# ITEM 8
# Structural Materials

# Structural Materials

Structural materials usable in the system in Item 1, as follows:

(a) Composite structures, laminates, and manufactures thereof, specially designed for use in the systems in Item 1 and the subsystems in Item 2, and resin impregnated fibre prepregs and metal coated fibre preforms therefor, made either with organic matrix or metal matrix utilizing fibrous or filamentary reinforcements having a specific tensile strength greater than $7.62 \times 10^4$ m ($3 \times 10^6$ inches) and a specific modulus greater than $3.18 \times 10^6$ m ($1.25 \times 10^8$ inches);

<u>**Notes to Item 8:**</u>

(2) The only resin impregnated fibre prepregs specified in (a) above are those using resins with a glass transition temperature ($T_g$), after cure, exceeding 145 degrees C as determined by ASTM D4065 or national equivalents.

**Produced by companies in**

- China
- Denmark
- France
- Germany
- Israel
- Japan
- Russia
- South Africa
- Sweden
- United Kingdom
- United States

***Composite structures, laminates, and manufactures***

**Nature and Purpose:** Composites and laminates are used to make missile parts that are often lighter, stronger, and more durable than parts made of metal or other materials.

**Typical Missile-Related Uses:** Composites and laminates can be used almost anywhere in ballistic missiles or unmanned air vehicles (UAVs), including cruise missiles. Uses include solid rocket motor cases, interstages, wings, inlets, nozzles, heat shields, nosetips, structural members, and frames.

**Other Uses:** Composite structures can be formed into almost any shape to meet required needs; they increase the speed of the production process and give great flexiblity to the final product. They are used in both civilian and military aircraft, recreational products (skis, tennis racquets, boats, and golf clubs), and in infrastructure (bridge repairs and small bridges).

**Appearance (as manufactured):** Composites take the shape of the object in which they are used, but they are light compared to metallic structures.

The reinforcement used to make a composite often results in a textile-like pattern on the surface of the object, especially when prepregged cloth is used. Even when cloth is not used, the linear pattern of the tape may still be present; however, a covering like paint sometimes conceals this pattern.

**Appearance (as packaged):** Composite structures are packaged much like other structures, with foam or other materials to protect them from surface abrasions or distortions from stress. Such protection is important because their surfaces are not as hard as metal, and their strength in non-designed directions is much less than that of metal.

**Produced by companies in**

- France
- Germany
- Israel
- Japan
- Russia
- South Africa
- United Kingdom
- United States

### *Resin Impregnated Fiber Prepregs and Metal Coated Fiber Preforms*

**Nature and Purpose:** Prepregs and preforms are the basic materials from which composites structures are made. Prepreg is the name given to a cloth-like material made of fibers and impregnated with resins. Prepregs are assembled over a form (e.g., a mandrel or mold) into the desired shape. Sometimes several layers are used to create laminates. Preforms are solid, three-dimensional, fiber structures with the same shape and roughly the same dimensions as the desired part and impregnated with resin. After curing, the preform is machined into the final configuration. Usually, the materials of interest are then cured to temperatures above 175°C to complete polymerization of the resin and to achieve a high glass transition temperature.

*Photo Credit: Cytec Fiberite, Inc.*

**Figure 8-1:** Examples of prepreg yarn.

**Typical Missile-Related Uses:** Prepregs and preforms are precursors to the composites and laminates that can be used almost anywhere in ballistic missiles and UAVs, including cruise missiles. Uses include solid rocket motor cases, interstages, wings, inlets, nozzles, heatshields, nosetips, structural members, and frames.

**Other Uses:** Prepregs and preforms allow composite structures to be formed into almost any shape to meet required needs. They are used in both civilian and military aircraft, recreational products, and in infrastructure.

**Appearance (as manufactured):** Prepregs are textile products that are impregnated with a pliable resin. They are manufactured in thin filaments, tapes from submillimeters to centimeters wide, and fabrics up to a few meters wide. They are usually stored on spools or in rolls, just like yarn or fabric. Three examples of prepreg yarn are shown in Figure 8-1. Other than a very slight yellow cast on some of the materials and the stiffness or stickiness of the yarn, this material looks much like unimpregnated yarn. An assortment of yarns, fabrics, and tapes is shown in Figure 8-2. Although a prepreg can still deform, it is considerably less capable of draping than a fabric, tape, or yarn that has no resin; however, they are all still deformable enough to be shaped into a composite structural part. Prepregs may be used to form the approximate shape of a desired part, called a preform. Examples of preforms for rocket nozzle skirts are shown in Figure 8-3. After heating and curing, these preforms are machined to their final shapes and finishes.

**Appearance (as packaged):** The fibrous materials discussed here must be refrigerated after impregnation with resin. Refrigeration prevents the resin from polymerizing and hardening before the prepreg is used to manufacture composite materials. If the temperature is held at about –20°C, the shelf life of the prepreg is approximately six months. To maintain sufficiently low temperatures during shipment, the prepreg material is packed in special containers for dry ice cooling, or it is shipped in mechanically refrigerated cargo containers. A packing configuration for shipment of prepreg material with dry ice cooling is shown in Figures 8-4 and 8-5.

*Photo Credit: Cytec Fiberite, Inc.*

**Figure 8-2:** Examples of fabrics, tapes, and yarns.

*Photo Credit: Aerospatiale Espace & Defense*

**Figure 8-3:** Preforms of rocket nozzle skirts.

*Photo Credit:* A Handbook for the Nuclear Suppliers Group Dual-Use Annex, *Report No. LA-13131-M (April 1996).*

**Figure 8-4:** Special cardboard container for holding dry ice packing around a carbon fiber prepreg tape spool during shipping. The dry ice is normally contained in a plastic bag packed around the spool.

*Photo Credit:* A Handbook for the Nuclear Suppliers Group Dual-Use Annex, *Report No. LA-13131-M (April 1996).*

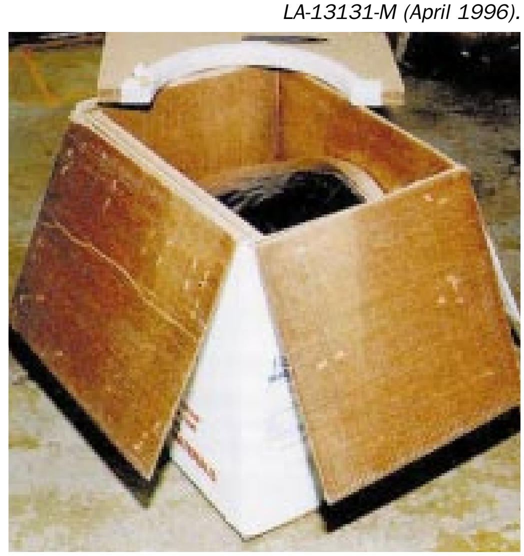

**Figure 8-5:** View of the prepreg shipping container with the lid open and the support yoke removed.

**Produced by companies in**

- France
- India
- Japan
- Russia
- United Kingdom
- United States

(b) Resaturated pyrolyzed (i.e., carbon-carbon) materials designed for rocket systems;

**Nature and Purpose:** Carbon-carbon is a composite of carbon fiber, usually made from pitch, rayon, or polyacrylonitrile (PAN), in a carbon-dominated matrix. It is usually made by using a high-content carbon resin as the initial matrix and then driving off the non-carbon elements through high heat. It is lightweight, highly heat-resistant, thermal-shock-resistant, and malleable for shaping as necessary.


**Figure 8-6:** A block of carbon-carbon material ready to be machined into a rocket nozzle. The larger cylindrical block is about 70 cm in diameter.

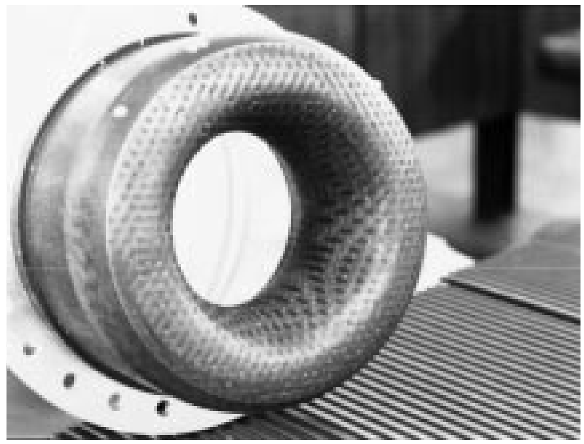

**Figure 8-7:** A carbon-carbon rocket nozzle throat showing the fabric pattern of the underlying fibers.

**Typical Missile-Related Uses:** Carbon-carbon materials are used for items such as rocket motor exit cones and nozzles, and RV nosetips, heat shields, and leading edges of control surfaces that must resist the effects of high temperatures and ablation.

**Other Uses:** Carbon-carbon structures are used in military and civilian aircraft applications such as high-temperature brake shoes, and in other applications requiring high strength and low weight such as wing roots. They can also be used for tooling requiring long life in severe, usually very high-temperature manufacturing environments, such as pouring ladles for steel, heaters for very high-temperature furnaces, and hot press tools.

**Appearance (as manufactured):** Typical carbon-carbon materials designed for rocket systems are black and have a patterned surface as a result of textile reinforcement. Nosetips and rocket nozzles are usually machined from blocks or billets or can be woven to shape. Blocks of material suitable for rocket systems and a machined rocket nozzle throat are shown in Figures 8-6 and 8-7, respectively. The nozzle throat shows the characteristic fabric pattern on its machined surface.

**Appearance (as packaged):** Before machining, blocks of carbon-carbon material are rugged enough to be packed in filler and shipped in cardboard boxes. Machined parts require careful packaging because, although the materials is resistant to breaking, it is not hard and can easily be gouged or scraped.

(c) Fine grain recrystallized bulk graphites (with a bulk density of at least 1.72 g/cc measured at 15 degrees C and having a particle size of $100 \times 10^{-6}$ m (100 microns) or less), pyrolytic, or fibrous reinforced graphites usable for rocket nozzles and reentry vehicle nose tips;

**Produced by companies in**

- Brazil
- Russia
- United States

**Nature and Purpose:** Fine-grain recrystallized bulk graphite is used to create very strong, heat-resistant parts. Graphite is the only known substance that doubles in strength as the temperature increases from room temperature to 2,700°C. Carbon particles are combined with pitch, a viscous coal tar residue, in a suitable mold and subjected to heat and pressure. The resulting block can be easily machined into the required part. It also has excellent thermal shock resistance and good thermal and electrical conductivity. Pyrolytic graphite is formed by high-temperature vapor deposition but is not widely used because its uneven thermal conductivity causes it to crack when heated.

**Typical Missile-Related Uses:** Fine-grain recrystallized bulk graphites are used for reentry vehicle nose tips, thrust tabs, and nozzle throats. A typical billet for a nosetip could be as small as several centimeters in each dimension.

**Other Uses:** Graphite is used in biomedical applications, in nuclear reactors, as a mold in casting and manufacturing metal parts, and for critically-dimensioned furnace fixtures. Graphite is also the preferred material for electrodes for electric discharge machining. When infiltrated with metals, graphite is used for brushes in electric motors and as bearings in many mechanical applications.

**Appearance (as manufactured):** Bulk graphite is a very fine, dark gray to black powder. The density of processed graphite ranges from 1.72 to 2.2 g/cc, the latter for pyrolytic graphite. Machined parts made from graphite are black and have a gloss dependent on the machining operation. Fine-grain graphite can be distinguished by its lack of surface pitting and some of the fine details that are often in the manufactured product. Graphite is much softer than metals; a ball point pen can dent the surface. Typical products that demonstrate these features are shown in Figure 8-8.

**Figure 8-8:** Various parts machined from fine grained bulk graphite.

**Appearance (as packaged):** These materials are packaged to protect their delicate surfaces and often to prevent any surface contamination. Typically, parts are placed in plastic bags or containers, which are packaged in materials normally used for fragile parts (i.e., bubble wrap, foam, etc.).

**Produced by companies in**

**Ceramic Composites**
- France
- Germany
- India
- Japan
- Russia
- United States

**Silicon Carbide Composites**
- France
- Japan
- United States

(d) Ceramic composite materials (dielectric constant less than 6 at frequencies from 100 Hz to 10,000 MHz) for use in missile radomes and bulk machinable silicon-carbide reinforced unfired ceramic usable for nose tips;

***Ceramic composite materials***

**Nature and Purpose:** Ceramic composite materials have strength and thermal properties sufficient for some use as heatshield materials. Unlike carbon-based materials, however, ceramics are insulators and do not conduct electricity, and electromagnetic radiation (e.g., radio waves) can pass through them. They are useful in protecting structures and equipment from high heat while still allowing communications to and from the vehicle.

Silicon-carbide reinforced ceramic composites are suitable for use to 1,200°C in an oxidizing atmosphere and to a somewhat higher temperature if coated. Silicon-carbide composites reinforced with filaments are very tough and, with a density of 2.3 g/cc, are considerably lighter than superalloys. These characteristics make them useable for reentry vehicle nosetips.

**Typical Missile-Related Uses:** Ceramic composite materials have been used in ballistic missile reentry vehicle antenna windows. Silicon-carbide unfired ceramic nosetips are hard and extremely heat-resistant; however, because they tend to chip but not break, they are not widely used.

**Other Uses:** High-heat-resistant ceramics are used in some gas turbine engines, automobile engines, furnaces, and solar energy receivers. Their uses include grinding rods and balls, furnace tiles, welding cups and nozzles, sandblast nozzles, and a variety of intricate parts for electronic applications. They are a common tooling material for use in manufacturing steps at elevated temperatures. Silicon-carbide reinforced ceramic composites are used in some military jet engines for thrust vector control flaps. Uses for all these materials are growing.

**Appearance (as manufactured):** Ceramic composite materials used in reentry vehicle antenna windows generally use ceramic filament reinforcement to prevent thermal-stress-induced failure. A block of 3-D silica-silica from which antenna windows are made may have a textile pattern evident on all surfaces. This material is often covered with a clear protective coating as a barrier to moisture. A silicon-carbide reinforced ceramic has the same pattern but is dark gray or black. All of these ceramic materials are very hard, much harder than other composites, and have a surface patterned like the textile reinforcement. They may be found in virtually any size between 1 mm discs and 50 cm cubes, which can be cut and ground to the required configuration by diamond tooling.

**Appearance (as packaged):** Because of their high cost and brittleness, these composites are packed in shock-absorbent materials. Since silica-silica material is also hygroscopic (i.e., it absorbs water), it is also packed in sealed bags of either mylar or other plastic, often with some type of a desiccant in the larger packing container. Some shippers also fill the sealed bags with dry nitrogen to protect the material from water absorption.

(e) Tungsten, molybdenum and alloys of these metals in the form of uniform spherical or atomized particles of 500 micrometer diameter or less with a purity of 97 percent or higher for fabrication of rocket motor components; i.e. heat shields, nozzle substrates, nozzle throats and thrust vector control surfaces;

**Produced by companies in**

- Germany
- Japan
- Russia
- United States

**Nature and Purpose:** These materials are controlled as powders, which can be formed into missile parts by pouring them into a mold and subjecting them to high heat and pressure (i.e., sintering). Parts made from these materials are very hard, dense, and strong. They also have extremely high melting temperatures: tungsten melts at 3,410°C and molybdenum at 2,610°C. Thus, finished parts are resistant to ablation in a high-heat and mass-flow environment such as those experienced in reentry or in missile exhausts.

**Typical Missile-Related Uses:** Because these materials are so dense and heavy, they tend to be used for smaller parts at critical points: reentry vehicle nosetips, nozzle throat inserts (but not the entire nozzle), and jet vanes, which are used to steer engine exhaust.

**Other Uses:** Tungsten powder is used in metal evaporation work, glass-to-metal seals, electrical contacts, and as an alloying element for steel. Tungsten carbide tool bits are critical for the metal working, mining, and petroleum industries. Molybdenum is an element used for powder metalurgy.

**Appearance (as manufactured):** Tungsten, molybdenum, and their alloys as spherical or atomized particles look like many other powder metallurgy products. The particles have a metallic sheen and flow freely because of their spherical shape. These materials are very heavy because both tungsten and molybdenum are high-density materials. Tungsten has a density of 19.3 g/cc, and molybdenum has a density of 10.2 g/cc. For comparison, iron has a density of 7.87 g/cc, and aluminum has a density of 2.7 g/cc.

**Appearance (as packaged):** These materials are packaged in sealed containers or drums to minimize contact with air and oxidation of the surface of the particles. The containers feel heavy for their size and are secured to a pallet or container to prevent movement.

**Produced by companies in**

- France
- Japan
- Russia
- Sweden
- United Kingdom
- United States

(f) Maraging steels (steels generally characterized by high nickel, very low carbon content and the use of substitutional elements or precipitates to produce age-hardening) having an Ultimate Tensile Strength of $1.5 \times 10^9$ Pa or greater, measured at 20 degrees C.

**Notes to Item 8:**

(1) Maraging steels are only covered by 8(f) above for the purpose of this Annex in the form of sheet, plate or tubing with a wall or plate thickness equal to or less than 5.0 mm (0.2 inch).

**Nature and Purpose:** Maraging steel is a particular alloy of steel noted for its high-yield strength. Typical formulations of maraging steel have relatively low carbon content (less than 0.03%) and relatively high nickel content (18 to 25%) as compared to most structural steels.

**Typical Missile-Related Uses:** The forms controlled by the MTCR (sheets, plates, and tubes) are generally used to make solid rocket motor cases, propellant tanks, and interstages.

**Other Uses:** These steels are used in special aircraft parts, submarine hulls, fencing blades, pipes, and reactors in the chemical and nuclear industries.

*Photo Credit:* A Handbook for the Nuclear Suppliers Group Dual-Use Annex, *Report No. LA-13131-M (April 1996)*

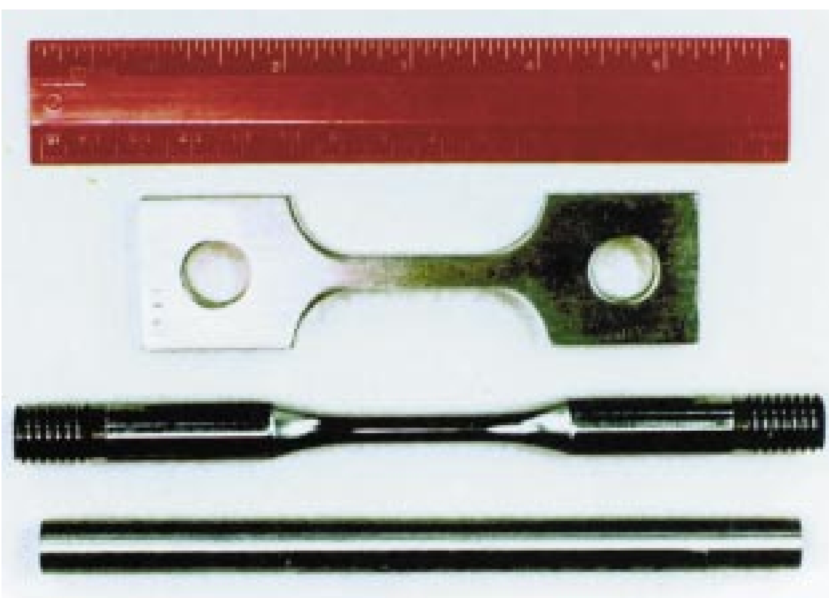

**Figure 8-9:** Top: stainless steel; middle: heat-treated maraging steel; bottom: zirconium tubing.

**Appearance (as manufactured):** Maraging steel has a lustrous gray color when clean and freshly prepared. If the metal has been subjected to an aging treatment to improve strength, it may have a dark oxide layer on the surface. This dark layer may also indicate that the maraging steel has been subjected to a controlled degree of oxidation in order to improve corrosion resistance during service. Heat-treated maraging steel and stainless steel and zirconium test samples are shown in Figure 8-9.

**Appearance (as packaged):** Maraging steel is often shipped in the low-strength, non-heat-treated condition so that it can be formed into the desired shape by the end user. It is bundled and shipped much like stainless steel, which it closely resembles. Sheets and plates are stacked and secured to a pallet. Tubes are bundled and secured to a pallet as well. Both may be covered with plastic sheet to protect them from the elements.

(g) Titanium-stabilized duplex stainless steel (Ti-DSS) having:
  (1) All the following characteristics:
    (a) Containing 17.0 to 23.0 weight percent chromium and 4.5 to 7.0 weight percent nickel, and
    (b) A ferritic-austenitic microstructure (also referred to as a two-phase microstructure) of which at least 10 percent is austenite by volume (according to ASTM E-1181-87 or national equivalents), and
  (2) Any of the following forms:
    (a) Ingots or bars having a size of 100 mm or more in each dimension,
    (b) Sheets having a width of 600 mm or more and a thickness of 3 mm or less, or
    (c) Tubes having an outer diameter of 600 mm or more and a wall thickness of 3 mm or less.

**Nature and Purpose:** Titanium Stabilized Duplex Stainless Steel (Ti-DSS) is a special alloy of stainless steel noted for its ease of welding and resistance to corrosive liquid propellant oxidizers. Typical formulations for Ti-DSS range from 17 to 23 percent by weight of chromium and 4.5 to 7.0 percent by weight of nickel, and such steel contains traces of titanium which, compared to other stainless steels, makes Ti-DSS particularly resistant to oxidizers such as Inhibited Red Fuming Nitric Acid (IRFNA). Additionally, Ti-DSS is a preferred material for liquid propellant missile applications because it is easily welded using common welding technology and, unlike other forms of stainless steel, does not require heat treatment after welding.

**Typical Missile Related Uses:** The forms controlled by the MTCR (ingots or bars, sheets, and tubes) are generally of sufficient size to be used to manufacture liquid propellant tanks and rocket engine plumbing.

**Other Uses:** There are very few known commercial uses for Ti-DSS. Although usable for many stainless steel applications, Ti-DSS is very hard, making it difficult to form into sheets or tubing. This makes it too expensive for common commercial applications. Additionally, although it is especially resistant to IRFNA, it does not perform well when exposed to other similarly corrosive materials such as chemical fertilizers.

**Appearance (as manufactured):** Ti-DSS is virtually identical in appearance to other stainless steels. It has a very fine grain, which usually requires a magnifying glass or microscope to view.

**Appearance (as packaged):** Ti-DSS is generally bundled and shipped much like other stainless steels. Sheets and ingots or bars are often stacked and secured to a pallet. Tubes are usually bundled and secured to a pallet as well. Both may be covered with plastic sheet to protect them from the elements.