fluid in the engines. Replacement of the lubricant would be done by using the fuel as the lubricant. This should pay off by simplifying the logistics, eliminating disposal costs for hazardous lubricant materials, saving weight (approximately 100 pounds per engine) by elimination of the lubricant equipment, and eliminating failures caused by thermal breakdown of the lubricant.

Chemically Reacting Fuels

These are chemical additives for fuel that are used to enhance a desired property.

Hydrogen. The ultimate clean-burning fuel is hydrogen. Investment in the technology is very long term, but has major advantages. The use of hydrogen opens up new possibilities for materials in engine design as the atmosphere is reducing instead of oxidizing as found in a conventional turbine engine. Problems due to hydrogen storage, drag caused by large hydrogen tanks, embrittlement, flammability, and thermal containment need to be addressed.

Hydrazine Elimination. A near-term need is elimination of hydrazine as a propellant for the auxiliary power unit (APU) in F-16 fighters. Hydrazine is toxic and carcinogenic. Its properties make its handling difficult, requiring an extensive logistics chain. There is an effort at Wright-Patterson AFB to find substitutes based on nontoxic ammonium salts, possibly an aqueous system. This effort should be encouraged.

11.4 Lubricants—Summary

Advancements in lubricants and seals, as well as sealants and other nonstructural materials are absolutely critical for the Air Force to meet mission requirements of aircraft and space vehicles of the future. Increasing the thrust to weight ratios of future turbine engines will require the development of efficient lubricants that can withstand these higher temperatures. New lubricants must be developed to reduce the propensity for coking of current engines and when new more efficient engines are fitted to aging aircraft. Turbine engine temperature requirements

are exceeding the capacity of state-of-the-art lubricants. Current synthetic polyol esters have an upper temperature limit of 400°F, while perfluoropolyalkylethers, which are under development for future advanced turbine engines, will have upper temperature maximums of 630°F to 700°F. Compatible sealing technology must also be developed hand-in-hand with advanced lubricants. Both liquid and solid lubricant technology developments, including technology for hard coats and wear resistant coatings will be necessary to meet the requirements of both expendable and man-rated engines of the future. Greatly improved liquid and solid lubricants must be developed to increase the lifetimes of spacecraft moving mechanical assemblies, such as control moment gyros and reaction wheels.

Thermal breakdown of lubricants is not currently a major maintenance problem for the USAF. However, future systems may be severely compromised due to lack of adequate lubricants or adequate development of new concepts. High-payoff items are:

- Near term: Increase the thermal stability of polyol ester lubricants to 450°F and increase the stability and capabilities of the perfluoropolyalkylethers and sealing systems to 700°F.
- Middle term: Investigate solid lubricant technology to provide lubrication to 1500°F to 1800°F. Eliminate lubricant completely by use of a single-fluid concept (100 pound weight savings per engine), coupled with endothermic fuel, or use vapor-phase lubricants. Note, however, that the single fluid concept is a very high-risk approach.
- Long term: Use magnetic levitation for motor parts and bearings. Note, however that solid or liquid lubricant may still be required for startup and shutdown.

The elimination of lubricants by use of the single-fluid concept would save approximately 100 pounds per engine. For the F-22 it is estimated that reducing engine weight per engine by one pound, would save 8.7 million gallons of fuel over the aircraft lifetime. The impact is large.

11.5 Recommendations—Lubricants

Both liquid and solid lubricants, wear-resistant coatings, seals, sealants, and other nonstructural materials are absolutely critical for successful Air Force operations in the future. Future systems may be severely compromised by a lack of adequate lubricants and seals or development of alternative concepts. To avoid this:

- Fund research on higher thermal stability in lubricants and seals.
- Encourage further exploration of a single-fluid concept for the elimination of lubricants.
- Continue current program on magnetic levitation and initiate effort to develop compatible solid lubricants.

11.6 Lubricants—Expanded Description

Lubricants

Thermal and oxidative stabilities and interactions with bearing/system materials are the issues. Innovative approaches are needed to achieve adequate materials for current and future aircraft engine designs and for spacecraft lubrication. Solid lubricants and wear-resistant coatings have the potential for replacement of liquids especially in expendable engines and for use in conjunction with magnetic levitation.

Magnetic Materials

The long term solution to many lubrication problems may be the use of magnetic bearings with solid lubrication. This is a long-term area for investment. The questions of weight and type of magnet (permanent or soft) need to be addressed.

12.0 Materials for Missile, Space, and Launch Systems

12.1 Introduction

Affordability is the key criterion for assessing the value of a new technology and its potential incorporation into military applications. Although enhanced performance continues to be a high priority, performance improvements must be achieved with affordable technologies. Affordability must be considered in terms of the life cycle cost of the system. This means that revolutionary materials and processes, which in some cases are more expensive than those currently in use, may have a favorable impact on a system's overall life cycle cost, and may also provide performance advantages.

A major obstacle to fully exploiting space is the high cost of getting there. Secretary of the Air Force Sheila Widnall has said that the highest selection criteria for replacing our launch fleet are "affordability, affordability, affordability." Therefore, a prerequisite for any future materials development effort is its potential payoff in lowering the cost of existing and future weapons systems. Because propulsion systems account for approximately 50 percent of total launch costs, the potential exists to dramatically reduce the cost of space and missile operations by the application of improved materials. Some technology areas that offer the possibility of meeting these needs include new energetic materials for propulsion systems and improved, lighter weight materials with higher temperature capability that allow the thrust to weight ratio of the system to be increased or allow the system to be operated at a more efficient temperature.

Opportunities for developing new energetic materials, including propellants, is discussed in a separate chapter of this report. This chapter describes other materials needs and potential developments that are critical for improving the affordability and performance of advanced missile, space, and launch systems.

Along with affordability, the other overriding consideration in future materials development is environmental compatibility and reduced environmental impact. The continually increasing environmental regulations on disposal practices and the content and handling of waste streams will limit the processes and materials that will be acceptable for future systems. This is of course the case for all of the materials applications discussed in this report, not just for missile, space and launch system needs. It is therefore an issue that must be emphasized by the leadership within the Air Force and DoD, in order to ensure that technologists developing new materials and processes adequately address environmental compatibility.

12.2 Materials for Improved Performance

The areas of highest payoff for space and missile applications in terms of performance are 1) lowering the weight and 2) improving the high temperature capabilities of advanced materials. Composites have become the materials of choice for certain applications because of their significant potential weight savings compared to conventional metallic structural materials. However, although significant improvements have been made, improving the high temperature capability of composites and metallic alloys must remain a key objective of future development efforts.

There are numerous components in rocket motors that can benefit from improved materials. In all cases, the key issues in the development of new materials and processes are affordability and environmental compatibility. In the case of structural materials, lower weight with equal or better strength and stiffness is the main goal, while high-temperature capability and improved reliability are also prime objectives. In solid rocket motors, the structural components for which new, lighter-weight, high-temperature materials would provide the greatest payoff are cases, nozzles, and insulation. In liquid rocket motors, improved high-temperature capability offers the greatest performance payoff, with improved mechanical strength and lower weight also being important. Some of the components in liquid rocket engines for which advanced materials development should be pursued include tanks, turbines, injectors, nozzles, hot gas manifolds, and preburners. For space structures and space rocket motors, low weight is the driver. Significant cost savings can be realized by replacing metallic components with lighter weight composites.

There is a critical need for advanced materials with adequate structural and transmissive properties for windows and radomes for hypersonic (Mach 5 - 10) missiles and aerospace vehicles. These types of materials would also serve in other applications like sensors, space structures, and solar propulsion systems. Materials with improved optical properties at certain wavelengths, such as that of CO₂ lasers (8-12 μ m), are also needed for supersonic applications (Mach 2 - 3). Advanced synthesis and processing of diamond films is one technical approach that may satisfy these needs. Improved methods of producing diamond-based structures could lower costs sufficiently to make diamond films or even diamond monoliths a viable option for future transparent materials applications.

Other needs unique to space systems are materials with improved resistance to radiation and atomic oxygen. Current efforts in this area are focusing on silicon- or aluminum-imbedded materials that form an oxide coating when attacked by atomic oxygen. Many other materials solutions may also become available.

There is considerable Air Force interest in running future liquid rocket engine oxidizer turbopumps oxygen-rich. Using them this way allows a lower turbine inlet temperature than fuel rich operation, and it eliminates a complex, heavy, multistage seal between the turbine and the impeller sections of the pump. The result is significant durability enhancement and thereby greater reliability. There is thus a need to identify and develop materials that are compatible with high-temperature, high-pressure gaseous oxygen in the turbopump and associated machinery. Likely candidates include metals, coated metals, and ceramics.

Another key area in which improvements to rocket propulsion are needed is turbopump engine bearings. Traditionally, vibrations experienced when the pump is cooled for liquid oxygen operation generate heat, leading to thermal runaway. Pump bearings are made of silicon nitride machined to a very fine finish with a low coefficient of friction in order to control temperatures during operation. There are two problems with this approach: 1) These bearings require high-quality silicon nitride produced only in Japan. 2) The precision production and machining required for the necessary surface finish are done in Germany due to the absence of a U.S. capability. There is no domestic source for these materials or components. Clearly, it is essential that our ceramics capabilities be markedly improved, not only for the production of high-performance materials but also in the high-level machining required to render these materials suitable for component application.

Developing approaches to combining high thermal conductivity, high modulus and low coefficient of expansion with improved strength in carbon-fiber composites is another important area. Thermal management and dimensional stability are often limitations in space structures. Simultaneously achieving the thermal properties, structural loads, and displacement requirements will lead to decreased system weight.

12.3 Materials Technologies Critical for Space and Missile Systems

Other materials technologies with the potential to produce performance and cost improvements in propulsion systems include the development of advanced adhesives and coatings, thin films and diamond manufacturing, environmentally compatible insulation, molecular self-assembly and nanoassembly of structures, microelectronic machines, microtube technology, high power density, uncooled electronics, advanced IR sensor materials, nonlinear optical materials for high speed on board data processing and transmission, and miniaturization of rocket and space components. Based on current efforts, it appears that specially designed hybrids (combinations of organics, inorganics, metals, ceramics) will be the materials of choice to satisfy the requirements for many of these advanced applications. Hybrid materials may also offer other advantages besides improved performance, such as the ability to design for lower sensitivity to impact or hostile action.

Adhesives and coatings. Development of adhesives and coatings that are more environmentally acceptable is currently a high priority for both military and commercial applications. While the impact to the environment of adhesives and coatings used for space and missile systems is extremely small compared to other uses (such as aircraft, or, even more significantly, commercial industry), it is important to recognize the effect of environmental regulations on the availability of existing specialty adhesives and coatings required by military aerospace systems and on the development of new systems for future needs. Complying with new laws and regulations to protect the environment while preserving the capability of existing and future systems will require a considerable investment in new technologies. It will also require leadership and foresight by senior management, who collectively must take the initiative in sponsoring the development of new technologies that provide environmental compliance without an unacceptable deterioration in the performance or cost of weapons systems.

Thin films and diamond technology. Improved thin films and more affordable diamond synthesis and processing are enabling technologies for numerous applications. Some benefits for aerospace systems include the development of high thermal conductivity substrates for a number of uses (e.g., thermal management in electronics), smart coatings that act as sensors and protective materials, diamond windows, diamond-coated bearings, diamond micromechanisms, and diamond-based thermionic devices.

Thermal insulation. Replacement of current insulation, which contain asbestos, with new, environmentally benign formulations is certain to be a high priority over the next decade. Some promising approaches include insulation based on high performance polymers such as Kevlar or oxy-silicates, or TPE-based formulations.

Molecular self-assembly and nanotechnology. The achievement of micron precision in fabricating new devices revolutionized the electronics industry during the 1960s and 1970s,

which in turn enabled development of a new generation of advanced weapons systems. Similar revolutionary advancements may be realized over the next decades through nanometer processing.

Nanostructured materials have significant promise for a number of applications, both military and commercial. For aerospace uses, nano-based processing could provide advanced electro-optic materials (discussed in Chapter 9.0), sensors (discussed in Chapter 13.0) and specialized structural materials, such as multispectral windows. Nano-assembly offers the possibility for creating multi-layer structures specifically designed on a molecular level. For example, current work is being conducted on multispectral windows such as shown in Figure 12.1 which consist of nanostructured silicon with specially designed dielectric properties imbedded in diamond or another high temperature substrate.

Multispectral Windows and Radomes for Space and Seeker Applications

(Concept of K.V. Ravi, Lockheed Missiles and Space, Palo Alto)

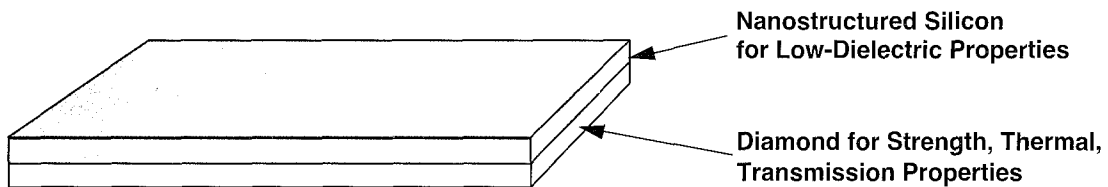


Figure 12.1 Nano-structured Multispectral Windows

Micro-electronic machines (MEMS)/miniaturization. MEMS promises to create a revolution in the capabilities of aerospace systems by combining the benefits of very small size, high performance, reliability and very low cost into one package. In space and missile applications, where size, cost, and intelligence are dominant considerations, the first MEMS systems are already finding application in the form of tiny, cheap inertial guidance units for smart munitions and micro-instruments for satellites. The ability to put on a single chip such devices as accelerometers, compasses, gyroscopes, pumps, fluid mixing systems, gas analyzers, cameras, and adaptive optical systems promise revolutionary improvements in every kind of complex technological system. The integration of hundreds, even thousands of microdevices into larger systems and structures offers still unexplored possibilities for self-monitoring, adaptability, and autonomous control. Figure 12.2 shows a microscale motor developed by Eckart Jansen of the MIT Microsystems Technology Laboratory.

Recent developments such as microtubes offer broad possibilities for micro-machine applications as well as potential uses in processing unique components, such as self-cooled nozzles or self-monitoring smart devices and structures. Some other potential propulsion applications

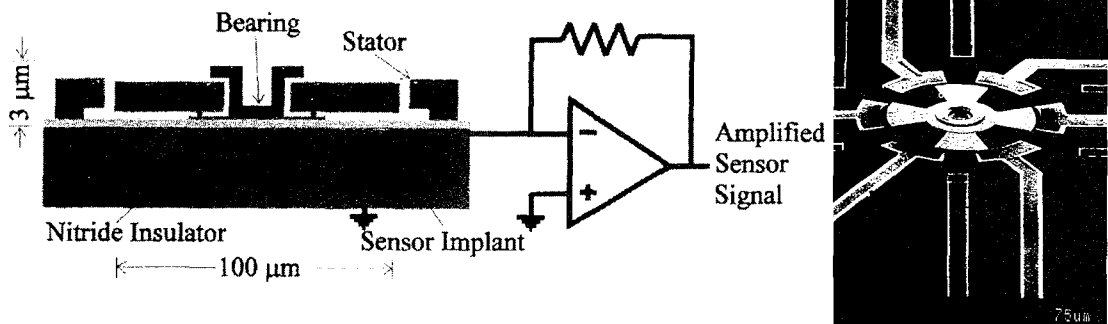


Figure 12.2 A microscale electric motor produced at the MIT Microsystems Technology Laboratory: a) diagrammatic b) imaged

for microtube composites include encapsulation, bondline venting of off-gases, microthin injectors, microcombustion chambers, and solar absorbing heat exchangers. Figure 12.3 shows a potential use of microtubes in high temperature insulation.

- **OBJECTIVE**

- Replace hygroscopic shuttle tile which requires sealing after each mission

- **APPROACH**

- Use microtubes to lower weight, increase insulation, increase temperature capability, and increase toughness

- **PAYOFF**

- Save hundreds of thousands of dollars/mission and greatly decrease turn-around time

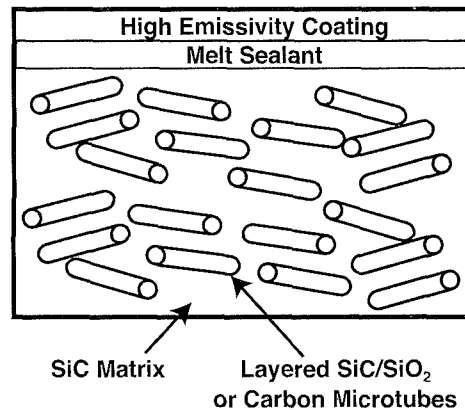


Figure 12.3 Microtubes in High Temperature Insulation (Photo courtesy of Phillips Laboratory

High Power Density Uncooled Electronics, Advanced IR Sensor Materials, Nonlinear Optical Materials for Data Processing and Transmission. High power density electronics based on wide-bandgap semiconductors have the potential for great payload weight savings because they can handle much more power than similar sized conventional semiconductors, or can deliver the same power in a much smaller and lighter package. They also have significant potential advantages in radiation hardness and reliability. Advanced IR sensor materials will increase the performance of surveillance payloads while reducing weight due to reduced cooling requirements. Nonlinear optical materials are the key to high speed on-board optical data processing and optical communication between satellites or between satellites and Earth. Millimeter-wave crosslink communication is also a high payoff, but potentially nearer term capability.

A consistent long-term investment in the fields of nanotechnology and miniaturization is strongly recommended. These fields offer great potential for enabling the development of new components and devices for aerospace systems and also have potentially broad commercial significance.

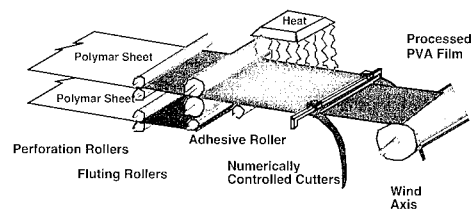
12.4 Far-Term Objectives

Far-term objectives for low-cost solid propulsion systems include development of functionally graded motors and integrated manufacturing techniques that allow rockets to be fabricated with a minimum of steps. Such methods may include fabrication of more than one rocket component (e.g., rocket propellant, insulation, case) concurrently, or with a single piece of equipment. Figure 12.4 shows a potential concept for low-cost manufacture of rocket motors. Functionally graded motors would provide a means for controlling the thrust of the rocket by changes in the internal composition of the propellant within the motor. Thermoplastic-based rocket propellants and rocket components would be inexpensive to produce and would allow the motor to be recycled rather than disposed of at the end of its service life.

Another far-term propulsion concept would require light weight, strong materials for use in cryogenic tanks. These tanks may contain liquid helium with energetic materials slurried in, or they may contain solid hydrogen or solid oxygen with energetic fuels or oxidizers embedded in the matrix. In conjectural designs for reusable launch vehicles (RLVs), there may be a large temperature delta of approximately 3000 K between external, leading-edge structures and the cryogenic tank. This will place tremendous loads on the materials.

TECHNOLOGY CHALLENGE:

Develop Revolutionary Approach For Manufacturing Rocket Motors in More Reliable, Safe, Cost Efficient and Environmentally Acceptable Manner



PAYOFF:

- **Significant Improvement Over Conventional Solid Motor Manufacture**
9 Steps vs 23
- **Environmentally Benign Solution Propellant**
- **Safer Manufacture**
- **Improved Performance (greater than 5%)**

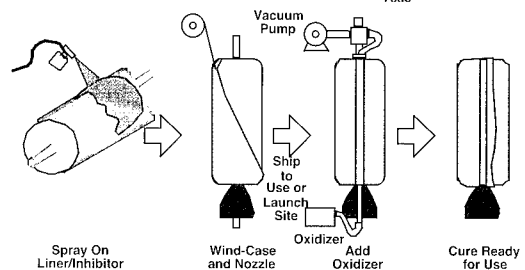


Figure 12.4 Concept for Concurrent Manufacture of Rocket Motor Components (Photo courtesy of Phillips Laboratory)

13.0 Function-Integrated Materials

13.1 Introduction

The Nature of Function-Integrated Materials

The technological selection of materials commonly targets a given collection of properties which define the materials' primary function in a system. For example, in an Air Force context, carbon-epoxy composites on an aircraft serve a structural function and are selected because they offer a good compromise on low density, high stiffness, and high strength. Piezoelectric materials, on the other hand, are not usually selected for a structural function but for their ability to perform mechanical-electrical energy transduction with high efficiency. The materials of optical fibers are selected of course because of their light transmission properties, but they do not have ideal mechanical flexibility and repair processability. Materials as we know them and use them at the present time are largely monofunctional. Many materials-enabled technologies can be envisioned for the future through synthesis of structures in which multiple functions are integrated by molecular design in one material. The best examples of function-integrated materials by design are in fact found in biology, and they remain generally an unrealized vision in technology.

The vision for function-integrated materials would be materials in which sensing functions using photons, mechanical forces, and magnetic or electric fields are built into the molecular structure within the boundary conditions of a secondary or even tertiary function related to structure or ability to interconvert energy. Such binary and ternary combinations of a material's functions by structural design has not really occurred technologically. A possible application of such materials in Air Force systems would be sprayable and adhesive batteries or solar cells for the wings of aircraft to convert solar energy to electrical power and store it, all while at high altitudes. These sprayable batteries would be, ideally, composite structures that have the processability of currently known materials and even have load-bearing capacity. Another relevant application would be sprayable, structural composites which have a switchable antenna function to receive and process information or be stealthy on demand. The concept can be extended to sprayable materials for tunable radomes and special sensors. To close the loop on function integration, the new materials that should be explored must be potentially recyclable. This is important not only for environmental purposes but also because function integration in materials will enable technologies at a cost. An extremely promising and unexplored group of materials for function integration are nanophased organics and nanophased composites.

Nanophased Metals and Ceramics

The materials community worldwide recognizes nanophased materials as one of the important frontiers for materials technology. Research on nanocrystalline metals and ceramics was initiated during the past two decades, and many potential opportunities have been identified. For example, superplasticity has been observed in nanocrystalline ceramics such as alumina. Another important property identified in laminated ceramic-metal nanostructures has been extremely high dielectric constant. Nanostructured ceramics could also play a very important role as thermal barriers in airframe and propulsion applications. A general advantage that could

be achieved in nanocrystalline metals and ceramics is high purity, which may be important in enhancement of mechanical properties. The properties of nanocrystalline intermetallics are still not very well known; this is due in part to the limited scale up of these materials to date. Nanocrystalline metals and ceramics could be important in Air Force technologies since they could play a key role in the development of higher temperature engines or other aircraft components. Ceramic-metal nanophased materials could also lead to new materials with super dielectric constants. This would enable a technology of highly efficient, miniaturized antenna arrays on air vehicles.

13.2 New Directions in Function-Integrated Nano-Structured Materials

Nanophased Polymers

Relative to metal and ceramic nanostructured materials, little is known about the properties of nanophased polymers and organic-inorganic nanocomposites. In the field of polymers, considerable attention has been given over the past two decades to microphase separated materials. These materials consist of block copolymers in which chemically different segments have fairly narrow distributions of molar mass. At equilibrium these polymers self-organize into microstructures with various geometries. However, ordering occurs very slowly or requires applied shear forces to increase the rates at which they order. These include, for example, lamellar structures, cubic superlattices, hexagonal phases in which similar segments segregate into cylindrical structures, and several bicontinuous structures which have been discovered more recently. The properties of these microphase separated polymers are still being investigated, however, common flexible copolymers require rather high molar mass to exhibit a thermodynamically stable microphase separated state. Thus, it will not be easy to make the transition into nanophased organics with common block copolymers. Special polymers with rigid segments or special molecular architectures will be required to truly access the nanometer regime. Furthermore, for certain applications it would be important to develop nanophased polymeric materials in which the nanostructures consist of single macromolecules and also have distinct shape. This concept is referred to here as "nanoparticle polymers" and is described in further detail later in this section.

If the Air Force had access to nanophased polymers, various technological quantum leaps related to materials could occur. These include ultralight materials for structural applications which may not require carbon fibers, glass fibers, or ceramic particles for reinforcement, materials recycling technologies, as well as the function-integrated materials described above. Certain molecular structures in nanophased organics could also be used as recyclable paints and adhesives. Nanophased polymers would also be important to Air Force technologies because such structures might be necessary to produce stable third-order nonlinear optical materials that utilize high-amplitude photons to transmit, process, and store information at rates several orders of magnitude faster than currently possible. These materials could serve as optical computers on air vehicles and being organic or composite in nature would not add significantly to the weight of aircraft, satellites, missiles, or rockets. Relative to silicon-based computer technologies, information processing with photonic organics is projected to be 10,000 times faster.

Solid energetic materials that would be molecularly designed to have nanometer or micron sized regions of all key ingredients is one additional outcome from nanophase polymers. The vision in this concept would be to generate the ability to design single-component solid propellants and explosives processable as macroscopically ordered structures. For example, energetic materials could be produced with nano- or micro- tubes of oxidizer in fuel matrices, oriented in a common direction within a charge. Alternatively, layered structures could be formed by self-assembly of a fuel-oxidizer block copolymer. Again, the structural chemistry or architecture of blocks would be key in achieving nanometer as opposed to micron sizes in structures. Such materials could bring spatial control of focused energy, homogeneous energy dissipation and safety, as well as enormous increments in specific impulse.

Nanoparticle Polymers: Processing and Recycling via Reversible Sintering, Molecular Nano-Composites. The polymeric materials of contemporary technologies contain long chain macromolecules which are typically coiled in solution or in the melt. When solidification occurs, these long molecules either fold if they crystallize or extend under flow when fibers are

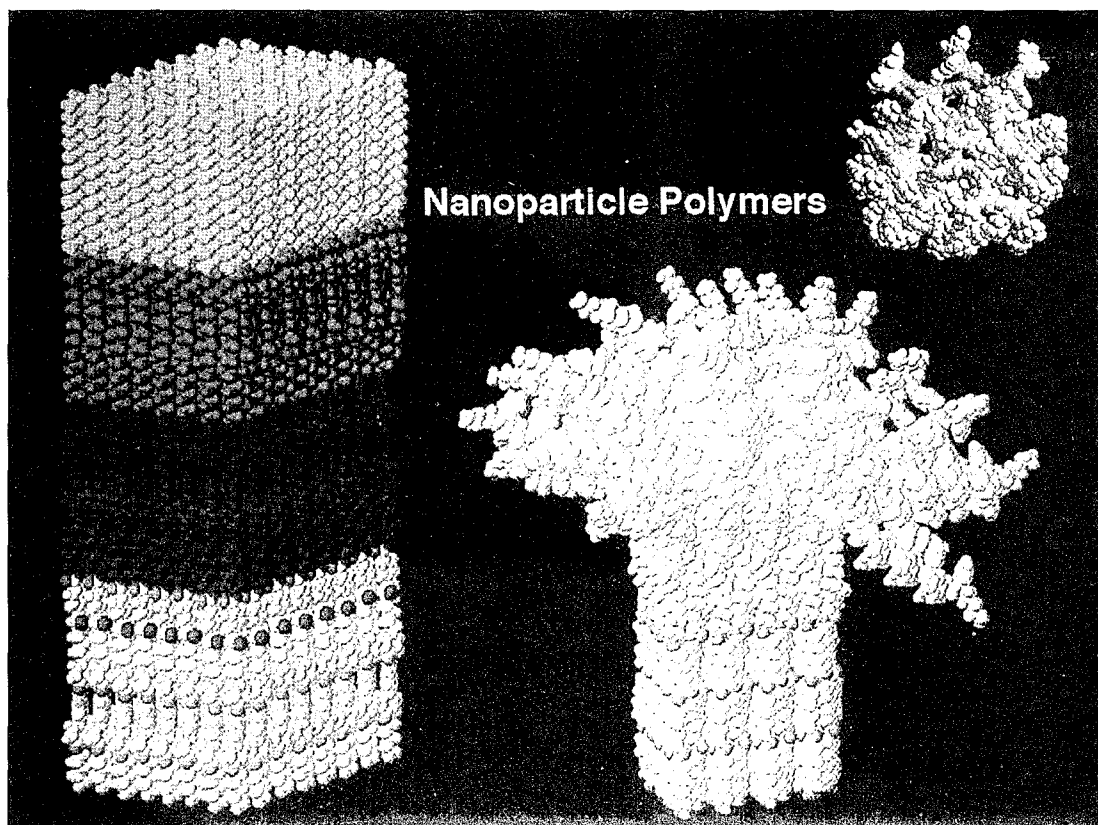


Figure 13.1 Molecular Graphics Rendition of Nanoparticle Polymers with Dimensions on the Order of Several Nanometers

produced. Missing among the large number of polymeric materials available today are materials composed of polymer molecules that resemble hard particles with nanoscale dimensions. The analogy to hard particles is based on the concept that such polymer molecules would have a well defined shape that never changes as materials transform from liquids to solids and vice versa. Such materials could be appropriately described as molecular object polymers or nanoparticle polymers and would have shapes generated irreversibly through covalent bonds. Figure 13.1 shows a molecular graphics rendition of three structures which could be considered nanoparticle polymers. In essence, nanoparticle polymers would be polymers that resemble nanocrystalline ceramics. The actual structures shown have been synthesized in academic materials chemistry laboratories but not yet in a scale large enough to allow a thorough investigation of their technological potential.

With technological access to nanoparticle polymers, we could revolutionize the nature and the processing techniques of lightweight, high-strength materials. For example, nanoparticle polymers could be sintered the way ceramics are sintered, except that this would be possible easily at very low temperatures and could involve reversible secondary bonds or ionic bonds. This process of organic sintering could be controlled by surface chemical modification of the nanoparticle polymer molecules. Most importantly, there is the opportunity to develop the concept of reversible sintering which should be of great importance in a recycling context. Desintering of macroscopic structures into nanoparticles could occur at temperatures slightly higher than those used in the original sintering process or by resuspension of the nanoparticles in water when ionic bonds are used as a means to sinter the macroscopic structure. Nanoparticle polymers would have by definition a covalent structure somewhat similar to that of crosslinked polymers, given that their molecular shapes would be sustained by a covalent structure. Crosslinked polymers, including the epoxy matrices of composites, as well as rubbers, cannot be recycled by solvation or melting. In this context the possibility of efficiently processing and recycling nanoparticle polymer materials is an exciting prospect. The final materials processed from nanoparticle polymers could take morphological forms that would resemble, for example, stacked and glued mica-like organic flakes or densely packed and oriented organic fibers of nanoscale diameter. One of the characteristics of such materials would be very high strength-to-density ratios, but many other novel properties could be imparted to the structures through molecular design of the nanoparticle.

Using a nanoparticle polymer technology, novel molecular composites could emerge for high-strength, lightweight airframe components. Such materials could use nanoparticles as the reinforcement, but use conventional polymers as the binding matrices. This would introduce additional degrees of freedom in tuning properties, since stiffness could be controlled through the nature of the matrix, and possibly property anisotropy and strength through the nanoparticles and their anchoring chemistry to matrix materials. Recycling for materials formulated as molecular composites could involve simply the depolymerization of very small quantities of conventional linear polymers serving as the interparticle glue. In these materials, as suggested before, crosslinking would be totally internal to the nanoparticles and therefore would not interfere with recycling as it does now in advanced composites based on epoxy matrices.

Work is starting in laboratories throughout the world to produce macromolecular structures that resemble hard nanoparticles two or more orders of magnitude larger than buckyballs. The magnitude of the effort is still very small, but most importantly ongoing work does not

necessarily envision the role of such macromolecular structures in advanced materials. Therefore, the possible revolution they could contribute to processing, recycling, and function integration in materials is really not part of the current vision. Research programs are needed that will target macromolecular particles as the components of advanced materials.

Nanophased Polymers and Damage-Resistant Electronic and Photonic Organics. Organic materials with conjugated structures can exhibit many useful properties for advanced technologies. These properties include third-order nonlinear optical properties, electrical conductivity, electroluminescence and photoluminescence among others. All of these properties are important for sensor development or energy conversion functions in materials. However, the problem with such materials is the fact that many electronically delocalized organic structures can be chemically unstable or have poor resistance to laser beam damage. Conjugated structures also tend to aggregate due to interactions such as carbon-carbon overlap, and this may significantly quench some properties. Strategies to protect these structures through molecular encapsulation need to be investigated, and this is where nanophased polymers of the nanoparticle type may play an important role. Specifically, it may be possible to design nanoparticles in which internalized delocalized structures are protected by robust molecular shells. This would also facilitate the processing of electronic and photonic organics using the sintering methodologies described above.

The role of molecular architecture in the effective encapsulation of conjugated structures needs to be investigated. Specific examples could include the use of dendrimeric structures or layered particles of various shapes of dimensions smaller than those of the wavelengths of interest in order to avoid scattering. In cases where long-range electronic conduction is desired, the encapsulation of the most sensitive conjugated structures needs to involve conducting shells, hopefully damage-resistant ones. Future optical computing sensing devices, and laser beam protection devices would benefit from a nanophase approach to the protection of environmentally sensitive structures.

Nanoparticle Polymers and Function-Integrated Materials

The potential of nanoparticle polymers in function-integrated materials is based on the possibility of designing molecularly two or more functions in the nanoparticle. For example, one could combine a sensing function, an energy transduction function, and a structural function in a given nanoparticle. Conventional polymers considered for second order nonlinear optics are entangled linear chains which have to be mixed with dye molecules and then poled in an external electric field in order to make an electro-optical sensor device. On the other hand, if the basic unit of the sensing material is the anisotropic plate nanoparticle, dye molecules could be pre-incorporated covalently inside the plate in a given orientation relative to local coordinates of the nanoplate. The macroscopic orientation needed to make the sensor would arise from the polar macroscopic stacking of plates. In addition to the sensing function, the nanoplate is also a useful structural element offering stiffness and planar anisotropy. Structurally, one could say that the nanoparticle is a microstructural unit cell of the material since its structure reflects the final microstructure and anisotropy of the macroscopic solid. A good case in point is the structural similarity between the anisotropic nanoparticles that resemble plates and the macroscopic material produced when the plates are condensed with a common stacking direction.

Nano-Composites: Molecular Dispersion of Organics in Semiconductors, Metals, and Ceramics

The composite materials that emerged over the past few decades and used presently in Air Force systems are mechanical mixtures of two or more components, typified by the dispersion of fibers in a polymer matrix. The performance and processing of these systems will probably continue to improve but many limitations will remain with regard to recycling, cost, and repair of structural components. Little is known at present about the properties that may emerge if organic molecules, including polymers, could be dispersed molecularly in ceramic or metallic lattices. In nature, for example, molecularly dispersed proteins toughen extremely brittle ionic lattices to a point where ductile fractures are observed. A good example of this phenomenon is biogenic calcium carbonate.

Research is proceeding in the U.S. and elsewhere on the intercalation of polymers in ceramic materials. For example, work is being carried out on the intercalation of both hydrophilic and even hydrophobic polymers in layered inorganic solids such as silicates and calcium aluminates. These materials have been shown to have enhanced mechanical properties such as higher toughness or compressive strength. The intercalation of the organic in these layered inorganics produces lamellar ceramic-polymer nanocomposites. Most of the synthetic methodologies are direct, that is, they involve diffusion of polymers between inorganic layers. Precipitation of the inorganic component from concentrated polymer solutions has also been explored as a different approach to intercalation and offers distinct advantages. In this case the precursor ions to the inorganic solid are dissolved in the polymer solution.

The precipitation of inorganic materials in organic media needs to be investigated further, including precipitation in ordered media. One of the interesting aspects of the precipitation approach is the possibility of having a liquid or viscoelastic precursor to the nanocomposite which would be of great importance in processing. Also, the precipitation approach could produce interfacial bonding between the nanophases through the possibility of molecularly dispersing the organic component in the inorganic lattice. This last issue also impacts our ability to design novel properties by close coupling of the nano-phases. Other possible avenues to produce interesting nanocomposites would be to explore the simultaneous spraying of metals and polymers on substrates.

Synthetic examples of nano-composites could offer not only novel mechanical properties, but also unique electrical, optical, and transport properties at weight ratios of organic and inorganic content which are not common in conventional composites. Novel electrodes and corrosion-resistant metals with relatively little organic content are additional examples of systems that could emerge from these materials. Molecular level dispersion of organics in inorganic materials also opens the possibility of finding thermodynamically stable composite materials; this is of obvious consequence to recycling of composites. In many instances, primarily in soluble materials, the composite solid state would reform spontaneously, thus offering facile recycling of high-value-added materials. The prospects for this area of advanced materials are promising, but this field will only develop through the interdisciplinary efforts of organic chemists, inorganic chemists, and materials scientists.

Nano-Composites and Function-Integrated Materials

Innovation in nanocomposites brings the potential for novel classes of function-integrated materials. One possibility is the creation of processable materials with energy storage functions coupled to structural functions. In the precipitation approach mentioned above, an organic matrix would be used as the precursor for nucleation of a nanostructured semiconductor that behaves as a solar cell. The precursors to these nanocomposites could be sprayable substances that are deposited on external or internal surfaces of air vehicles. After spraying, semiconductor nanophases could grow through vapor infiltration of a reactant or through changes in temperature. Synthetic routes of this type have been tried in laboratory scale and demonstrated to be feasible in principle. A possible technology to emerge from this would be composite structural coatings that can behave as solar cells and energy storage devices, an important technology for an aircraft that can orbit at 100,000 feet.

Superlattice Molecular Materials

A closely related concept to nanophased polymers and composites which is not equally recognized as a possible frontier for advanced materials, is that of superlattice materials. Such materials, fully organic, inorganic, or organic-inorganic composites would consist of molecular clusters a few nanometers in size that self organize into large superlattice arrays. An example of a superlattice molecular material is the colloidal array. Synthesis of highly charged, monodisperse colloidal arrays from monomeric precursors demonstrates self-assembly occurring during emulsion polymerization. Examples of organic and inorganic superlattices are already known but remain laboratory curiosities at the present time. Recent developments in thin-film assembly make possible preparation of superlattice molecular materials. Electrostatic self-assembly is a thin-film preparation procedure involving immersion of substrate into solutions containing charged materials. The simplicity and versatility of the electrostatic self-assembly technique allows for the preparation of new combinations of incompatible precursors. The resulting multilayer can be composed of any combination of polymers, inorganic colloids, small molecules, enzymes, and inorganic materials. If necessary, films prepared this way can be annealed to form robust films with light-emitting and electrical conducting properties. Sensor technologies could be impacted greatly by developments in the field of superlattice materials over the next few decades. The vision for the connection between superlattice materials and sensor technologies has two different directions. One relates to the potential ability of superlattices of nanostructures to bind agents from the environment, chemical or biological, with a high degree of specificity and in sufficient amounts to make detection possible. The other direction relates to the use of superlattices, organic or inorganic, as nanolithographic tools. This would impact on our ability to miniaturize complex electronic or future photonic devices to a size that makes them invisible.

Biomimetic Materials

Imitation of the synthesis and processing and properties of function-integrated materials found in biological systems comprises the field of biomimetics. Recent examples include biomineralization and spider silk. Biological composites such as bones and teeth consist of a polymeric matrix reinforced by an inorganic phase. Synthetic factors comprising biomineralization include strong binding by the organic matrix of the inorganic reagents, good solvation of the

inorganic reagents by the polymer and an ordered, regular polymer environment to induce nucleation. Inorganic crystal phases normally requiring high temperatures and pressures can be prepared at room temperature and atmospheric pressure by this method. Spider silks are prepared in nature by conversion of an aqueous protein precursor solution into an oriented fiber. Imitation of this process would require preparation of cloned silk protein prepared by bacteria and conversion of precursor into fibers. Highly tensile spider silk fibers will have applications as energy-absorbing materials. Also, knowledge of silk biosynthesis has application in the synthesis of oriented polymeric fibers.

Bacteriorhodopsin is a light-sensitive protein found in halophilic bacteria. It undergoes a photocycle similar to the photocycle found in vision. Bacteriorhodopsin has been processed into thin film form and optical device concept demonstrations have been performed including dynamic holography, spatial light modulator, second-order nonlinear optical material, artificial retina and optical data storage. The wavelength sensitivity of this material can be modified by preparing tailor-made bacteriorhodopsins by genetic engineering or chemical modification of the chromophore.

13.3 Conclusions and Recommendations

The field of function-integrated materials is key to materials-enabling technologies for the Air Force. The development of this field using molecularly designed nanostructures will require synthetic research aimed at finding molecular architectures that can form functional nanoparticles, both organic and inorganic. This will be important both for nanophased polymers but also in the search for superlattice materials. The mechanisms to facilitate scaleup of these new materials in order to characterize their properties will be a key element for success. The development of the area will also require finding synthetic methods for nanocomposites that accomplish molecular dispersion of polymers or organic molecules in metals, semiconductors, and ceramics.

14.0 Energy Generation and Storage

The Air Force has a continuing need for more efficient and system-compatible energy generation and storage devices. By far the most important energy generation devices used on aircraft are auxiliary power units (APUs), which are characterized by reasonable power densities (greater than 100 kW/kg) and moderate energy densities that are determined by the amount of fuel on board (typically greater than 70kW hr/kg for a three-hour flight). Although batteries with better performance characteristics are available (Table 14.1), we do not see any other technology replacing the APU or engine-driven electric generators for aircraft power, even in the "more-electric aircraft" (MEA) or the "all-electric aircraft" (AEA). The reason is simply that potentially competing technologies (e.g., batteries and supercapacitors) are so inferior in low-temperature start-up characteristics that we cannot envision technological advances over the next few decades that would change this conclusion. Instead, it appears that the rational approach to enhancing reliability for MEA or AEA is to employ redundant APUs.

Table 14.1 Specific Energy, Specific Power, and Cycling Characteristics of Potential Aircraft Power Systems

	Specific Energy (W·hr/kg)	Specific Power (W/kg) ¹	Cycle Life ^{**}
Supercapacitor	<10	<600	--
Li/Solid Polymer Electrolyte	250	100-400	<150
Ni/Hydrogen	65-80	600-900	30,000+
Ni/Metal Hydride	175	200-400	1000+
Ni/Cadmium	80-100	600-900	10,000+
Lead/Acid	30-50	600-900	30,000+
Flywheel	20 [@]	Very High [#]	•
APU	70 ^{\$}	>100	Very Large

(*) Typical values. (**) Cycle life decreases with increasing depth of discharge. (!) Highly dependent on design and on method of determination (pulse vs. steady-state). (@) Scales with

There are opportunities for impressive advances in airborne power generation for MEA/AEA applications that depend on advances in magnetic materials. These include development of superior soft magnetic materials possessing simultaneously high strength, high critical temperature and high magnetic strength, and low electrical loss for advanced motor and generators

directly integrated with small and large turbine engines for airborne power and self-starting aircraft, and advanced hard magnetic materials for bearing applications on these same systems.

Impressive improvements seem possible. Examples are twice the mechanical strength, and an order of magnitude lower electrical loss for soft magnetic materials for 550°C operating temperatures and an increase in operating temperature for hard magnetic materials from 300°C to 450°C, with extended life at these temperatures and a factor of two increase in energy product. In the long term, there are real possibilities for nano-structure or mesostructure technologies to provide superior advanced magnetic materials. Laminated solids would replace the present physical stack of laminations separated by a thin insulator in core materials for generators and motors. Near-term, diffusion bonding techniques for metal-to-metal and ceramic-to-ceramic interfaces would improve the stiffness and strength of core materials. We should note, however, that our conclusion with regard to the future of batteries in MEA and AEA applies strictly to the primary power source, and not to internal engine and APU start functions, or to power conditioning. Advanced batteries and supercapacitors will almost certainly be employed for these secondary functions, particularly as efforts are made to reduce the reliance of aircraft on ground support equipment. The state of development of advanced batteries and supercapacitors, and the likely courses of development of these technologies in the future, are reviewed later in this section.

Perhaps the greatest need in the Air Force for advanced energy storage is for spacecraft. Energy generation and storage is required for a wide variety of missions, ranging from low earth orbit (LEO), surveillance (optical, IR, and radar), information processing, asset mapping, directed energy weapon systems, geosynchronous communications and GPS. The power requirements range from a few kilowatts for passive systems to greater than 10 MW for directed energy systems, and include both continuous power and pulsed power. A number of energy generation and storage technologies are possible, including:

- Photovoltaics
- Thermionics
- Nuclear thermoelectrics
- Flywheels
- Tethers (a long wire cutting the Earth's magnetic field—used on the Navy's Transit satellite 20 years ago)
- Secondary batteries
- Supercapacitors
- Superconducting rings

Each of these technologies offers advantages and disadvantages which render them more or less appealing for specific applications. Several are summarized below.

The most commonly used technology is photovoltaic electricity generation with secondary battery storage. Photovoltaic conversion has been in use for more than 30 years and is likely to be the mainstay power source for the great majority of space systems for the next 50 years.

The current technology is based on silicon p-n junctions, in which primarily single-crystal materials are used. Because of electron-hole recombination, which is promoted by defects (grain boundaries, dislocations, impurities), the quantum efficiency is low (less than 15 percent in the laboratory, less than 10 percent in the field for polycrystalline materials), and slightly higher for single-crystal materials, which requires the use of excessively large solar arrays. Also, the cost of producing photovoltaic materials of optimum properties is very high, so that the cost per kilowatt of produced power is also high.

While photovoltaics will remain the mainstay of power generation in space systems over the next five decades, as noted above, we expect that significant advances might be made in photovoltaic materials that will result in higher conversion and lower fabrication cost, which will translate into higher energy densities and lower specific power cost. These anticipated developments include more extensive use of compound semiconductors with high conversion efficiencies. One way to enhance the performance of solar cells is by tuning the semiconductor band gap to match the solar spectrum. This increases the portion of the sun's energy that can be converted to electricity. There are many new single layer and multilayer compounds that have yet to be explored for designing new high efficiency solar cells.

As an example of the payoff in this area, multi-junction solar cells composed of GaInP/GaAs/Ge have demonstrated a record breaking conversion efficiency of 27 percent. The photoabsorption in the solar cell can also be enhanced by using textured surfaces and anti-reflection coatings. The textured surfaces are designed to increase the optical path length through thin semiconductor layers increasing the probability that all the incident photons will be absorbed. Silicon solar cells with these surface treatments have recently demonstrated conversion efficiencies of 24 percent.

Another means for higher efficiency is to discover semiconductor materials which generate more than one electron per photon, through hot electron or Auger generation processes. These types of materials are predicted to have conversion efficiencies approaching 50 percent.

In addition to conversion efficiency, an important property for solar cells in space applications is radiation resistance. In space, solar cells often experience high radiation environments, especially during solar flares. To provide longer lifetimes for spacecraft, materials must be selected which are less susceptible to damage by radiation, which degrades the power performance of the solar cell. The disadvantage of high-efficiency semiconductor solar cells is the cost per cell. However, this increased cost can be offset by the reduced launch costs associated with lighter weight arrays that require less stowage volume.

Synthesis of photo-stable, low cost, organic p-n junctions offers high payoff. Many conjugated organic systems (polyacetylene, polythiophene, polyaniline, and polyphenylene, to name a few) are already doped to produce p-type or n-type materials. Because these materials may be readily processed as thin films using inexpensive processing technologies, it is possible to envisage low-cost p-n junctions in the form of large-area thin films being fabricated. The major problems are that many of these polymers have poor photostabilities and exhibit low conversion efficiencies; however, it is fair to note that the efficiencies are no lower than they were for silicon-based materials at a comparable stage of development. The photostability problem may be difficult to solve, because the degradant is the hot hole, which is an entity formed within the

p-n junction on photoabsorption. For space applications, these materials need to be radiation resistant and thermally stable as well as photo-stable. It is clear that new materials, possibly doped conjugated inorganic systems, for example, $-(\text{SN})_x^-$, $-(\text{SiN})_x^-$, $-(\text{PN})_x^-$, should be explored, because the potential payoff is very high.

Synthesis of composite photovoltaic materials, in which an inorganic semiconductor is contained within a functional matrix also offers potentially high payoff. The matrix may be developed to enhance the conversion efficiency by converting the energy of hot electrons and holes that escape from the particle surfaces into thermal energy or it could be devised to screen the semiconductor from the more energetic photons in the spectrum.

In all of these technologies it is evident that computationally designed materials will play increasingly important roles. Thus we are now on the verge of being able to tailor the electronic properties of compound semiconductors by first-principle calculation (i.e., solving Schroedinger's equation). This capability will allow us to specify systems and compositions that more exactly meet our needs than is possible with current systems.

For LEO craft, the battery cycles between charge and discharge every 90 minutes, and must do so for at least 30,000 cycles corresponding to a life of five years. Currently, the only batteries that are capable of delivering this cycle life are nickel-hydrogen and advanced nickel-cadmium for small systems requiring less than 1.5 kW. In both cases, the cycle life is a function of temperature and of the depth of discharge, with cycle life decreasing as more energy is extracted from the battery per cycle. The degradation in cycle life results from restructuring of the nickel positive electrode, and it is irreversible. In order to achieve the desired cycle life, the depth of discharge must be limited to about 40 percent of the theoretical value. This means that a significant amount of inaccessible active mass must be carried into space. Given that the energy densities of these battery systems are already low (65-80 W-hr/kg), the inaccessible active mass (60 percent) further reduces the effective energy density (to 26-32 W-hr/kg) and hence reduces the balance of payload for the mission. To put the problem into perspective, consider a satellite that has a lower power storage requirement of 30 kW-hr. Because of the need for long cycle life, the effective capacity of the nickel-hydrogen battery is of the order of 28 W-hr/kg.

Battery and supercapacitor technology is rapidly evolving (Figure 14.1), with the developments being driven by the need for zero-emission automobiles. In the U.S., this effort is being supported by the U.S. Advanced Battery Consortium (ABC), a partnership between the DOE and the "Big Three" automobile manufacturers (GM, Ford, and Chrysler). The ABC has identified advanced lead-acid and nickel-cadmium as the near-term batteries, but both have energy densities impractically low (less than 100 W-hr/kg) for the MEA. The middle-term technology has been identified as nickel-metal hydride, which has demonstrated an energy density of about 175 W-hr/kg. This battery shows good cycling characteristics, but the potential for developing the energy density to 500 W-hr/kg seems small to nonexistent. The ABC has identified lithium/solid polymer electrolyte/intercalation cathode (Li/SPE/IC) batteries as the most promising long-term technology, and already batteries of this type have attained energy densities in excess of 250 W-hr/kg, with claims of energy densities as high as 400 W-hr/kg being made on occasion. However, these latter claims are almost certainly based on the masses of the active material alone and do not take into account packaging. In any event, on the basis of specific energy the

Li/SPE/IC systems appear to be promising long-term candidates for back-up power sources for the MEA.

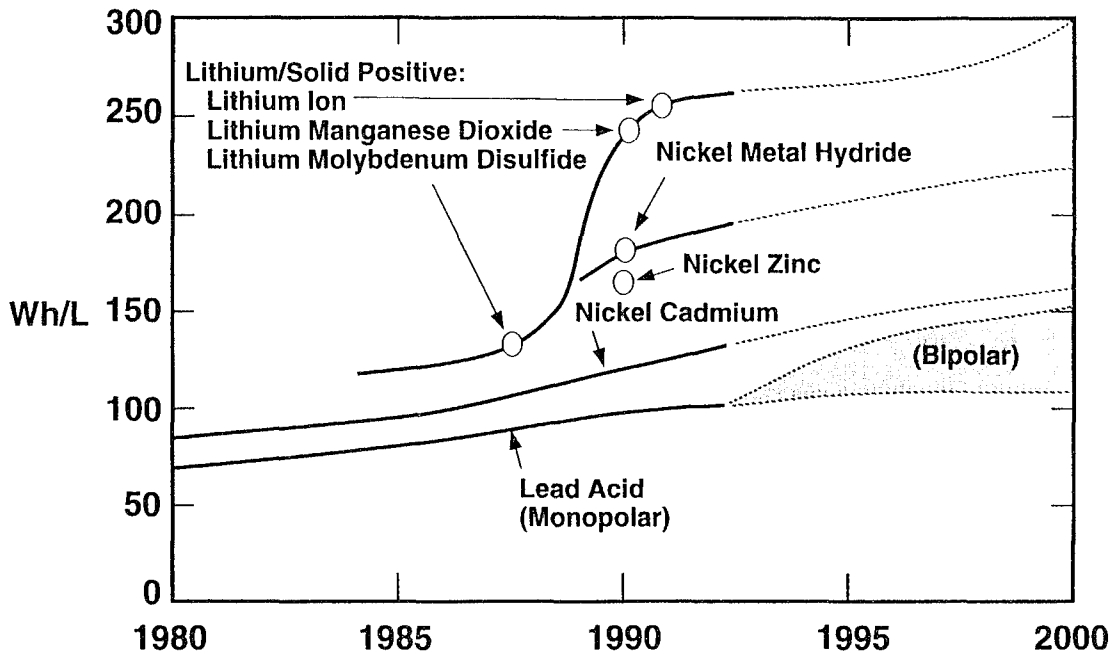


Figure 14.1 Battery and Supercapacitor Technology Trends: 1980-2000

While the energy densities of the Li/SPE/IC systems appear attractive, they generally have low power densities and poor cycling characteristics. The latter problem arises from the fact that the lithium metal anode does not cycle well, and test cells have managed to achieve cycle lives of only about 100 cycles before failure. However, it is fair to note that cycle life as a characteristic is generally developed late in the overall development of a battery, so that we might reasonably look towards a life in excess of 1000 cycles within the next few decades. One approach to enhancing the cycle life has been to use a Li-C intercalation anode. Because the maximum loading of the carbon corresponds to LiC_6 (i.e. 3 gm of lithium to 72 gm of carbon), this approach significantly degrades the energy density of the battery. So far, a Li/SPE/IC battery having high energy density, high power density, and a long cycle life, the combination of requirements for the BUPS for a MEA, has not been developed. Furthermore, the prospects that such a battery will be developed within the next two decades are small. This option must be viewed only as long-term for an MEA main power source battery.

With regards to supercapacitors, the ABC middle-term goals for specific power and specific energy are greater than 500 W/kg and greater than 5 W-hr/kg respectively. The ABC long-term goals—greater than 20 years—for these parameters are greater than 1600 W/kg and greater than 15 W-hr/kg. The prospects for achieving these latter goals in the near term are good, and at least one laboratory claims to have exceeded these performance characteristics. A specific power of 1600 W/kg implies a capacitor bank of a little over 300 kg to meet the power requirement of 500 kW, so that the weight of the battery is 1070 kg (236 pounds). If, on the other hand, the

nickel-hydrogen battery could be discharged to 100 percent of theoretical capacity and still retain the cycle life, the weight of the battery becomes 430 kg (940 pounds). Assuming a launch cost of \$10,000 per pound, the additional inactive battery weight costs \$14M. Thus, a huge penalty is paid per launch to ensure adequate cycle life.

The cycle life is the Achilles' heel of many secondary battery systems, and the cycle life requirement of 30,000 cycles for a LEO satellite can be met only by nickel-hydrogen, advanced nickel-cadmium, and possibly lead-acid. Before progressing with this discussion it is worth examining why electrode degradation occurs.

Charge storage in secondary batteries occurs via reversible charge transfer reactions that result in the formation and annihilation of chemical species. Some of these reactions are dissolution processes (e.g., on discharge of a cadmium electrode in a nickel-cadmium battery) in which case restructuring of the active mass occurs on recharge deposition and subsequent cycling. Other species are solids, $\text{Ni}(\text{OH})_2$ and NiOOH as in alkaline nickel electrodes, and each of the solids has a different molar volume. Charge cycling generates cyclic stresses, which gradually fracture the active mass and hence disrupt the transfer of electrons and ions through the electrode structure. Unfortunately, this process is irreversible so that when the capacity is reduced below a tolerable level, the battery must be discarded. Electrode degradation is the principal problem facing developers of advanced Li/SPE/IC batteries.

Superconducting Rings

Superconducting rings provide an intriguing concept for energy storage, and this technology is now being commercialized for use as a standby power source. Both conventional (niobium-based) and high-temperature (oxide-based) superconductors have been used or proposed. However, the energy density is low and it appears that this technology is not suitable for flight operations unless other parts of the system are also operated at cryogenic temperatures.

Flywheels

Flywheels are an attractive mechanical energy storage technology actively being developed for zero-emission automobiles. Flywheel systems are now being considered for space systems. Although the energy density is low for rotating disks in the 200 pound class (approximately 20 Whr/kg), when compared with batteries (Table 14.1), the energy density squares with the mass so that a ten-fold increase in the mass of a disk rotating at the same angular velocity would result in a one hundred-fold increase in the energy density. Thus, large flywheels become very attractive as high energy density power sources, because energy densities in excess of 1 kW-hr/kg can be envisioned. Other advantages of flywheels include:

- An effectively infinite life
- Low losses with ultralow-friction (magnetic) bearings
- Very high specific power that is determined only by the ability of the generator to extract energy from the system.

However, flywheels generate considerable gyroscopic forces that need to be recognized when designing the flight system. Another problem is that flywheels still have too great a "self-discharge" rate. The important materials issue is to devise materials that have high densities and are able to withstand very high centrifugal stresses. Composite materials are promising in this regard.

Nuclear Systems

Nuclear thermoelectric and thermionic power sources have been employed on spacecraft, although the reluctance on the part of designers and the public to accept nuclear power, even in the form of isotope heating, has severely limited these systems. While the conversion efficiencies are low (approximately 6 percent for thermoelectrics and approximately 20 percent for advanced thermionics), the energy and power densities of the sources can be very high, and hence they are attractive on purely technical grounds. The materials issue with these systems is enhancement of the conversion efficiency. The general opinion is that both the thermoelectric conversion efficiency and the thermionic conversion efficiency will continue to improve, but that no spectacular improvements are on the horizon.

Tethers

A tether is a long wire, attached to a satellite, that produces power by induction from the earth's magnetic field. This system is flight proven (on the Navy's Transit satellite), and it works well. However, its low energy density and low power density are not suitable for most space power applications. One interesting problem is that as energy is extracted from the earth's magnetic field, the satellite slows down. To compensate, it is necessary to provide periodic boosts using conventional rockets. Accordingly, the weight of the rocket must be included in any energy density or power density calculations.

Fuel Cells

Fuel cells are electrochemical devices that continuously convert chemical energy directly into electrical energy, so that in many respects they share features with batteries. However, unlike secondary batteries, fuel cells are not electrically recharged and hence they do not cycle in the conventional sense. Because they are continuous energy converters, the effective energy density is determined by the relative masses of the converter (the cell) and the fuel and oxidant. As the relative mass of the latter increases, the energy density of the system becomes increasingly determined by the energy density of the fuel and oxidant, multiplied by the conversion efficiency.

A most attractive feature of a fuel cell is that the efficiency is not determined by Carnot's theorem, which applies to heat engines. In the case of fuel cells, the efficiency, ϵ , is given by:

$$\epsilon = \Delta G / \Delta H = 1 - T(\Delta S / \Delta H)$$

where ΔG , ΔH , ΔS and T are the changes in Gibbs energy, enthalpy, and entropy of the cell reaction, and the Kelvin temperature, respectively. Typically, for a H_2/O_2 fuel cell, the efficiency is approximately 0.65 compared with about 0.3 for an internal combustion engine. Practical efficiencies of 0.5 have been achieved in phosphoric acid cells and in polymer exchange membrane cells of the type used in the Gemini and Apollo programs. Note that if S/H is negative, the

efficiency can exceed unity. In this case, heat is transferred into the cell from the surroundings in response to the positive change in entropy of the reaction. We know of no practical cell where this is observed.

Fuel cells are used extensively on manned spacecraft, and have been the primary power source for all spacecraft since Gemini. These cells are of the proton exchange membrane type and employ hydrogen as the fuel and pure oxygen as the oxidant. This is a well-established technology, and it works well in spacecraft because of the low sensitivity to cost compared with other applications, such as automobiles. Even so, the cost is high—greater than \$50,000/kW—which can be traced to the need to use noble metal catalysts at high loadings, the high cost of the membrane, and the low volume of production. However, there are other potential applications of interest to the AF. These include standby power, power for supporting ground-based facilities such as radars, and as ground power for servicing aircraft. The advantages of ambient temperature fuel-cells for these applications is that they are silent and have very low IR signatures. However, they become even more attractive if they can employ a liquid fuel, rather than gaseous hydrogen, and air as the oxidant. Again, this technology is highly developed in that systems are available commercially that produce hydrogen fuel for the cell by reforming hydrocarbons or partially oxygenated fuels, such as methanol. However, the reformer is a high temperature system that emits IR radiation as well as CO, CO₂, and low levels of NO_x. What is needed is an ambient temperature fuel cell that employs a liquid fuel directly without the need to reform.

Direct oxidation of methanol in fuel cells is being actively explored by DOE and by various companies, mostly with DOE funding. To date, these efforts have met with only very limited success, with the principal impediment being the lack of a good electrocatalyst for the anode (fuel electrode). The conventional noble-metal catalysts cannot support high enough current densities at sufficiently low overpotentials to yield useful powers.

One approach is to increase the temperature, but this can be done only at the loss of LO. In the case of PEM cells, electrolyte dehydration limits the cell temperature to 80 - 100°C, which is too low to yield useful power using currently available electrocatalysts. What is needed is a revolution in electrocatalysis to produce materials upon which the oxidation of methanol or liquid hydrocarbons is fast. Various materials, such as tungsten bronzes, and activated carbons, are being explored, but to date little success has been achieved. While the Air Force may choose not to directly invest in this effort, it should keep abreast of developments because of the potentially high payoff.

One solution to this problem might be to use a highly soluble, easily oxidized organic fuel, such as sugar, in conjunction with a suitable enzyme (adenosine tri-phosphate) as the catalyst. This cell would emulate, in a simple way, the utilization of sugars by higher organisms and hence represents a biologically inspired system.

Appendix A

Panel Charter

The mission of the Materials Panel is to identify key materials technologies that will have a profound impact on Air Force operations and systems into the first several decades of the 21st century. The panel will focus on identifying and quantifying the payoff to the Air Force in terms of advanced capabilities, reliability, supportability, disposability, and affordability of future Air Force Systems.

Appendix B

Panel Members and Affiliations

SAB Members

Professor Digby Macdonald ,Chairman
The Pennsylvania State University

Dr. Robert Hughes
Bechtel Environmental, Ins.

Ad Hoc Advisors

Professor R. Judd Diefendorf
Clemson University

Professor Hamish Fraser
The Ohio State University

Dr. Robert Schmitt
SRI International

Professor Samuel Stupp
University of Illinois, Urbana Champaign

Government Participants

Mr. Tobey Cordell
Wright Laboratory

Dr. Douglas Dudis
Wright Laboratory

Executive Officers

Major Robert Frigo
Wright Laboratory

Major D. Mark Husband
Wright Laboratory

Major Michael Reagan
USAF Scientific Advisory Board

Technical Editor

2Lt Douglas Vander Kooi
George Washington University

Appendix C

Panel Meeting Locations

Date	Location	Organizations Represented
6-7 April 95	Wright-Patterson AFB, OH	Materials Directorate, Wright Lab
2 May 95	Marietta, GA	Lockheed Aeronautical Systems Company
3-5 May 95	Maxwell AFB, AL	USAF Scientific Advisory Board Spring General Membership Meeting
8 June 95	West Palm Beach, FL	Pratt and Whitney Company
22-23 June 95	Washington DC	Air Force Office of Scientific Research Office of Naval Research Naval Research Laboratory Advanced Research Projects Agency Central Intelligence Agency
29-30 June	Wright-Patterson AFB, OH	Propulsion Directorate Materials Directorate
6-7 July	Palo Alto, CA	SRI International Propulsion Directorate, Phillips Lab Thiokol Aerojet Crystallume Chemical Systems Division Lockheed Palo Alto Research Lab ARACOR

Appendix D

List of Acronyms

Acronym	Definition
ABC	Advanced Battery Consortium
ADN	ammonium dinitramide
AEA	all-electric aircraft, All Electric Aircraft program
AFOSR	Air Force Office of Scientific Research
AIAA	American Institute of Aeronautics and Astronautics
AMRAAM	Advanced Medium Range Air to Air Missile
AN	ammonium nitrate
APU	auxiliary power unit
ARPA	Advanced Research Projects Agency
ASIP	Airframe Structural Integrity Program
BMDO	Ballistic Missile Defense Organization
BUPS	back-up power source
CAT	computer-aided tomography
CBM	condition-based maintenance
CBW	chemical and biological weapons
CCD	charge-coupled device
CFD	computational fluid dynamics
CL-20	a propellant/explosive oxidizer
CMC	ceramic matrix composites
CTE	coefficient of thermal expansion
CVD	chemical vapor deposition
DFA	damage function analysis
DFE	design for environment
DoD	Department of Defense
DOE	Department of Energy
DTA	damage tolerance analysis
EMI	electromagnetic interference

EPA	Environmental Protection Agency
FMS	foreign military sales
FSU	former Soviet Union
GOX	gaseous oxygen
GPS	global positioning system
GSO	geosynchronous orbit
HAP	hazardous air pollutants
HEDM	high energy density matter, High Energy Density Materials program
HEMT	high electron mobility transistors
HMX	high melting explosive
HPT	high-pressure turbine
HSCT	high speed civil transport
HUD	heads-up display
HYTECH	Hypersonic Technology program
Isp	specific impulse
ICE	internal combustion engine
IHRPT	Integrated High Payoff Rocket Propulsion Technology program
IHPTE	Integrated High Performance Turbine Engine Technology program
IM	insensitive munitions
IR	infrared
IRNFA	an oxidizer
LCA	life-cycle analysis, life-cycle assessment
LEO	low earth orbit
LO	low observability, low observable
LOX	liquid oxygen
LPT	low-pressure turbine
MBE	molecular beam epitaxy
MEA	more-electric aircraft, More Electric Aircraft program
MEMS	microelectromechanical system
MEMS	micro-electronic machine system
MIC	metastable interstitial composite

MICOM	Army Missile Command
MMC	metal matrix composites
MMH	monomethyl hydrazine
MOU	memorandum of understanding
NASP	National Aerospace Plane Program
NDE/I	nondestructive evaluation/inspection
NIST	National Institute of Standards and Technology
NLO	non-linear optics
NMEL	New Materials Exploration Loop
NSF	National Science Foundation
NWV	New World Vistas
O&M	operations and maintenance
ODC	ozone-depleting chemicals
OMC	organic matrix composites
ONR	Office of Naval Research
PDLC	polymer dispersed liquid crystal
PDM	programmed depot maintenance
PEM	proton exchange membrane
PSAN	phase stabilized ammonium nitrate
QPA	qualitative process algorithm
R&D	research and development
REFTECH	refurbishment technology
RF	radio frequency
RFC	retirement for cause
RLV	reusable launch vehicle
SAB	Scientific Advisory Board
SCFN	spherical convergent flap nozzle
SERDP	Strategic Environmental Research and Development Program
SETAC	Society of Environmental Toxicology and Chemistry
SFC	specific fuel consumption
SOA	state-of-the-art

SPE	solid polymer electrolyte
SQUID	super conducting interference device
SSTO	single stage to orbit
T ₃	compressor discharge temperature
T ₄₁	high pressure turbine inlet temperature
TEX	an oxidizer
TNAZ	trinitro-azetidine
TOGW	take-off gross weight
TPE	thermoplastic elastomers
UDMH	unsymmetrical dimethyl hydrazine
USAF	United States Air Force
UV	ultraviolet
VOC	volatile organic compound