A Survey of Emerging Materials for Revolutionary Aerospace Vehicle Structures and Propulsion Systems

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Abstract

The NASA Strategic Plan identifies the long-term goal of providing safe and affordable space access, orbital transfer, and interplanetary transportation capabilities to enable scientific research, human and robotic exploration, and the commercial development of space. Numerous scientific and engineering breakthroughs will be required to develop the technology required to achieve this goal. Critical technologies include advanced vehicle primary and secondary structure, radiation protection, propulsion and power systems, fuel storage, electronics and devices, sensors and science instruments, and medical diagnostics and treatment. Advanced materials with revolutionary new capabilities are an essential element of each of these technologies. A survey of emerging materials with applications to aerospace vehicle structures and propulsion systems was conducted to assist in long-term agency mission planning. The comprehensive survey identified materials already under development that could be available in 5 to 10 years and those that are still in the early research phase and may not be available for another 20 to 30 years. The survey includes typical properties, a description of the material and processing methods, the current development status, and the critical issues that must be overcome to achieve commercial viability.

Key Words

aerospace, structure, propulsion, electronics, radiation, thermal protection systems, materials, metals, intermetallics, polymers, ceramics, carbon nanotubes, composites
Introduction

The mission of NASA is to advance and communicate scientific knowledge and understanding of Earth, the solar system, and the universe; to advance human exploration, use, and development of space; and to research, develop, verify, and transfer advanced aeronautics, space, and related technologies. To fulfill this bold mission, NASA has adopted the following long-term goals:

- create a virtual presence throughout our solar system and probe deeper into the mysteries of the universe and life on Earth and beyond,
- use our understanding of nature’s processes in space to support research endeavors in space and on Earth,
- conduct human and robotic missions to planets and other bodies in our solar system to enable human expansion,
- provide safe and affordable space access, orbital transfer, and interplanetary transportation capabilities to enable research, human exploration, and the commercial development of space, and
- to develop cutting-edge aeronautics and space systems technologies to support highway in the sky, smart aircraft, and revolutionary space vehicles.

Perhaps the most challenging of the above goals is human exploration of space beyond low Earth orbit. There are formidable barriers that are currently limiting human presence in space including technology deficiencies and mission affordability. Numerous scientific and engineering breakthroughs will be required to develop the technologies necessary to overcome these barriers. Critical technologies include lightweight vehicle primary structure and durable materials for thermal protection systems, effective radiation protection for long-duration missions, advanced propulsion and power systems, electronics, sensors and science instruments, and in-space health diagnostics and medical treatment. New materials with revolutionary capabilities are an essential element in each of these critical technologies.

A survey of emerging materials with applications to aerospace vehicle structures and propulsion systems was conducted. The purpose of the survey was to assist in long-term agency mission planning and to provide guidance in developing an appropriate research investment strategy. The comprehensive survey identified materials already under development that could be available in 5 to 10 years as well as those that are still in the early research phase and may not be available for another 20 to 30 years. The guiding philosophy of the survey was to identify materials that may offer dramatic improvements in properties. Implicit in this philosophy is an optimistic view of the best case properties and a successful resolution of the critical technical issues.

This report documents the findings of the survey. For each of the twenty-three advanced materials and eight reference materials included in the survey, typical properties are tabulated along with a description of the material and processing methods, the current development status, and the critical issues that must be overcome to achieve commercial viability. The report is organized by applications to aerospace vehicle structures and propulsion system components. The report also presents the results of several systems analysis studies that highlight the enormous potential of one revolutionary new material, carbon nanotubes. The report concludes...
with two appendices that provide a detailed description of each material and its current developmental status.

**The Format of the Survey**

The survey of emerging materials was originally conducted to assist in long-term agency mission planning and to provide guidance in developing an appropriate research investment strategy. The guiding philosophy of the survey was to identify materials that may offer dramatic improvements in properties. The survey was organized by applications (vehicle structure and propulsion system), fundamental material systems (metals, ceramics, polymers, and their composites), and estimated time to maturity (near-term, intermediate-term, and far-term). Specific properties for each material are tabulated using a standard set of properties. The appendices provide a complete description of each material, the processing method(s), current state of development, and the critical issues that must be resolved for the material to become viable for aerospace applications.

A standard set of properties is reported for each material. These specific properties were selected for comparison purposes only. It is recognized that many other properties not reported such as compression modulus and strength, fatigue, creep, and fracture toughness may represent design constraints for specific components of aerospace vehicle systems. The ground rule for including a material in the survey was that actual properties of the material have been measured and reported. The decision was made to report properties of a specific material (composition and processing method) rather than broad ranges of properties for a material system. The organizing philosophy is that properties of an actual existing material gives greater credibility to the survey with regard to supporting future mission planning. Implicit in this philosophy is an optimistic view of the best case properties and a successful resolution of the critical technical issues.

Since NASA missions are being planned over a long time horizon, the survey included materials that may mature in the near term (5-10 years), intermediate-term (10-20 years), as well as recently discovered materials still in the early stages of exploratory research. These newly discovered materials will require breakthroughs in processing methods and may take 20-30 years to become fully mature for aerospace vehicle applications. The attribute “manufacturability” was selected as a measure of the current state of development (maturity) of each material system. The NASA technology readiness level (TRL) scale was selected as a quantitative measure of manufacturability. The NASA TRL scale, see Table 1, ranges from 1 to 9, with 1 representing the early stages of research and 9 representing proven maturity for aerospace applications. From a NASA programmatic point of view, TRL 1-3 represents research, TRL 3-5 represents focused technology development, 5-7 represents advanced technology development, and TRL 7-9 represents advanced prototype systems development and demonstration in flight conditions.

**Materials for Aerospace Vehicle Structure**

One of NASA’s most important goals is to reduce the cost of access to space by a factor of 10 in the near-term and a factor of 100 in the far-term. This challenging goal can only be met
by developing a reusable launch vehicle that can perform many missions much like today’s commercial and military aircraft. Concepts for second and third generation reusable launch vehicles (RLV), illustrated in Figure 1, are currently under development. (The NASA Space Shuttle is considered to be the first generation reusable launch vehicle.) These future launch vehicles are not achievable without dramatic breakthroughs in the properties of structural materials. With the technology challenges of an RLV in mind, properties of advanced metallic and non-metallic material systems were surveyed. Representative properties of metals and metal matrix composites (MMC) are tabulated in Table 2 [1-7]. Aluminum 2219-T87, which is used extensively in current aerospace vehicle structures, was selected as a reference material for comparison purposes. Properties of carbon-based materials and polymer matrix composites are tabulated in Table 3 [8-18]. Aluminum 2219-T87, several carbon fibers (M46J and IM7), and a carbon fiber reinforced polymer (CFRP) composite used in a NASA spacecraft (M46J/7714A) were selected as reference materials. All materials tabulated in Tables 2 and 3 are described in Appendix I. The specific modulus and specific strength of the materials in Tables 2 and 3 are also plotted in Figure 2. (Please note that the data in Figure 2 are plotted on a log-log scale.) As is readily apparent in Figure 2, dramatic improvements in properties are potentially achievable if the identified materials can be developed to commercial viability. For example, in the next 5 to 10 years, polymer matrix composites such as the IM7/8552 material system are expected to become mature for numerous aerospace primary structure applications. The key to achieving this potential will be the combination of compelling technology pulls and the associated resource investments. In the long-term, single crystal, single wall carbon nanotubes (SWNT), open symbol in Figure 2, and polymer matrix and aluminum matrix composites reinforced with SWNT (NtFRP and Nt/Al, respectively) offer orders of magnitude improvements over aluminum 2219-T87. However, the technology readiness level (TRL) of these materials systems is quite low, estimated to be at 1 on the NASA TRL scale, and breakthroughs in production and scale-up methods will be necessary. Nonetheless, the enormous potential of nanostructured materials is extremely attractive.

An emerging application for advanced high-temperature metallic alloys is the thermal protection system (metallic TPS) of reusable launch vehicles (RLV). Metallic TPS represents an attractive alternative to the rigid ceramic tile material systems currently used as the TPS for the space shuttle orbiter and other atmospheric entry spacecraft. Lee-side metallic TPS will not need coating for 1000°F operation. Also, metallic TPS typically will not require high temperature seals or adhesive development. From an operational point of view, metallic TPS is a particularly attractive way to significantly reducing operational costs of an RLV. Metallic TPS are inherently all weather, durable, and impact resistant. Unlike ceramic TPS tile systems, metallic TPS will not require waterproofing or other restorative processing operations between flights and may be removed for subsurface inspection, thereby minimizing ground handling. Finally, metallic TPS are applicable to all vehicles and have the potential to save considerable vehicle weight, especially when used as part of an integrated aeroshell structural system.

Metallic TPS development requirements encompasses alloys for up to 1800 °F operation including Ni, Fe, and Cr based alloys and intermetallics for 2000 °F + operation including Be, Ti and Ni based systems. Alloy development also includes ultra low density metallics such as porous materials, metallic foams, and nanostructured alloys. Properties of selected materials are included in Table 2. Process development requirements are needed for functionally graded
(materials with spatially-varying and direction-dependent properties) and hybrid material systems and innovative process methods for sheet and foil product forms including direct cast, spray deposition, and laser sintering. Requirements for surface modifications include functionally graded layers and nano-laminates for aeroshells, and environmentally compliant surfaces and/or coatings. Concept and design development requirements are leading to integrated thermal/mechanical/insulation substructures for aeroshells and integrated cryotank/substructure/TPS/aeroshells. The critical technical issues include process and production scale-up methods for flight hardware and optimized durability and damage tolerance attributes.

Materials for Propulsion Systems Components

Second and third generation propulsion system concepts under development for reusable launch vehicles (RLV) are illustrated in Figure 3. Properties of advanced metallic and non-metallic material systems were surveyed. Representative properties of metals and metal matrix composites are tabulated in Table 4 [19-20]. Inconel 718 is used as the reference material for comparison purposes. Properties of ceramics, ceramic matrix composites and carbon fiber reinforced polymer matrix composites (CFRP) are tabulated in Table 5 [21-29]. Inconel 718 and the Nextel N720 ceramic fiber were selected as the reference materials. All materials tabulated in Tables 4 and 5 are described in Appendix II. The specific modulus and specific strength of the materials in Tables 4 and 5 are also plotted in Figure 4 relative to their use temperature. As illustrated in Figure 4, dramatic improvements in use temperature and modest improvements in strength and modulus are potentially achievable if the identified materials can be developed to commercial viability. For example, in the next 5 to 10 years, intermetallics and advanced nickel-based metallic alloys look very promising. In the long-term, ceramic matrix composites and nanostructured metals offer significant property improvements over the current baseline materials. However, the technology readiness level (TRL) of these materials systems is quite low, estimated to be at 1 to 3 with some limited demonstrations in the 4 to 5 range on the NASA scale from 1 to 9, and breakthroughs in production and scale-up methods will be necessary. For many applications, long-life protective coatings will also be required in order to meet the demanding propulsion operational requirements.

Case Study: The Potential Benefits of Structural Materials Derived from Carbon Nanotubes

The general field of nano-science and technology offers the potential to be the next great technological revolution. Of particular interest to NASA is the confluence of the three great megatrends, information technology, biotechnology, and nanotechnology, as illustrated notionally in Figure 5. In the field of materials science, we may see a paradigm shift from the traditional materials role of developing metals, polymers, ceramics, and composites to a revolutionary role of developing nanostructured, functionalized, self-assembling, and self-healing materials. Looking into the future, the theoretical potential of these revolutionary classes of new materials will create breakthroughs that will enable technology developments that are barely imaginable today. In the aerospace field, these new technologies may make space travel routine and enable human exploration of space beyond our current practical limitation of low
Earth orbit. Imagine the possibilities if there was a material to replace aluminum that is an order of magnitude stiffer and two orders of magnitude stronger! Dramatic breakthroughs in manipulating matter will be required to develop this technology. Perhaps the most exciting outcome will be the realization of self-assembling, self-repairing, adaptive, intelligent, multifunctional materials. The key to realizing this dream may be the development of the molecular assemblers, perhaps approaching the versatility of the DNA molecule, so that matter may be manipulated an atom at a time.

Material systems based on carbon nanotubes are a particularly attractive new class of materials. Carbon nanotubes are cylindrical molecules composed of carbon atoms in a regular hexagonal arrangement, closed on both ends by hemispherical endcaps, as shown in the insert in Figure 5. On the basis of computer simulations and limited actual experimental data [30-45], some specific forms of carbon nanotubes appear to possess extraordinary mechanical, thermal, and electrical properties, see Tables 6 and 7. If the properties of carbon nanotubes observed at the molecular level can be translated into useful macro-scale materials, the potential benefits to the aerospace industry include applications to vehicle structures, propulsion systems, thermal management, energy storage, electronic and computing, sensors and devices, and biological and medical. Systems analysis studies [46] were conducted to quantify some of these benefits in specific applications of interest to NASA. The results of those studies are summarized below.

**Properties of carbon nanotubes and composites used in the systems analysis models**

Computer simulation results and limited experimental studies show that small diameter, single-walled carbon nanotubes may possess elastic moduli in excess of 1 TPa, and strengths approaching 200 GPa. If small diameter, single-walled tubes can be produced in large quantities, and incorporated into a supporting matrix to form structural materials, the resulting structures could be significantly lighter and stronger than current aluminum alloys and carbon fiber reinforced polymer (CFRP) composites used in conventional aerospace structures. As tabulated in Tables 6a and 6b and Table 7, the properties of single-wall carbon nanotubes (SWNT) and multi-wall carbon nanotubes (MWNT) reported in the literature [30-45] exhibit quite a range in values. The properties of SWNT (from Table 3) used in the systems analysis studies reported herein are as follows:

- **Tensile Modulus**: 1200 GPa
- **Tensile Strength**: 6 GPa in a composite
- **Elongation**: 1% in a composite
- **Density**: 1.20 g/cm³

These properties were selected because they are typical of the theoretical and experimental values reported in the literature without overstating the expectations.

The specific modulus and specific strength of several aerospace materials currently used in structural components of aerospace vehicles are plotted in Figure 2. The CFRP Composite is a high modulus, high strength fiber in a toughened polymer matrix with a quasi-isotropic laminate stacking sequence and a 60% fiber volume fraction. (See Appendix I for a detailed
description of the materials plotted in Figure 2.) Theoretical properties of the carbon nanotube fiber reinforced polymer (NtFRP Composite) were calculated using standard micromechanics equations. The NtFRP is assumed to be the same laminate as the CFRP and the strength was limited to 2.5 GPa (1% strain) to reflect current structures design practices, as tabulated in Table 3. The single crystal bulk material (SWNT) plotted in Figure 2 represents the theoretical potential of nanostructure carbon and will require several breakthroughs in nanotube production to achieve. This highly perfect, single crystal, bulk material, not requiring a matrix binder, is viewed as theoretically possible. As is evident from Figure 2, the polymer composite reinforced with nanotubes offers a significant advantage over conventional aluminum and carbon fiber reinforced polymer composites.

**Benefits to Aerospace Structure Quantified by Systems Analysis Studies**

The theoretical properties of the nanotube reinforced composite (NtFRP) were used in a simple, systems analysis model [46] of a reusable launch vehicle shown in Figure 6. The computed vehicle dry weight results are shown in the accompanying bar chart in Figure 6. Two cases were analyzed to show the benefit of substituting aluminum with CFRP (case 1) and with NtFRP (case 2). Dramatic reductions in weight were achieved in both cases. The results shown assume that the wings, body, and cryogenic propellant tanks are replaced with CFRP composites (case 1) and with NtFRP composites (case 2). Simplifying assumptions were made regarding design issues such as the amount of minimum gage structure and applications of stiffness versus strength critical design criteria. While these assumptions can be varied, the results plotted in Figure 6 were based on 0% minimum gage, 50% of the structure is strength critical and 50% is stiffness critical. Because of the dramatic reduction in structural weight due to the lighter materials, the vehicle can be resized resulting in even greater reductions in the vehicle dry weight. (These projected weight savings do not consider materials substitutions for other components such as the engines, thermal protection system, or subsystems.)

An aircraft engine application was also analyzed [46]. A typical gas turbine engine for a 300 passenger aircraft, shown schematically in Figure 7, was selected as the current baseline for the analysis. As the accompanying bar chart shows, significant weight reductions are potentially achievable with nanostructured materials. The low temperature applications were based on the use of NtFRP composites for the nacelle, fan, low-pressure compressor components (blades, stator vanes, case, and ducts), and the bypass ducts. The high temperature applications were based on the use of boron-nitride nanotube reinforced silicon carbide ceramic matrix composites for the high-pressure compressor, combustor, turbine components (blades, stator vanes, case, and ducts), and the nozzles. While theoretically possible, boron-nitride nanotubes have not been produced and properties are not available in the literature. Therefore, the boron-nitride nanotube reinforced silicon carbide ceramic matrix composite system was not included in the materials survey. However, properties were estimated so that the potential benefit due to revolutionary improvements of high temperature materials could be illustrated. The properties were estimated to be 3.6 GPa tensile strength, 535 GPa tensile modulus, and 3.70 g/cm³ density based on the known properties of boron and silicon carbide. Referring to the results plotted in the bar chart in Figure 7, the potential benefits in engine applications due to carbon nanotubes is somewhat modest due to their use in the low temperature range. However, the benefits that may be
achieved by both carbon nanotubes in lower temperature applications and boron-nitride and silicon carbide nanotubes in high temperature applications are very significant.

Significant weight savings benefits may also be achieved by designing spacecraft using NtFRP composites. The Mars Global Surveyor (MGS) was selected for illustrative purposes because a systems analysis model [46] already existed. The MGS spacecraft is shown in Figure 8. The baseline materials used in the structure and propulsion system were selected for substitution by NtFRP. These components comprise about 40% of the gross weight of the baseline spacecraft. The systems analysis results for the gross weight of the spacecraft is compared in the bar chart in Figure 8. The bar labeled MGS is the baseline weight for the actual MGS spacecraft. The bar labeled NtFRP Structures is the result of the materials substitution and resizing the spacecraft, but retaining the same science instruments. The predicted reduction in structural weight is about 50% while the gross weight savings potential of the spacecraft is still a significant 20%.

Observations

The above results focus primarily on the role of carbon nanotubes in reducing structural weight. While these results are very dramatic, they only touch on the potential of nanotechnology to revolutionize aerospace vehicles and spacecraft. The breakthroughs that are conceptualized by the “nanotechnologists” will enable future NASA missions now currently inconceivable. These future missions may only be achieved by micro/nano-miniaturization of all subsystems. Materials need to be developed that are functionalized to optimized desired mechanical, electrical, thermal, magnetic, or optical properties. The development and optimization of multifunctional materials and structures need to be perfected through nanoscale fabrication technologies. Self-diagnostic and self-repairing materials are essential for long duration space missions.

Summary and Conclusions

Numerous scientific and engineering breakthroughs will be required to develop the technology required to achieve NASA’s long-term goals. Critical technologies include advanced vehicle primary and secondary structure, radiation protection, propulsion and power systems, fuel storage, electronics and devices, sensors and science instruments, and medical diagnostics and treatment. Advanced materials with revolutionary new capabilities are an essential element of each of these technologies. Numerous advanced materials have been identified for applications to aerospace vehicle structures and propulsion system components. Many of these materials could be available in 5 to 10 years but others are still in the early research phase and may not be available for another 20 to 30 years. Twenty-three advanced materials were included in the survey along with typical properties, a description of the material and processing methods, the current development status, and the critical issues that must be overcome to achieve commercial viability.
The key findings in the survey are as follows:

1. In the near-term, numerous advanced materials exist that have attractive properties and can mature to a TRL of 6+ within 5 to 10 years or less, but only with a compelling technology pull and the associated resource investment.

2. In the far-term, biomimetic, nanostructured materials, especially carbon nanotubes, are attractive for many application but dramatic breakthroughs will be required to realize the potential of the materials systems within the next 10-20 years.

3. Structural materials for vehicles: a factor of 2 gain in weight savings can be achieved by carbon fiber reinforced polymers, metal matrix composites, and intermetallics; carbon nanotube reinforced polymers (and metals) may offer a factor of 10 gain in weight savings.

4. Structural materials for propulsion components: ceramics offer modest increases in use temperature and significant weight savings over metallic or refractory metal alloys; advanced metallic alloys and intermetallics may offer a factor of 2 gain in weight savings but only modest temperature improvements; polymer matrix composites, including carbon nanotubes, may offer significant weight savings.

In conclusion, a cautionary note is advisable. It is frequently true that a new material looks the most attractive when you first see the properties! The history of new materials development is that when the final design “-ilities” get worked the weight goes up, the use temperature goes down, and the operational environment limits performance. Finally, applications of new materials must be evaluated in a systems context. For example, advanced structural design methods and highly efficient structural concepts will be required to fully exploit the potential benefits of biomimetic, nanostructured, multifunctional materials in revolutionary aerospace vehicles. Also, the building-block approach to manufacturing scale-up will be essential to validate the advanced materials and concepts.

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References


Appendix I. Description of Materials for Aerospace Vehicle Structure

TiAl Alloy [20,21]

*Description*
A light weight replacement for Ti and Ni alloys in structural applications in oxidizing environments

*Processing Method(s)*
Complex airfoils, housings and cases are made by casting. Sheet, rods, fasteners, disks are made by ingot/powder preforms plus hot working.

*Current State of Development*
Lower strength, stiffness limited parts are more mature. Higher strength alloys have not been tested to same level.

*Critical Issues*
Damage tolerance is only moderate and must be confirmed for specific applications. Hydrogen resistance is expected to be poor.

Alumina (Al$_2$O$_3$) fiber/ Aluminum Metal Matrix Composite [1]

*Description*
Low cost precursor materials in tape or wire form of fibers (Al$_2$O$_3$ or SiC) in aluminum matrix. Precursor forms are thin and flexible for laying into composite or selectively reinforcing metallic structures. Useable temperature range exceeds polymer matrix composite and Al alloys. Reduced weight attained through improved structural efficiency and higher specific properties. Aluminum matrix composites are believed to offer inherently superior cryogenic containment.

*Processing Method(s)*
Braze in air to form composite panel or to selectively reinforce metallic structures. Composite panels can be manufactured by continuous laser brazing of tapes using fiber winding techniques. Composite panels can also be fabricated by laying up tape followed by hot pressing.

*Current State of Development*
Al$_2$O$_3$ continuous fiber in pure Al matrix wire in use for electrical line supports to extend distance between cable supports. Continuous laser brazing using fiber winding techniques under development for fabricating curved composite panels. Other processing methods using aluminum alloys are possible.

*Critical Issues*
Limited availability of precursor tapes and/or wires. Process development and scale-up issues for fabrication of composite panels from precursor materials need to be studied further.
Aluminum alloy foam core structures [3,13]

Description
Open and closed cell aluminum alloy foams with controlled densities (up to 95% porosity) and varying pore sizes (up to 200 ppi) for use as the core of sandwich structures, castings and extrusions.

Processing Method(s)
Syntactic foams produced by compaction and/or sintering of metal powder precursors. Reticulated foams produced by direct foaming of liquid metal and/or castings.

Current State of Development
Applications include damage containment, acoustic damping, thermal management (aircraft), secondary structures, e.g. telescopes, heat exchangers (space vehicles), energy absorption (automotive), armor piercing protection (military).

Critical Issues
Forming to complex configurations, core-to-face sheet and panel-to-panel joining for primary structure applications.

Aluminum Beryllium (Al-Be) alloys [2,4,6]

Description
Ultra-low density Al-Be binary alloys (2.1 g/cm³) and Al-Be-Mg ternary alloys (2.3 g/cm³) comparable with polymer matrix composites.

Processing Method(s)
Powder metallurgy using cold isostatic pressing (CIP), extrusion followed by cross-rolling to sheet.

Current State of Development
Binary alloy (Al-62Be) has been produced and used in limited aircraft applications for decades (YF12, F-16). Ternary alloys (e.g. Al-40Be-5Mg) are under research and development.

Critical Issues
Cryogenic fracture toughness of binary alloy is low. Tensile and fracture toughness at cryogenic, ambient and elevated temperatures need to be established. Potential cryotank and TPS application if mechanical and thermal properties at extreme temperature ranges (-250°C to 500°C) are favorable.

Titanium alloy foam core sandwich structure [3,13]

Description
Ultra-low density foams (up to 95% porosity) fabricated from advanced titanium alloys. Provides structural efficiency, weight reductions, and enhanced performance for hot structures.

Processing Method(s)
Deposition of titanium-based material onto polymeric foam pre-forms, followed by high-temperature processing to remove organic volatiles. Spray deposition of hollow titanium-based
spheres followed by sintering. Direct foaming of molten titanium-based materials. Other techniques include gas entrapment solid state processing.

**Current State of Development**

Only limited development activities are ongoing. Titanium foams are currently produced from conventional titanium alloys using vapor deposition onto polymeric foam preforms. Foams are not currently produced in intermetallics such as titanium-aluminides and titanium-beryllides

**Critical Issues**

Deposition of lightweight intermetals without losing low-density elements through volatilization. Development and scale-up of high-deposition-rate processes for large-scale production of foam. Development of useful levels of ductility in intermetallic foams. Joining processes for incorporating foams into sandwich structure.

### Silicon Carbide (SiC) fiber/ Beryllium Metal Matrix Composite [4,5,6]

**Description**

Continuous SiC fiber reinforced beryllium with 0.0056 in. diameter fibers, 30-40 volume percent fiber. Dual coating on fibers for fiber/matrix compatibility at high temperatures.

**Processing Method(s)**

Methods include tape cast powder with binder and vacuum hot press (VHP) or hot isostatically press (HIP), plasma spray Be on drum-wound fibers and VHP or HIP, foil/fiber/foil layup and VHP or HIP.

**Current State of Development**

Largest piece ever made is approximately 15 cm x 23 cm x 6 ply. Room temperature mechanical properties need to be developed. Material system has not been actively developed anywhere in the free world since 1989.

**Critical Issues**

There is a public mind set against Be use because of past toxicity issues. Fiber/matrix interactions need to be addressed and also need better fiber exhibiting minimum reaction with Be during high temperature processing and service, or stable fiber coatings.

### Carbon Nanotube (NT) fiber/ Aluminum Metal Matrix Composite [7]

**Description**

Short carbon nanotube (NT) fiber reinforced aluminum alloy.

**Processing Method(s)**

Mechanically mix NT with Al alloy powder. Vacuum hot press (VHP) and/or extrude.

**Current State of Development**

Very small quantities produced in laboratory. A few experimental tensile data. Preliminary microstructures exist with 2 mm long NT (ropes) and a 10 volume percent fiber in pure Al matrix. Properties were computed by limiting the strain to 0.7%.
Critical Issues
NT production, availability in bulk; longer NT; NT dispersion, alignment control in matrix; other matrix metals

Carbon Fiber Reinforce Polymer (CFRP) Composite [8-11]

Description
The carbon fiber reinforced polymer composite (CFRP) is the IM7/8552 material system, a toughened epoxy resin reinforced with unidirectional carbon fibers or a woven preform. The IM7 fibers are intermediate modulus carbon filaments. The 8552 epoxy is a damage-resistant system, recommended for structural applications requiring high strength, stiffness, and damage tolerance. The properties in the table are taken from the Hercules Development Data Sheet and correspond to a [0/+45/-45/90]s quasi-isotropic (Q-I) laminate stacking sequence and a 60% fiber volume fraction.

Processing Method(s)
Conventional thermoset resin equipment and techniques can be used to process IM7/8552 prepreg tape. The laminates fabricated out of prepreg tape are typically cured in an autoclave at 350 °F.

Current State of Development
CFRP are fully mature for some applications but not yet fully mature for all aerospace structural applications. Numerous CFRP composites have been developed by industry to a TRL of 9. The successful liquid hydrogen cryogenic tank on the DC-XA was fabricated out of IM7/8552. However, we are still encountering unanticipated failure modes when composites technology is extended to a new large-scale structural applications, for example the X-33 liquid hydrogen tank.

Critical Issues
Relatively immature design and analysis practices, manufacturing scale-up, and nondestructive inspection for bonded construction are some of the primary technical issues that currently limit the full potential of CFRP’s.

Single Wall Carbon Nanotubes (SWNT) [26-45]

Description
A single-wall carbon nanotube (SWNT) is a graphene sheet rolled into a cylindrical shape so that the structure is virtually one-dimensional with axial symmetry. Tube diameters vary between about 0.7 nm to 10.0 nm. Multiwall carbon nanotubes (MWNT) are concentric cylinders of individual SWNT’s with various diameters. The SWNT are thought to be held together by relatively weak frictional forces. A single crystal SWNT refers to a membrane of aligned, long, continuous SWNT’s which were formerly held together by van der Waal forces, coalescing into a crystalline form which arises from decreased entropy during continued alignment.

Processing Method(s)
The laser vaporization synthesis method uses a laser to vaporize a graphite target and nanotubes form in the condensing vapor of the heated flow tube at 1200°C. The carbon arc method uses carbon rod electrodes and vaporizes the carbon atoms into a plasma at >3000°C with the nanotubes forming on the negative electrode. The high-pressure gas-phase growth process
(HipCo) uses high temperature (900-1200°C) and pressure (10-100 atm) to create a highly turbulent gas mixture that nucleates carbon nanotubes from a mixture of CO and a Fe/Ni carbonyl catalyst. Carbon nanotubes grow from metal clusters that form during this process.

**Current State of Development**

SWNT’s have been fabricated at discontinuous lengths approaching microns and ropes of entangled SWNT’s have been fabricated into paper-like mats.

**Critical Issues**

Production of large quantities of useable nanotubes with macroscale lengths has not yet been achieved.

---

**Carbon Nanotube Fiber Reinforced Polymer (NTFRP) Composite [33,46]**

**Description**

Carbon Nanotube containing composites are estimated to have about 20% loading of the nanotubes or they will be crossplied materials that will afford no more than about 20% of the unidirectional nanotube properties because of processing/interface problems. The strength of the SWNT was limited to about 1% strain or about 10 GPa.

**Processing Method(s)**

Processing will involve dispersing nanotubes in binders which will be molecular in nature, perhaps monolayers with hundreds of nanometers to micron in thickness. Layups and fabrication will have to be non-conventional and are yet to be determined. Processing of complex forms should offer no major technical problems. The long-term hope is that molecular self-assembly can be employed which will create ‘near perfect’ molecular order.

**Current State of Development**

To date only crude prototypes have been made where carbon nanotubes have been dispersed at low levels up to about 5% in room-temperature-curing epoxies and other polymers.

**Critical Issues**

Carbon nanotube scaleup is in its infancy with only gram quantities available for experimentation. The ability to disperse nanotubes in binders has not been fully developed as is the case for all other processing issues. Fiber spinning is beginning to show promise as a method to produce continuous fiber from short nanotubes.
Appendix II. Description of Materials for Propulsion System Components

**TiAl Alloy [20, 21]**

*Description*
A light weight replacement for Ti and Ni alloys in structural applications in oxidizing environments.

*Processing Method(s)*
Complex airfoils, housings, and cases are made by casting. Sheet, rods, fasteners, disks are made by ingot/powder preforms plus hot working.

*Current State of Development*
Successful aircraft engine tests provide technology for space transportation applications. The technology is more mature for applications requiring lower strength and stiffness. Higher strength alloys have not been tested to the same levels.

*Critical Issues*
Damage tolerance is only moderate and must be confirmed for specific applications. Hydrogen resistance is expected to be poor.

**Advanced Ni Single Crystal [20,21]**

*Description*
New single crystal alloys for jet engine turbine blades continue to push capability to higher temperatures.

*Processing Method(s)*
Directional solidification

*Current State of Development*
Very mature for jet engine applications but not mature for space transportation.

*Critical Issues*
Hydrogen resistance must be evaluated. Specific alloy selection for space transportation issues need to be addressed.

**Advanced Ni Poly Crystal [20, 21]**

*Description*
Advanced Ni alloys are made by powder metallurgy and used for compressor and turbine disks. Higher strength and temperature capability compared to today’s alloys used in aircraft engines and space shuttle main engines.
**Advanced Cu Alloy [19]**

**Description**
Advanced Cu-alloy with improved temperature capability for thrusters, rocket nozzles, nozzle ramps, and other high heat flux applications, without sacrificing damage tolerance.

**Processing Method(s)**
Powder metallurgy (PM) and hot isostatic pressing (HIP), extrude, rolling

**Current State of Development**
Rocket test firings have demonstrated feasibility. Durability still needs to be examined. Coatings for extending life and performance need more work.

**Critical Issues**
Coating reliability and performance limits need more definition. Applications other than thrust cells are immature.

---

**Gr/Cu Composite [19]**

**Description**
High strength, conductivity, stiffness, lightweight material for hypersonic leading edges, actively cooled structures, radiators, heat pipes

**Processing Method(s)**
Pressure casting and Physical Vapor Deposition (PVD)

**Current State of Development**
Unidirectional plies are well developed and characterized. Woven composites are less mature but offer fewer weaknesses.

**Critical Issues**
Transverse properties are usually poor.

---

**Nano Structure Ni Alloy (Ns Ni) [47]**

**Description**
Nano structured nickel alloys with nanoscale grain size are projected to have twice the strength, twice the damping capacity, and twice the hydrogen resistance relative to conventional alloys.
**Processing Method(s)**
Cryomilling and powder metallurgy (PM)

**Current State of Development**
Material systems have not been developed to date. Projections are based on similar results in other metals.

**Critical Issues**
Processing feasibility needs to be confirmed. Concerns also exist about low temperature damage tolerance.

---

**NT / Cu Composite [47]**

**Description**
Cu alloys with nanotubes, buckyballs, or diamond reinforcements are projected to have extremely high thermal conductivity, good stiffness and low weight.

**Processing Method(s)**
Powder metallurgy (PM), Casting

**Current State of Development**
Materials cannot be fully explored until nano-reinforcements are more readily available.

**Critical Issues**
Availability of nano-reinforcements and development of processing methods

---

**W, Nb, Mo Alloys [no reference]**

**Description**
Refractory metals offer the highest temperature capability available in a metal. High densities and poor hydrogen and oxygen resistance limit uses. Materials are uniquely attractive for deep space missions and nuclear propulsion.

**Processing Method(s)**
Cast and wrought or powder metallurgy are common. Chemical vapor deposition has also been used on rocket thrusters.

**Current State of Development**
Technology was worked heavily in the 1960’s and 1980’s. Alloys and processing are well developed. Coating efforts and alloy development for oxidation resistance are less mature but still hold promise.

**Critical Issues**
Environmental resistance and coating reliability
Nextel 720 fiber/alumino-silicate (Al₂O₃SiO) Ceramic Matrix Composite [22-25]

**Description**
Nextel 720 fabric/alumino-silicate (Al₂O₃SiO) matrix, ~48% fiber volume, no interface coating, uses controlled matrix porosity for composite toughness

**Processing Method(s)**
Sol-gel derived matrix infiltrated into woven Nextel 720 fabric. Sol-Gel is a process where micron-size particles are dispersed in a liquid and a solid is formed through chemical reaction rather than melting. Infiltrated fiber weaves are laid up on tooling with final shape. Complex shape is vacuum bagged, then consolidated at low temperature and pressure (<150°C and <15 GPa). Free standing post-cure at ~1000°C to 1100°C.

**Current State of Development**
Materials have been tested in exhaust systems for military applications. Large parts have been fabricated and tested in engines.

**Critical Issues**
With currently available low temperature fibers, composite processing and use temperatures are limited to ~1100°C. With fibers that have greater thermal stability, processing temperature could be increased and mullite could be formed as the matrix. A mullite matrix and oxidation resistant fiber coating would lead to an oxide CMC with greater thermal stability and possibly higher mechanical properties.

**Carbon Fiber Reinforce Polymer (CFRP) Composite [8-11]**

**Description**
Improvements in matrix chemistry (polymer backbone and end-caps), better control of the resin-fiber interface, and the use of novel reinforcement approaches (e.g., alumino-silicate clay reinforced polymers) are expected to lead to improvements in mechanical performance, processability and long-term durability at high temperatures.

**Processing Methods**
New developments in resin chemistry will enable processing by a variety of methods including prepreg-based methods (autoclave processing, compression molding, and automated tow placement) and resin infusion approaches (resin transfer molding, resin film infusion).

**Current State of Development**
Current high temperature systems have limited long-term durability at temperatures above 290°C. Processing of these conventional high temperature materials is limited to prepreg based methods.

**Critical Issues**
Need to identify/optimize resin chemistry to enable resin transfer molding processability without sacrificing high temperature performance and long-term durability.
C/SiC Ceramic Matrix Composite [22-25]

Description:
Carbon fibers offer high temperature capability with the high modulus and oxidation resistance of a silicon carbide (SiC) matrix.

Processing Method(s):
Chemical Vapor Infiltration (CVI) is used for high strength. The process is well understood and has the largest database. Melt Infiltration (MI) is used for highest thermal conductivity and lowest porosity. Polymer Infiltration Pyrolysis (PIP) is used as the initial processing at low temperatures. It can also be used to form large complex shapes.

Current State of Development:
C/SiC has been examined for use in forming blisks, nozzles, combustors, nozzle ramps, cooled components, leading edges, and control surfaces as well as other components. Work is being performed to determine the effects of oxidation on composite life. Variations are being made in each of the different processing approaches to determine ways to increase composite properties, densify thick sections, and improve oxidation resistance.

Critical Issues:
Critical issues include life prediction methods, processing of components, reliability/reproducibility/uniformity, coefficient of thermal expansion mismatch between fiber and matrix, and oxidation resistance, including coatings.

SiC / SiC Ceramic Matrix Composite [22-25]

Description:
Because of inherent oxidation resistance, low density, high strength, and creep-rupture resistance, continuous fiber-reinforced ceramic matrix composites based on SiC fibers and SiC matrices can thermally outperform superalloys and thus are strong candidates for advanced hot structural components.

Processing Method(s):
Variety of small diameter SiC-based fiber types, commercially available in multifilament tows, are woven or braided into 2D and 3D architectures. Interphase coatings, typically based on carbon or boron nitride, are deposited on fibers by chemically vapor infiltration either before or after architecture formation. SiC-based matrices from a variety of different precursors are infiltrated into coated fiber architectures by various combinations of gas, polymer, slurry, and/or molten silicon to achieve as dense a matrix as possible.

Current State of Development:
The feasibility of first generation SiC/SiC composites have been examined in a variety of industrial, military, and commercial engine applications. Identified deficiencies, which are currently being addressed by a variety of governmental programs include insufficient long term stability of constituents at high temperatures, particularly in moist combustion environments, fiber weave-ability for complex-shaped components, and high acquisition costs. Significant
progress has been made recently by the development of stoichiometric SiC fibers, Si-doped boron nitride interphases, dense melt-infiltrated matrices, and oxide-based environmental barrier coatings.

Critical Issues:
Components exhibit poor processibility and property reproducibility. Composites lack interphase stability, particularly at intermediate temperatures. Fiber architectures need to be developed for component scale-up. Fiber and composite fabrication costs are high. Low projected market volume contributes to instability of the fiber and composite vendor base.

NT / Polymer Composite [33, 46]

Description
Properties of nanotube reinforced high temperature polymers are estimated at a nanotube loading level of about 20 weight percent. The limited data published to date on nanotube reinforced polymers suggests that optimum levels of nanotube loading are in the range of 10 to 20 weight percent. Properties of these material systems are assumed to be primarily reinforcement (nanotube) dominated and are estimated at 20% of the theoretical properties of the nanotubes. These estimates assume good NT-polymer adhesion.

Processing Methods
Novel processing methods and binder/sizing chemistries need to be developed to insure homogeneous distribution of nanotube reinforcements throughout the polymer matrix. Molecular level control of nanotube orientation and interactions with the matrix material is highly desired to obtain optimal properties and performance.

Current State of Development
There is sparse published data on nanotube reinforced polymers. Literature reports to date have been on crude composites from epoxies or acrylates at a nanotube loading level of up to 5 weight percent.

Critical Issues
Need to develop an affordable, reproducible method to make large quantities of nanotubes with controlled size, geometry, chirality and purity. In addition, the proper chemistries have to be developed to control nanotube dispersion in the matrix without adversely affecting the mechanical integrity of the nanotubes.
Table 1. The NASA Technology Readiness Levels (TRL)

- TRL 1: Used on Aerospace Vehicle
- TRL 2: Prototype Development/Qualification
- TRL 3: Specifications Performance Verification
- TRL 4: Quality Control Product Form Development
- TRL 5: Scale-up, Processing Property Verification
- TRL 6: Material Preparation Property Screening
- TRL 7: Advanced Prototype Systems & Flight Demonstration
- TRL 8: Advanced Technology
- TRL 9: Focused Technology
- TRL 10: Research
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<thead>
<tr>
<th>Property</th>
<th>Aluminum 2219-T87 (handbook)</th>
<th>TiAl (measured)</th>
<th>TiC / SiC (measured)</th>
<th>Ti/Al Be (measured)</th>
<th>Ti Foam (theoretical)</th>
<th>SiC / Be (estimated)</th>
<th>NT / Al Composite (theoretical)</th>
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<tr>
<td>Tensile Strength</td>
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<td>Tensile Modulus</td>
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<td>210 GPa</td>
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<td>280 GPa</td>
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<td>1.7 %</td>
<td>0.8 %</td>
<td>20 %</td>
<td>5 %</td>
<td>5 %</td>
<td>3 %</td>
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<td>Carbon Fiber IM7 (handbook)</td>
<td>CFRP Q-I M46J/7714A Terra Spacecraft</td>
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<tr>
<td>Tensile Strength</td>
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<td></td>
<td></td>
<td>(60 GPa exp.)</td>
<td></td>
<td></td>
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<td>58 GPa</td>
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</tr>
<tr>
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<td>1.0 %</td>
<td>1.8 %</td>
<td>1.0 %</td>
<td>1.58 %</td>
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<td>15 % (6 % exp)</td>
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<td>18 W/mK</td>
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<td>17 W/mK</td>
<td>320 W/mK</td>
<td>400 W/mK</td>
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<td>Use Temp.</td>
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Table 5. Properties of Ceramic, Ceramic Matrix Composites, and Polymer Matrix Composites for Propulsion Applications

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<tr>
<th>Property</th>
<th>Reference 1</th>
<th>Reference 2</th>
<th>5-10 yrs</th>
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<tbody>
<tr>
<td></td>
<td>Inconel 718</td>
<td>Nextel N720</td>
<td>CFRP</td>
<td>Composite</td>
<td>SiC / SiC</td>
<td>Composite</td>
<td>NiFRP</td>
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<tr>
<td>Tensile Strength</td>
<td>1.03 GPa</td>
<td>2.1 GPa</td>
<td>0.18 GPa</td>
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<td>0.6 GPa</td>
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<td>2.5 GPa</td>
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<tr>
<td>Tensile Modulus</td>
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<td>260 GPa</td>
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<td>83 GPa</td>
<td>250 GPa</td>
<td>240 GPa</td>
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<td>Elongation</td>
<td>14 %</td>
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<td>&lt;1%</td>
<td>2.4 %</td>
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<td>Density</td>
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<td>30</td>
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</tr>
<tr>
<td>Thermal Cond’ty</td>
<td>15 W/mK</td>
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### Table 6a. Strength and Modulus of Carbon Nanotubes

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<th>Value</th>
<th>Units</th>
<th>Range</th>
<th>Simulated</th>
<th>Measured</th>
<th>Technique</th>
<th>Equipment</th>
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**SWNT** = single-wall nanotube  
**MWNT** = multi-wall nanotube
Table 6b. Strength and Modulus of Carbon Nanotubes, continued

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<th>Range</th>
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<th>Equipment</th>
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SWNT = single-wall nanotube  
MWNT = multi-wall nanotube
### Table 7. Thermal and Electrical Properties of Carbon Nanotubes

<table>
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<tr>
<th>Thermal Property</th>
<th>Value</th>
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<td>Thermal Comparator Constantan Rod</td>
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<th>Measured</th>
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Figure 1. Next generation reusable launch vehicles
Figure 2. Structural materials for aerospace vehicle applications
Rocket Combined Cycle System (3rd Generation)

Aerospike Propulsion System (2nd Generation)

Pulse Detonation and Turbine Combined Cycle (3rd + Generation)

Figure 3. Next generation propulsion systems
Figure 4. Materials for propulsion systems applications
Figure 5. A revolution in materials development
Figure 6. Results of a systems analysis study of a reusable launch vehicle
Figure 7. Results of a systems analysis study of a jet engine
Figure 8. Results of a systems analysis study of a spacecraft.
A Survey of Emerging Materials for Revolutionary Aerospace Vehicle Structures and Propulsion Systems

Charles E. Harris, Mark J. Shuart, and Hugh R. Gray

NASA Langley Research Center
Hampton, VA 23681-2199

The NASA Strategic Plan identifies the long-term goal of providing safe and affordable space access, orbital transfer, and interplanetary transportation capabilities to enable scientific research, human, and robotic exploration, and the commercial development of space. Numerous scientific and engineering breakthroughs will be required to develop the technology required to achieve this goal. Critical technologies include advanced vehicle primary and secondary structure, radiation protection, propulsion and power systems, fuel storage, electronics and devices, sensors and science instruments, and medical diagnostics and treatment. Advanced materials with revolutionary new capabilities are an essential element of each of these technologies. A survey of emerging materials with applications to aerospace vehicle structures and propulsion systems was conducted to assist in long-term Agency mission planning. The comprehensive survey identified materials already under development that could be available in 5 to 10 years and those that are still in the early research phase and may not be available for another 20 to 30 years. The survey includes typical properties, a description of the material and processing methods, the current development status, and the critical issues that must be overcome to achieve commercial viability.