Misra M (1990) Towards unobtainium [new composite materials for space applications]. Aerosp Compos Mater 2(6):29-32

TOWARDS UNOBTAINIUM

Space offers a unique challenge for material scientists because of the extreme environment. For example, Space Station Freedom, during its 30-year life, will undergo approximately 175,000 thermal cycles from +250 to −250° F as the structure moves in and out of the Earth's shadow. Re-entry vehicles for Earth and Mars missions, travelling at speeds as high as 17,000 mph, may encounter temperatures that exceed 3,000° F. In addition, the emergence of Strategic Defense Initiative (SDI) systems has created an unprecedented demand for space structures with critical dimensional stability for extremely high pointing accuracies.

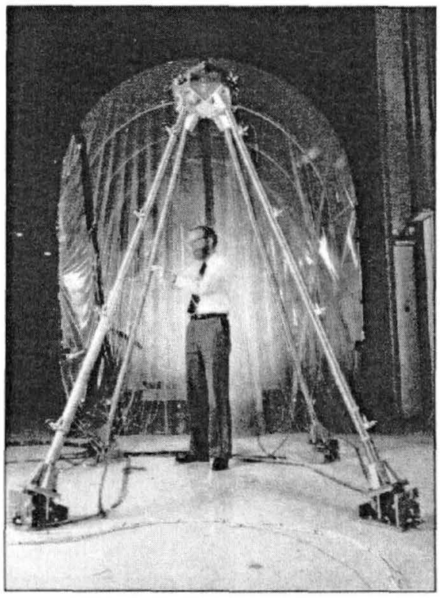
Materials for space applications must be light to reduce launch costs, which can range from US $6,000 to US $13,000 per lb. A high stiffness-to-density ratio is needed to raise the fundamental frequency of manoeuvrable structures and minimise active and passive controls. High material damping is also required to control vibrations caused by manoeuvring or onboard disturbances. A low or near-zero coefficient of thermal expansion (CTE), combined with high thermal conductivity, provides resistance to thermal deformation during repeated thermal cycles. Long-term stability when exposed to atomic oxygen (in LEO), and ultraviolet and charged particles (in GEO) is critically important. For certain systems, the capability to survive laser and nuclear particle beams is a key element for a successful mission. After reviewing such material property requirements, some scientists facetiously claim their quest is to find the one material that can satisfy all these needs – 'unobtainium'. In reality, no one material can be optimum for all applications. The goal is to develop various materials, each optimal for its specific use.

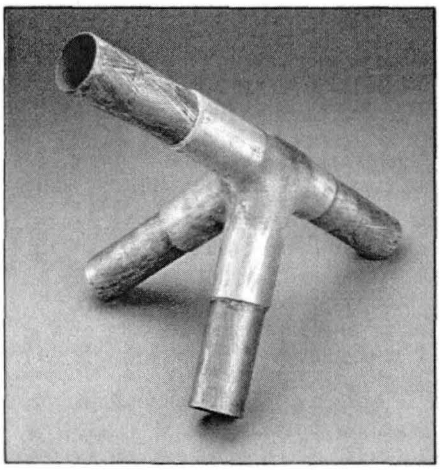
The Martin Marietta Astronautics Group has several continuing research and development tasks directed toward advanced, engineered materials:

- Advanced composites for light, stiff, highly damped, and dimensionally stable structures;
- High-temperature materials for re-entry vehicles;
- Shape memory alloys (SMA), which are adaptive composites for 'smart' structures;
- Light alloys for propellant tanks;
- Surface modifications, including diamond films, for tribological (friction-resistant) and protective coatings.

Martin Marietta is well advanced in engineered materials for space applications.

Graphite/Mg is being considered for several SDI applications. Martin Marietta built this representative space structure from the material (below). Attachment fittings were also made of graphite/Mg.





It is expected that in future spacecraft, all these technologies will be needed.

Graphite/epoxy composites have been the key ingredients in light space structures for decades. New long-life and stringent survivability requirements for advanced space systems highlight some problems associated with graphite/epoxy composites. Most thermoset composites are hygroscopic; moisture absorption and subsequent desorption can degrade them. Outgassing in space vacuum can also contaminate optical systems and restrict their performance. Microcracking caused by thermal cycles can be a critical problem. In addition, thermoset composites are difficult to mass produce and repair.

During the past 10 years, thermoplastic matrix composites have received significant attention as replacements for conventional thermoset composites. The major difference between these materials is their chemical compositions. Thermoplastics consist of repeating, long-chain molecules (monomers) with a fixed chemical structure (inert or nonreactive); thermoset materials are composed of complex molecules that cure by reaction (crosslinking and bonding) in the presence of a catalyst. This fundamental difference allows thermoplastic composites to be fabricated by a rapid heat-melt-solidify cycle as compared with the often lengthy heat-reaction-cure cycle for thermoset composites. As a result, thermoplastic composites exhibit an inherent capability to be rapidly processed and offer significant increases in production and decreases in manufacturing costs. In addition, because thermoplastics do not chemically react and set, they can be reprocessed by simply applying heat and pressure.

Several fibres, including glass and graphite, have been incorporated into thermoplastic matrices such as polyetheretherketone (PEEK), polyetherimide, polyether sulfone, and polyphenylene sulfide. High-strength or high-stiffness graphite fibres such as AS4, IM6, and P75 are most widely used. When combined with reinforcing fibres, these materials offer extremely high strengths and stiffnesses, and low densities. For example, AS4/PEEK exhibits a strength of approximately 100 ksi with a density of 0.063 lb/cu in. Compared with an equivalent strength, high-performance steel with a density of 0.284 lb/cu in, it is five times lighter. Compared to an aluminium density of 0.10 lb/cu in, it is 1.5 times lighter. ▶

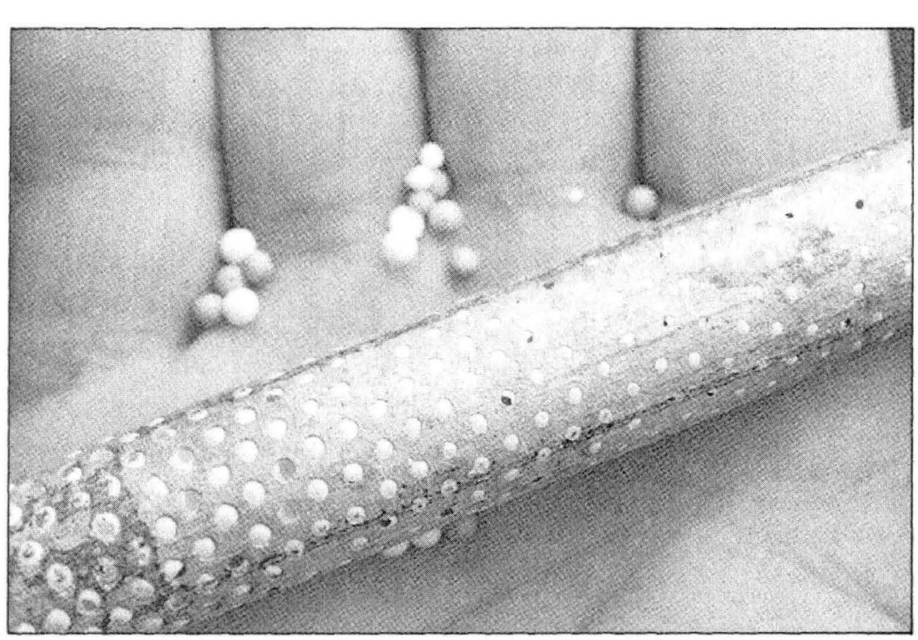
The chemical composition of thermoplastics provides improved toughness and survivability in the natural space environment compared with thermoset matrix composites. Even though graphite/thermoplastic composites seem to possess tremendous potential for space applications, additional analysis is needed to quantify outgassing and survivability.

Compared with thermoset composites, in which the epoxy matrix is simply a load-transfer medium between the fibres, metal matrices contribute significantly to overall composite properties. As a result, metal matrix composites (MMCs) offer no moisture absorption, no out-gassing, high specific stiffness combined with near-zero CTE, high thermal and electrical conductivities, higher material damping, and resistance to thermal distortion and microcracking. Based on their outstanding properties, graphite/Mg composites were selected for the Zenith Star space-based laser experiment's metering truss structure, which has one of the most stringent pointing and dimensional accuracy requirements of any spacecraft.

MMCs possess attractive properties for space applications and are near-optimal materials. However, the applications have been limited thus far because of the difficult fabrication processes required. Most fibres, such as boron, graphite, and SiC, react with the common metal matrices. For example, graphite fibre will react with the aluminium matrix, forming deleterious aluminium carbide at the interface, degrading the fibre, and embrittling the composite. Therefore, a barrier coating must be applied to the fibres.

Furthermore, to create a strong interfacial bond, the metal matrix should wet the fibres or form beneficial intermetallic compounds to provide a strongly adherent metallurgical bond, such as in the cast graphite/Mg process. To date, developing diffusion barriers and wettable coatings has been limited to a few fibre and matrix systems. Consequently, most of the research work has focused on B/Al, graphite/Al, graphite/Mg, graphite/Cu, and SiC/Ti, for which such coatings are available.

The first successful application of continuous fibre-reinforced MMCs (B/Al) was the Space Shuttle orbiter's fuselage stiffeners because of this composite's high stiffness. Similarly, the Hubble Space Telescope has a graphite/Al structural antenna support boom. Graphite/Mg is being considered for several SDI applications. A representative space structure was fabricated by the Martin Marietta Astronautics Group's Space Systems Company using graphite/Mg tubes and fittings. Graphite fibres such as P130X, which have a thermal conductivity approximately four times greater than that of copper, have been developed recently by Amoco. Composites using these fibres with a copper or aluminium matrix can offer thermal conductivity that is two times greater than that of copper and a weight that is approximately half that of copper. These composites are extremely attractive for space applications such as radiators, heat sinks, and electronics packaging.



Discontinuous metal matrix composites are closed-cell metallic foam structures in which the ceramic microballoons form the interior wall.

DISCONTINUOUS-REINFORCED MMC

The efficiency of reinforcement in a composite is reduced as the aspect ratio (length to diameter) if the reinforcement is reduced. However, dispersion of particulates or whiskers in metal matrices can significantly increase specific stiffness and reduce the CTE. For example, a 20 per cent volume fraction of SiC particles in a 2124 Al matrix can increase the composite modulus to approximately 19.9 Msi (compared with 10 Msi for the matrix) without significantly changing overall density. To date the most common discontinuous reinforcements for space applications have been SiC, Al_2O_3, TiC, TiB_2, B_4C in Al, Mg, Ti, Cu, and intermetallic matrices.

Most discontinuous MMCs are fabricated using powder metallurgy processing and thus are not cost-effective. Recent developments at Duralcan, in the casting technology of SiC in an Al matrix, have reduced costs to a reasonable price of US $2 to US $5 per lb. One example of an application for SiC/Al is a precision gimbal for an optical system that requires a rigid, light material with low CTE, and good wear resistance.

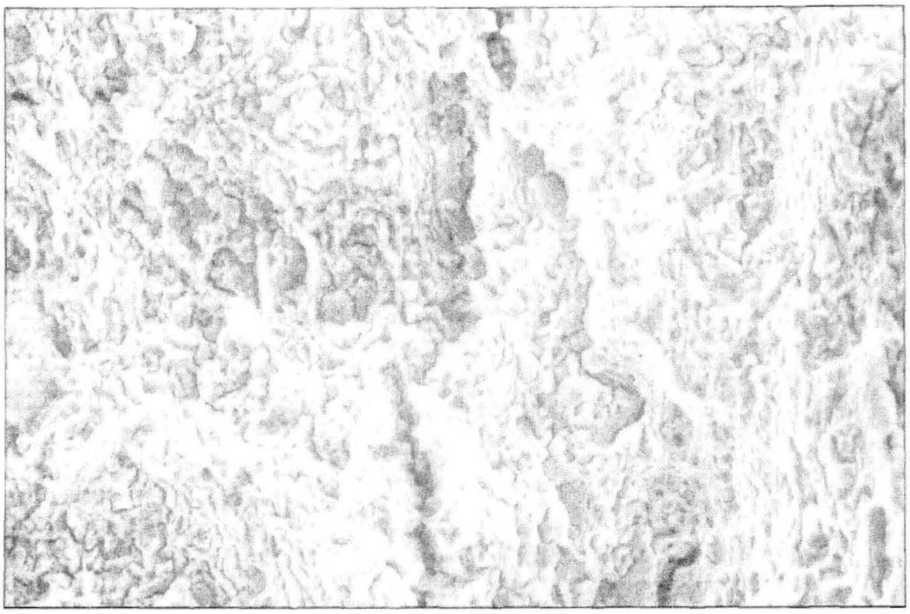
Scientists at the Martin Marietta Laboratories in Baltimore, Maryland, have developed a new exothermic dispersion (XD) process based on the principles of combustion synthesis to fabricate discontinuous-reinforced composites. Self-propagating, high-temperature synthesis (SHS), or combustion synthesis, was developed by Soviet scientists in the early 1970s to fabricate intermetallic and ceramic compounds such as nickel aluminides and TiB_2. Basically, the process uses the heat generated (exothermic) when the constituents react. The XD process expands upon the original SHS concept to form composites with unique mechanical properties.

SHS is an inexpensive process to form intermetallics and ceramics. However, there are several problems associated with it, such as oxide contamination, porosity, and agglomeration. As a result, the final XD product has similar problems. Systematic research is being conducted at the AMAX Research Center in collaboration with the Martin Marietta Laboratories to resolve some of these issues. The team has been successful in reducing oxide content to lower levels during fabrication of XD TiAl.

Reinforcements other than TiB_2 are being examined for aluminium matrices, and have been used to overcome problems associated with the poor dispersion of TiB_2 in aluminium.

In another recent development, discontinuous MMCs have also been produced by incorporating ceramic microballoons into a metallic matrix. Ceramic microballoons are low-density, hollow spheres of alumina, silica, zirconia, or carbon. These materials have inherently high compressive strength and low CTE. Discontinuous MMCs have been fabricated by a vacuum casting process, and exhibit low density, high compressive strength, high compressive strain to failure, and good damping characteristics. The compressive strengths of these composites can be modified by using micro-balloons of different wall thickness-to-diameter ratios, and heat-treating the matrix to the T6 condition.

Similar to syntactic organic foam, a discontinuous MMC is closed-cell metallic foam in which the ceramic microballoons form the interior wall of the cell. The Martin Marietta Astronautics Group is developing methods to fabricate these composites with tailored material properties by using an optimum combination of ceramic microballoons and metallic matrices. For example, fine carbon microballoons have been preferentially incorporated at the inner surface of an aluminium alloy by the centrifugal casting process to produce self-lubricating composites. With high specific compressive strength, high damage tolerance, and good damping, these composites are also candidates for structural platforms, cones, submarine hulls, impact-resistant shields, and energy-absorbing systems for aerospace and marine applications.



The fracture toughness of Weldalite is increased by the secondary cracking, parallel to the crack front, effectively relieving the through-thickness constraint.

HIGH-TEMPERATURE MATERIALS

Aerospace products such as re-entry vehicles, high-performance missiles, and hypersonic aircraft could require light materials capable of operating in the 1,800 to 4,000° F temperature range. Candidate materials for such applications are carbon-carbon (C–C) composites, ceramics, intermetallics, and intermetallic composites.

The first C–C composite was discovered accidentally by the Vought Aircraft Company in 1958 when an organic matrix composite was inadvertently pyrolised into charred composites. The resulting material exhibited several beneficial structural characteristics. There are now several methods for fabricating C–C composites. Basically, a carbonfibre preform is impregnated with carbonaceous matrix and pyrolised at temperatures of 1,500 to 2,700° F several times to produce a densified structure, which is subsequently carbonised (1,800 to 2,700° F) and graphitised (2,700 to 5,000° F) to produce a high-performance C–C composite.

The predominant feature of C–C composites is their ability to retain room-temperature strength (80 ksi) at temperatures up to 3,700° F. They possess good tensile and compressive strength, low creep rate at high temperatures, high thermal conductivity, and are capable of resisting thermal shocks from −250 to +3,000° F.

Because of their excellent high-temperature properties, C–C composites have been used for rocket nozzles to withstand high-temperature erosion and abrasion without being incinerated. Other applications include Space Shuttle nose cones and leading edges, brakes for aircraft and high-performance cars, thermal radiators, and survivable space structures.

One major problem associated with C–C composites is poor oxidation resistance at temperatures above 850° F. Thus, C–C composites require protective coatings, typically ceramic, such as SiO_2 and SiC. These coatings generally perform well up to 2,800° F. Research is continuing to increase this temperature capability with multilayer coatings to prevent diffusion of carbon and oxygen through these layers.

INTERMETALLIC COMPOUNDS

Intermetallic compounds, with their excellent high-temperature mechanical properties and low density as compared with conventional alloys, are the combination of two or more metals that form with an ordered crystal structure. Interest in these materials has increased in recent years because conventional metallic alloys do not retain their mechanical properties at temperatures above 1,200° F.

Recent research in intermetallic compounds has focused on developing aluminides for high-temperature structural applications. These compounds, composed of aluminium and another metal such as iron, nickel, or titanium, combine low density with good high-temperature strength and stiffness.

An intermetallic system based on beryllium-containing compounds has also received increased attention. These compounds are unique because they retain strength and stiffness to almost their melting temperature, which can be as high as 3,560° F. Furthermore, unlike the aluminides, beryllides are extremely oxidation resistant. Most of the work on these compounds has focused on beryllium-rich beryllides such as $NbBe_{12}$, Nb_2Be_{17}, $TiBe_{13}$, and Ti_2Be_{17}.

The problem with most intermetallic compounds is that their room-temperature damage tolerance is low because of their sensitivity to contamination. Oxides, carbides, and other contamination can severely limit ductility and decrease fracture toughness. Recent advances in processing have improved the consistency of the materials and their associated properties.

Complex crystal structures also limit the low-temperature damage tolerance of these compounds. In the case of the aluminides, ductility can be improved by alloying with elements that improve the ability of dislocations to move through the lattice or limit the effect of brittle grain boundaries. In the case of the beryllides, which offer a limited number of slip systems even at high temperatures, alloying additions may not be effective in improving ductility. An alternative approach to improving the damage tolerance of these compounds is to form them into microlaminated structures with several micron-sized layers. Each interface acts to absorb the energy of a propagating crack, thereby increasing the structure's damage tolerance. This technique has been successfully used to increase the toughness of high-strength steels and ceramics such as alumina.

The use of intermetallics in aerostructures could be necessary to overcome the hostile environments that future space systems will encounter. These compounds show promise in meeting aerospace industry needs.

SHAPE MEMORY ALLOYS

SMAs undergo a reversible crystalline phase transformation that is the basis of the 'shape memory effect'. (One of the better known is Nitinol, a Ni-Ti intermetallic alloy that derives its name from its two elements and the agency that discovered it in the 1960s – the US Naval Ordnance Laboratory.) The low-temperature phase is a twinned, martensitic structure that is capable of large strain deformation (in excess of 10 per cent in some alloys) with relatively little force (~10 ksi). The high-temperature phase is a cubic-based, austenitic structure with mechanical behaviour that is similar to conventional metals. When the martensite is deformed and then heated, the original heat-treated shape is recovered. However, if the deformed martensite is constrained during heating, high-recovery stresses evolve (>100 ksi is possible in some alloys). A combination of the two allows SMAs to produce mechanical work with the application of heat.

SMAs also demonstrate the 'pseudoelastic effect' in which martensite can be stress-induced in an alloy at high temperature that otherwise would be austenitic. This effect allows large, recoverable strains to be induced at high levels of stress, making SMAs capable of storing many more times the strain energy afforded by spring steel. Shape memory and pseudoelastic effects can be better explained by understanding that the existence of each phase in a SMA depends on the combination of free energy available from temperature, stress, and strain.

Experimental mapping of domain boundaries, and analytic modelling theory have allowed analysis and design of shape memory-based mechanisms and devices. This has been particularly beneficial in designing integrated actuators for vibration and shape control of large space truss structures. The hysteretic nature of these materials has also been used in passive damping applications in which martensite acts much like a viscoelastic material.

Historically, the problem associated with proper application of these alloys is greater than just their nonlinearity and hysteresis. Transformational cycling of the alloys produces additional effects of creep, ▶

fatigue, and material property drift. These effects are being studied to provide the basis for effective alloy processing and 'training' before application. For example, the Martin Marietta Astronautics Group is using isothermal strain cycling of SMA wire to stabilise creep and material property drift before consolidation into composite materials. These 'smart' composites must show reproducible response to electrical heating through thousands of cycles. Smart composites using SMA reinforcement wires can actively attenuate acoustic noise in structures by having fundamental control over structural stiffness. Strain-compliant SMA composites can also be used as integrated members in truss structures, performing passive and active roles in vibration and shape control.

Scientists at Martin Marietta Laboratories have invented an ultrahigh-strength Al-Cu-Li alloy called Weldalite 049. A relatively high copper-to-lithium ratio compared with other Al-Li alloys promotes precipitation of the T1 (Al_2CuLi) phase. In addition, nucleation aids such as silver and magnesium are added to obtain uniform and fine dispersion of the strengthening phase. Consequently, an unprecedented yield strength of 100 ksi can be achieved for both the T6 and T8 tempers, with good fracture toughness for a 92 ksi yield strength. Weldalite has comparable weldability to other Al-Cu alloys and offers higher mechanical properties that can be exploited in cryogenic tanks.

Diamond and diamond-like carbon (DLC) coatings have generated considerable interest in such diverse applications as tribological materials, microelectronics, atomic oxygen protection, laser- and nuclear-hardened surfaces, abrasion-resistant lens and dome materials, and more consumer-oriented applications such as wristwatch crystal surfaces (nonscratch), windshield surfaces (nonpitting), and magnetic disc coatings (long life).

These applications take advantage of the desirable properties of diamond (such as the highest hardness of any known material, low coefficient of friction, very high thermal conductivity, high dielectric strength, and transparency in the ultraviolet, visible, and infra-red regions). Unfortunately, the most commonly used deposition methods, plasma-assisted or plasma-enhanced chemical vapour deposition (PECVD), generate high substrate temperatures (normally 1,500 to 1,800° F, but in some cases as low as 850° F), and many of the potential substrates cannot even survive these temperature excursions, much less maintain their properties.

At the Martin Marietta Astronautics Group, direct ion beam deposition has been used to deposit amorphous carbon and DLC onto molybdenum, zinc selenide, 440C steel, and an aluminised plastic at room temperature. Several forms of carbon have been deposited onto these materials. Qualitatively, DLC with amorphous carbon have been produced using CH_4+ ions and showed a visually transparent surface similar to the reported physical characteristics of diamond. Similarly, carbon-plus from a CO source produced a clear, electrically insulating, amorphous carbon and microcystalline graphite film. Thus, it is possible to produce amorphous carbon-plus graphite structures as well as graphite with diamond or DLC structures for tribological applications such as bearings and gears.

Applying DLC to 440C steel surfaces reduces the coefficient of friction (μ) by 60 per cent. The low μ value of 0.11 at the highest load is very close to the values confirming the solid lubricating nature of DLC. In addition, the wear surfaces exhibited very little damage compared to the untreated steels.

Films containing DLC are expected to exhibit even greater tribological performance. As the ion beam technique is advanced, the applications for these tailor-made surfaces will rapidly grow.

Space provides a definite challenge and a unique opportunity for material scientists. To meet this challenge, new engineered materials are being investigated continuously. However, a co-operative effort involving different engineering disciplines such as structural design, dynamics, thermal analysis, and fabrication will be needed not only to produce truly engineered materials, but also to effectively use them on systems. ■

Editor's note

Mohan Misra is manager of materials and structures at Martin Marietta's Space Systems Company. This article first appeared in the Astronautics Group Journal Volume 1, 1990.