Carbon-Carbon Composites: Emerging Materials for Hypersonic Flight

An emerging class of high-temperature materials called carbon-carbon composites are being developed to help make advanced aerospace flight become a reality.

Conceive of a sleek, futuristically shaped aerospace vehicle racing through the atmosphere at many times the speed of sound. Molecules of air continuously bombard the skin of the vehicle, driving its temperature up. Temperatures reach 2000°F, 2500°F, 3000°F, and even higher depending on the location on the vehicle.

An aerospace engineer engaged in designing such a vehicle would discover that lightweight materials capable of extended service at these extreme temperatures are simply not available. However, an emerging class of materials called carbon-carbon composites are presently under development to fill this need. Participating significantly in this development are the National Aeronautics and Space Administration (NASA) and the Department of Defense.

In comparison with other materials, carbon-carbon (C-C) composites are relative newcomers, having been discovered by accident in the late 1950's. Since then, these materials have been developed and improved, and are currently used in a variety of specialty applications which include friction applications as aircraft brake discs, propulsion applications as rocket nozzle throats and exit cones, and military applications as missile nose tips. Possibly the best known use of carbon-carbon composites is on Space Shuttle where it is used to protect the nose cap and leading edges of the wings from the searing heat of entry from space into the earth's atmosphere. In this role, they prevent the extreme heat generated during re-entry from reaching the main metallic structure of the Shuttle.

Because of the high-temperature strength and low density of carbon-carbon composites, aerospace engineers would like to use these materials in even more advanced applications. One application of considerable interest is as the structure of the aerospace vehicle itself rather than simply as a protective heat shield as on Space Shuttle. But suitable forms of these materials have yet to be developed. If this development can be successfully accomplished, advanced aerospace vehicles such as the National Aero-Space Plane (NASP) and other hypersonic vehicles will be closer to becoming a reality.

What Are Carbon-Carbon Composites?

Carbon-carbon (C-C) composites constitute a special subclass of composite materials. In simple terms, a composite is a material that contains both a reinforcing material to provide strength and stiffness, and a matrix material, or "glue", to surround and hold the reinforcement in place. Many types of composites exist; one everyday example is reinforced concrete in which steel rods constitute the reinforcement and the concrete is the "glue".

Somewhat more sophisticated composites are the familiar fiberglass

(NASA-TM-[illegible]) CARBON-CARBON COMPOSITES: EMERGING MATERIALS FOR HYPERSONIC FLIGHT (NASA) [illegible] CSCL 11D N90-[illegible]
Unclas G3/24 029[illegible]

composites used for fishing poles and other sporting goods, as well as automobile bodies and boat hulls and interiors. The reinforcing material in fiberglass composites is the glass fibers and the matrix material is a plastic. Carbon-carbon composites are those special composites in which both the reinforcing fibers and the matrix material are essentially pure carbon.

Fabrication

Fabricating C-C composites is time consuming and expensive. Many steps are required and commercial production times range from three to nine months, sometimes longer for material requiring special processing. Costs can run from a low of about $100/pound to well over $5000/pound depending on the size and complexity of the parts involved and the amount of processing required.

To fabricate a C-C part, one starts by first fabricating a carbon-resin part. Generally, the resin used is a phenolic resin, the same resin used in laminating plywood. Layers of carbon cloth coated with the uncured resin are stacked and formed into the desired shape using special fixtures to maintain its shape. Then the part is cured by heating in a pressurized oven, or autoclave, to temperatures near 325°F.

Following curing, the carbon-resin part is placed in a furnace and heated to a temperature near 1500°F to decompose the resin, leaving the carbon cloth bound loosely in a residue of carbon char. This resin decomposition process is called "carbonization". To prevent the part from burning up, the air in the furnace is replaced with an inert gas, typically nitrogen. For some applications, the part may be heat treated to higher temperatures, sometimes as high as 4500°F.

Although at this point in the fabrication process one has a true C-C part for the first time, the part is of little use as a structural material because the matrix of carbon char is porous and weak. Additional processing, called densification, is required to fill these pores and increase strength. Resin infiltration and carbonization, and chemical vapor deposition are the two basic methods employed.

In the resin-infiltration method, the part is immersed in liquid phenolic resin and pressure is applied to force the resin into its pores. The part is then removed from the resin, wiped clean, and cured in an oven. Then follows another carbonization. This cycle of impregnation, cure, and carbonization is typically repeated three or more times until the desired properties are obtained. Sometimes petroleum or coal tar pitch is used for densification in place of the phenolic resin.

In the chemical-vapor-deposition method, the porous part is heated in a reactor to near 2000°F in the presence of a hydrocarbon gas such as methane. The methane gas enters the pores and decomposes on contacting the hot part, depositing carbon within the pores. Several days to several weeks may be required to complete this process.

Regardless of which of the two densification methods are employed, the carbon reinforcing fibers ultimately become bound within a matrix of essentially pure carbon and the desired strength is achieved.

If oxidation protection is required for the intended end application, additional processing is necessary; otherwise, the part is ready to enter service at this point.

The Challenge of Oxidation Protection

Carbon burns, i.e., oxidizes, readily in air at high temperatures. Coal is one common form of carbon, and coal is known to be a good fuel. Carbon-carbon composites will similarly oxidize in high-temperature air unless they are adequately protected. Thus, the challenge facing materials scientists amounts to this: how can one prevent this material, which is a good fuel, from burning in high-temperature air? Because C-C composites offer such outstanding advantages as high-temperature structure--advantages that are not available in other materials--the challenge has been accepted.

Oxidation Protection Concepts

Materials scientists are exploring various approaches for achieving the necessary oxidation protection. Research is intensive, and, although many variations exist, most oxidation-protection concepts include certain basic features. In most concepts, the first line of defense consists of an oxidation-resistant coating. This coating is typically a layer of silicon carbide about 0.01 inches thick. Silicon carbide is particularly useful because it forms an extremely thin layer of protective silica glass when exposed to high-temperature air. This thin layer blocks further oxygen attack of the silicon carbide coating, and the coating, in turn, encapsulates and protects the C-C structure.

Unfortunately, all is not this simple. Both the silicon carbide coating and the C-C structure being protected expand and contract with changes in temperature during service. Since the extent of this expansion and contraction is not the same for these two materials, many fine cracks form in the coating. Oxygen can enter through these cracks and attack the C-C structure.

To prevent this attack, a second line of defense is employed. This defense consists of glazes applied to the surface of the coated part and glassy sealants within the pores of the C-C structure. The purpose of the glazes is to fill the cracks in the coating and, hence, block access of oxygen to the C-C structure, while the purpose of the glassy pore sealants is to coat the interior surfaces of the pores and prevent direct contact of oxygen with the carbon.

Still, all is not resolved. Carbon begins to oxidize at a significant rate at temperatures as low as 1000°F, and glazes and sealants which are effective over the broad temperature range encountered in flight have not yet been developed. Hence, a third line of defense is needed. This third line of defense consists of various additives distributed within the carbon matrix. The purpose of these additives is twofold: consume any oxygen reaching the C-C structure, and form additional quantities of protective glasses within the pores. Unfortunately, these additives are activated by oxidation and during this activation some matrix carbon is also oxidized with a resulting loss of mechanical properties of the C-C part.

Occasionally a fourth line of defense is employed. Oxidation-resistant coatings may be applied to the reinforcing fibers themselves, or additives may even be distributed within them. These approaches are highly experimental.

Were it not for the fact that the first line of defense, the silicon carbide coating, developed cracks, none of the additional defenses would be needed. Therefore, materials scientists are trying to reduce or eliminate coating cracks by formulating coatings of different composition and by employing transition layers between the coating and the C-C core. To date, no approach has been fully successful.

Many variations of the above schemes have been explored. The basic goal remains the same, however: to develop adequate oxidation protection in high-temperature air without compromising the desirable mechanical properties of the C-C structure being protected.

Space Shuttle

On Space Shuttle, an oxidation-resistant carbon-carbon (ORCC) composite is used to protect the nose cap and the leading edges of the wings from temperatures as high as 2500°F as the Shuttle reenters the earth's atmosphere from orbit. The ORCC material is bolted to the vehicle main structure, standing off in front of it to protect it from the extreme heat of reentry. This ORCC material, designed to be serviceable for up to 100 missions, has performed well and in accord with expectations. This material is the only reusable ORCC composite in service today.

Advanced Hypersonic Vehicles

Since ORCC composites have done an outstanding job on the Space Shuttle, aerospace engineers would like to employ them in even more demanding applications. On Space Shuttle, the ORCC composite does not form part of the vehicle structure, but serves as a heat shield only. However, if both the vehicle structure and the heat shield could be integrated together with one single material serving both functions, one could realize a substantial savings in weight. Such an integrated system is referred to as "hot structure". Plans for advanced hypersonic vehicles depend on the availability of a suitable hot structure. Presently, ORCC composites are the main candidates for this purpose, but no suitable advanced forms of ORCC composites are yet available.

Requirements for hot structure are more demanding than for a heat shield material. It is clearly not practical to replace main vehicle structure periodically the way one could replace a much smaller, removable heat shield. Hence, design engineers demand longer life capability from a hot structure component than the 100 missions for Space Shuttle ORCC parts. Also, skin temperatures predicted for advanced hypersonic vehicles are considerably higher than for Space Shuttle, approaching 3000°F, and possibly higher. Increased strength is also needed if ORCC composites are to serve as efficient primary structure.

What alternatives are there to employing ORCC composites for hot structure? If more conventional materials had to be depended on, design engineers would have to employ some method of cooling to maintain the structure at temperatures low enough to enable their use. But such cooling systems are complex and heavy. For example, heat exchangers, pumps, and a myriad of fine cooling passages would be required. Estimates of the weight associated with cooled metal structure range from 4 to 11 times the weight for carbon-carbon composites. Such heavy cooling systems would seriously compromise vehicle performance and even prevent certain performance objectives from being met.

There is no question that the problems faced in developing advanced forms of structural ORCC composites are great. But the potential payoffs also are great. In fact, some consider ORCC composites to be essential to the successful development of the U.S.'s best known proposed advanced aerospace vehicle, NASP.

Other Applications

As mentioned briefly earlier, C-C composites are currently used in various applications. Mostly, these are specialty applications related to the aircraft, military, or aerospace arenas where the performance available only from C-C composites is the primary consideration rather than cost.

One example of an application of quite a different nature exploits the fact that carbon is a material that is highly compatible with human tissue. Because of this compatibility and the high strength and low weight of C-C composites, interest is growing to use these composites as artificial bone implants.

The largest commercial market for unprotected C-C composites is aircraft brakes. In these applications, C-C composites are used as the friction discs in the brake system. Weight savings compared with steel can be substantial, as high as 60 percent. Because brake temperatures on typical landings are below 900°F, oxidation is not a serious issue and lifetimes of 3000 landings are possible.

Military and aerospace applications are far more demanding. Typical applications include missile nose tips and rocket nozzle throats and exit cones. Service life in these single-use applications is short--minutes to a few hours--and unprotected C-C is employed. Although the C-C component erodes during service, this erosion is accounted for in the design of the component, ensuring that the mission is completed before all the material is consumed.

Oxidation-resistant carbon-carbon composites are less mature materials but they offer significant performance payoffs for manned, reusable aerospace vehicles. Applications, already discussed, include the thermal protection material for NASA's Space Shuttle and airframe structure for advanced hypersonic vehicles. Other applications where reusability and long life are required include turbine engine rotors and other propulsion components in aircraft turbine engines.

Additional Challenges

Developing a high-strength, oxidation-resistant C-C composite is only the first step in meeting the challenge. Additional challenges must also be overcome before aerospace design engineers can utilize these composites in their vehicle designs.

For airframe structure, engineers need large panels, on the order of 4 feet by 10 feet. Most will need stiffeners and will be in a variety of complex shapes. Processing equipment and advanced processing methods not available today are needed to fabricate these panels in sufficient size and with consistent and uniform high quality essential to aircraft structure.

Design engineers strive towards the lightest structure possible since lighter structure provides greater payload capability or greater fuel capacity for increased vehicle range and mission flexibility. If stronger ORCC composites can be developed, they can be made thinner--and, hence, lighter weight--for a given load carrying capability. Current minimum thicknesses are on the order of 0.07 inch.

For a complete fuselage or wing structure, engineers need effective methods to attach and join various parts together. Some fasteners may be exposed to the same high-temperature environment as the ORCC itself. Hence, improved fasteners and joints need to be developed.

These and other problems need resolution. They are currently being addressed b NASA's Langley Research Center, the Department of Defense, and private industry. Much current research is being conducted under the sponsorship of the National Aero-Space Plane Joint Program Office in a concerted effort to find effective solutions as quickly as possible. I believe these solutions will be found. Some day, carbon-carbon composites--these materials with their rather curious name--will eventually make their mark by contributing to the reality of hypersonic flight.

Howard G. Maahs is Assistant Branch Head of the Applied Materials Branch, Materials Division, at the NASA Langley Research Center, Hampton, Virginia.

LIST OF ILLUSTRATIONS

(1) [Hypersonic vehicle photo]
One example of an advanced aerospace vehicle operating at hypersonic speeds is shown in this artist's rendition. Hypersonic speeds are those speeds in excess of five times the speed of sound. For comparison, the supersonic Concorde flies at only up to twice the speed of sound. At hypersonic speeds, aerodynamic heating can become severe causing the surface to glow red to white hot.

(2) [Hypersonic vehicle isotherms]
Representative maximum temperature isotherms (in °F) are shown for a conceptualized hypersonic vehicle. Local temperatures depend on vehicle configuration, flight trajectory, and speed. No lightweight structural materials are available for use at temperatures above about 1600°F.

(3) [Specific strength]
Strength is an engineering property of considerably importance. A convenient means of ranking different materials for structural applications when both high strength and low weight are important is the strength of the material divided by its density. This figure reveals that at temperatures above about 1600°F, carbon-carbon composites are unrivaled by other known materials.

(4) [Fabrication processing]
Many steps are required to fabricate carbon-carbon composites. This block diagram indicates the basic steps involved in fabricating unprotected carbon-carbon materials. Many variations are possible.

(5) [Laying up impregnated fabric]
Fabrication of a carbon-carbon part starts by first fabricating a carbon-resin part. In this photograph, a carbon cloth impregnated with an uncured phenolic resin is being smoothed down on a gently contoured mold plate. Additional layers of cloth will be stacked until the desired thickness is reached. Each layer is smoothed as it is laid down using a heat gun as an aid in softening the tacky phenolic resin. Finally, the laid-up part will be cured in an autoclave. (Source: LTV Missiles and Electronics Group)

(6) [Pyrolysis fixture and I-beam]
Special fixtures are employed to maintain the shape of carbon-carbon parts during cure and carbonization. A simple structural shape, an I-beam, is shown at the right while the special fixturing (made of graphite) used to maintain this shape during carbonization is shown at the left. (Source: LTV Missiles and Electronics Group)

(7) [Space Shuttle]
The nose cap and wing leading edges of the Space Shuttle reach temperatures of 2500°F. They are oxidation-resistant carbon-carbon composites. Although popular attention has focused mostly on the ceramic tiles which protect the lower surfaces of the vehicle, these tiles are not serviceable at the higher temperatures experienced by the nose cap and wing leading edges.

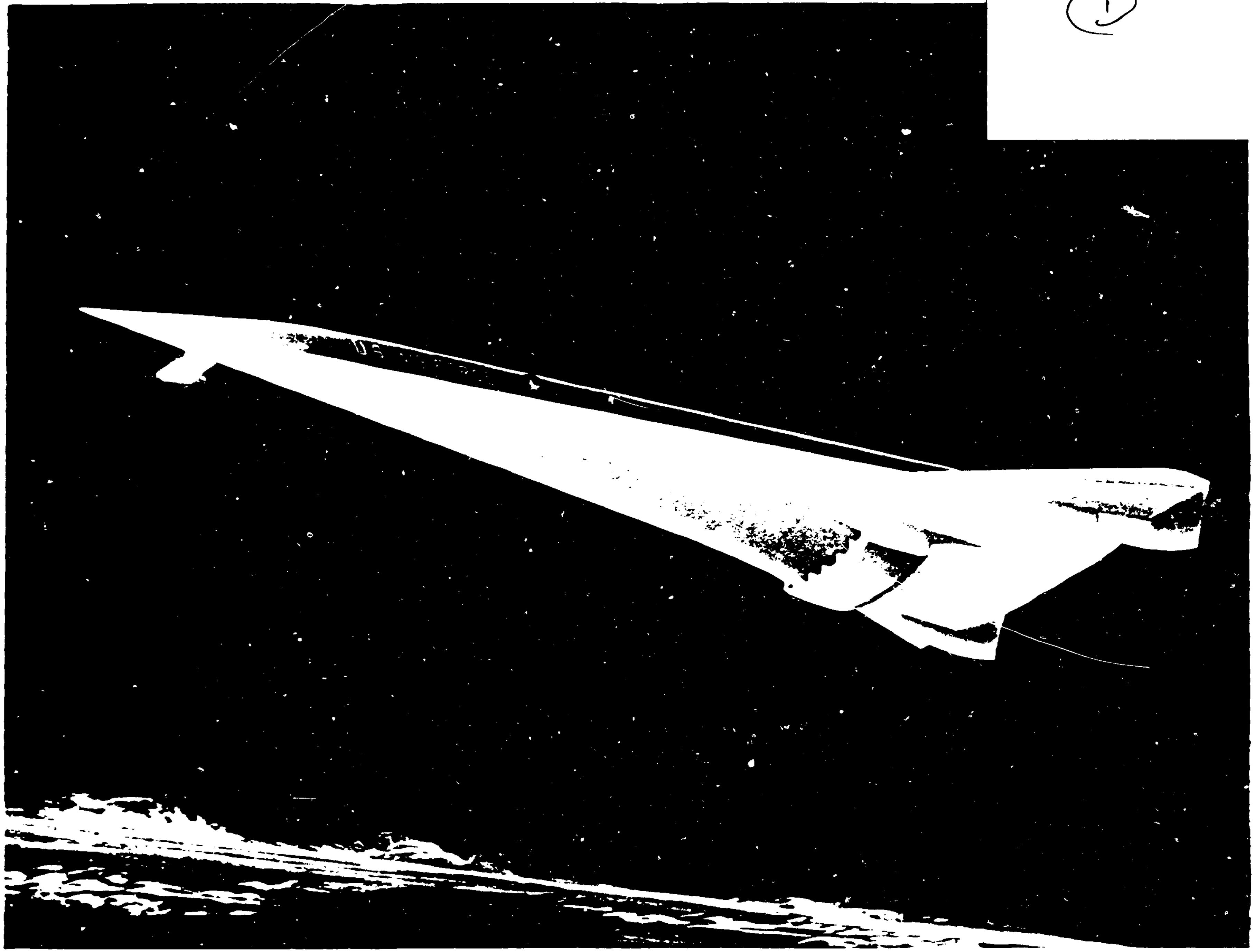
(8) [Leading edge attachment]
The oxidation-resistant carbon-carbon wing leading edge of the Space Shuttle is attached to the wing structure in sections. The forward wing spar with attachment hardware is shown at the right. A portion of the curved carbon-carbon heat shield is visible at the left. In flight, the main airflow approaches from the lower left. The protective cover over much of the heat shield is used to prevent accidental damage during assembly and inspection. (Source: NASA Johnson Space Center)

(9) [Oxidation-protection schemes]
Numerous schemes have been explored for protecting carbon-carbon composites from oxidation. The basic features of most of these schemes are depicted in this schematic drawing (not to scale). Many variations of these basic features exist.

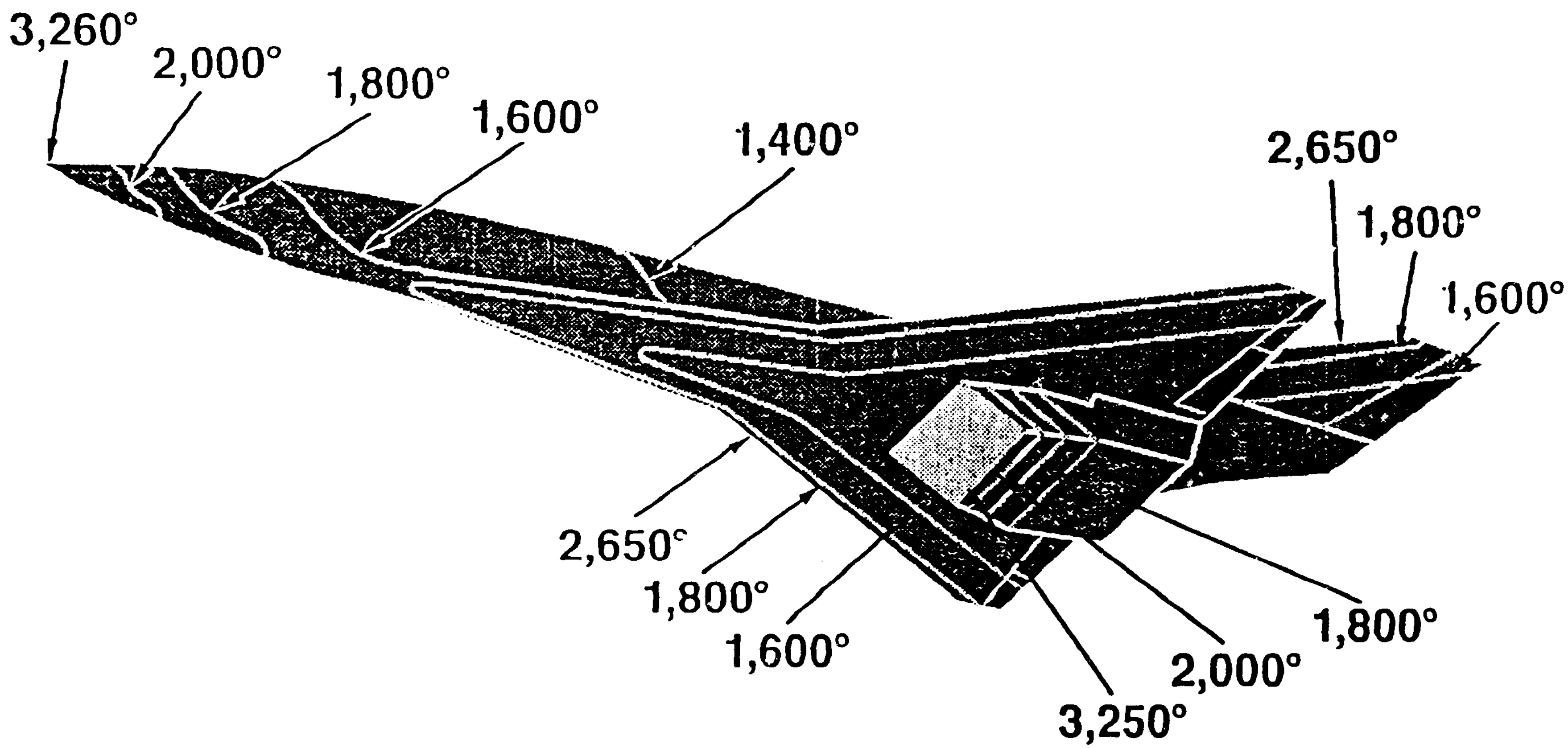
(10) [Stiffened panel]
Efficient airframe structure requires large, stiffened panels in complex shapes. This small, 12-inch long panel illustrates the complex shapes which can be fabricated from carbon-carbon composites. (Source: BFGoodrich Aerospace & Defense Divison)

L-72-7123

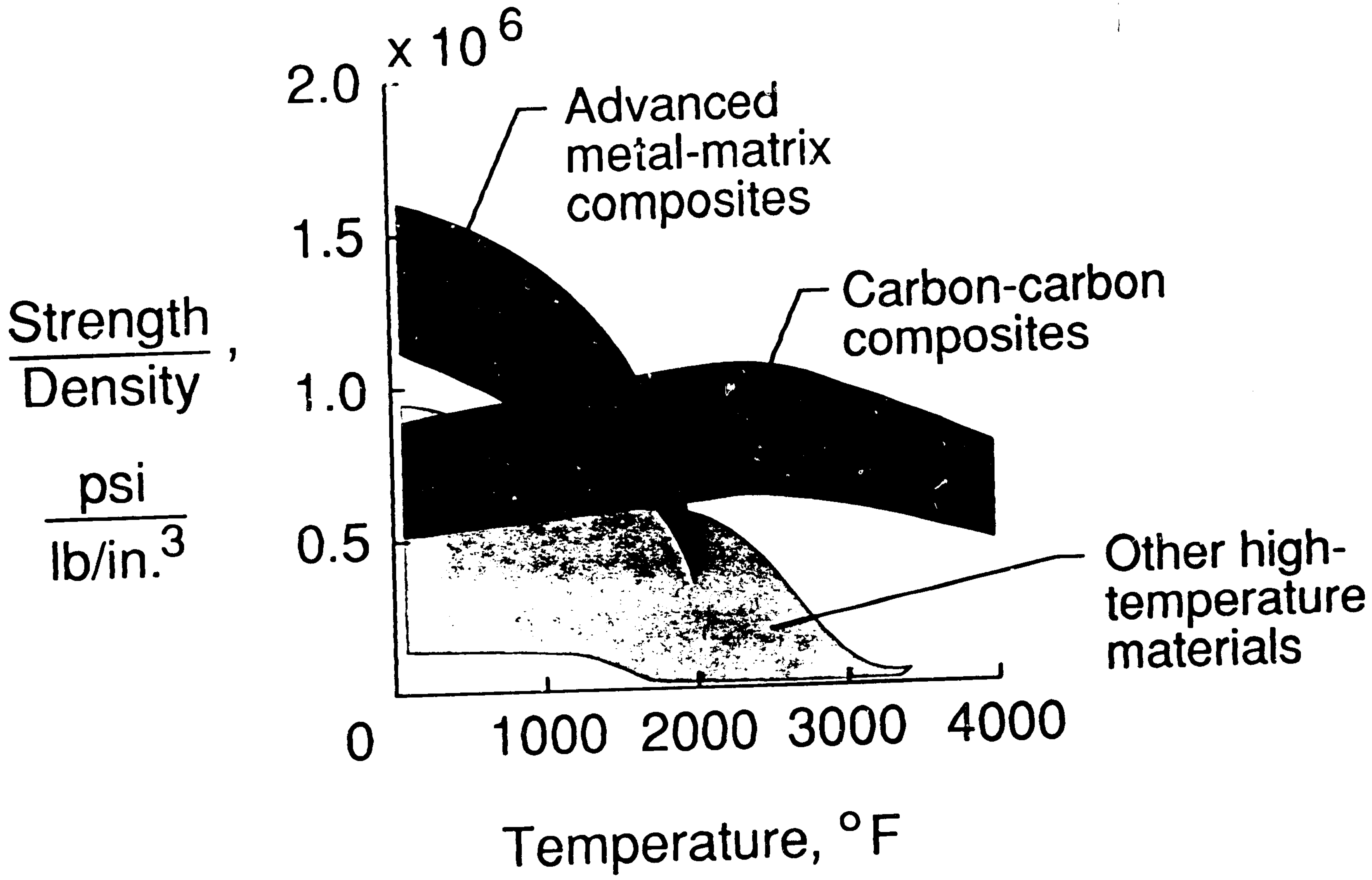
1



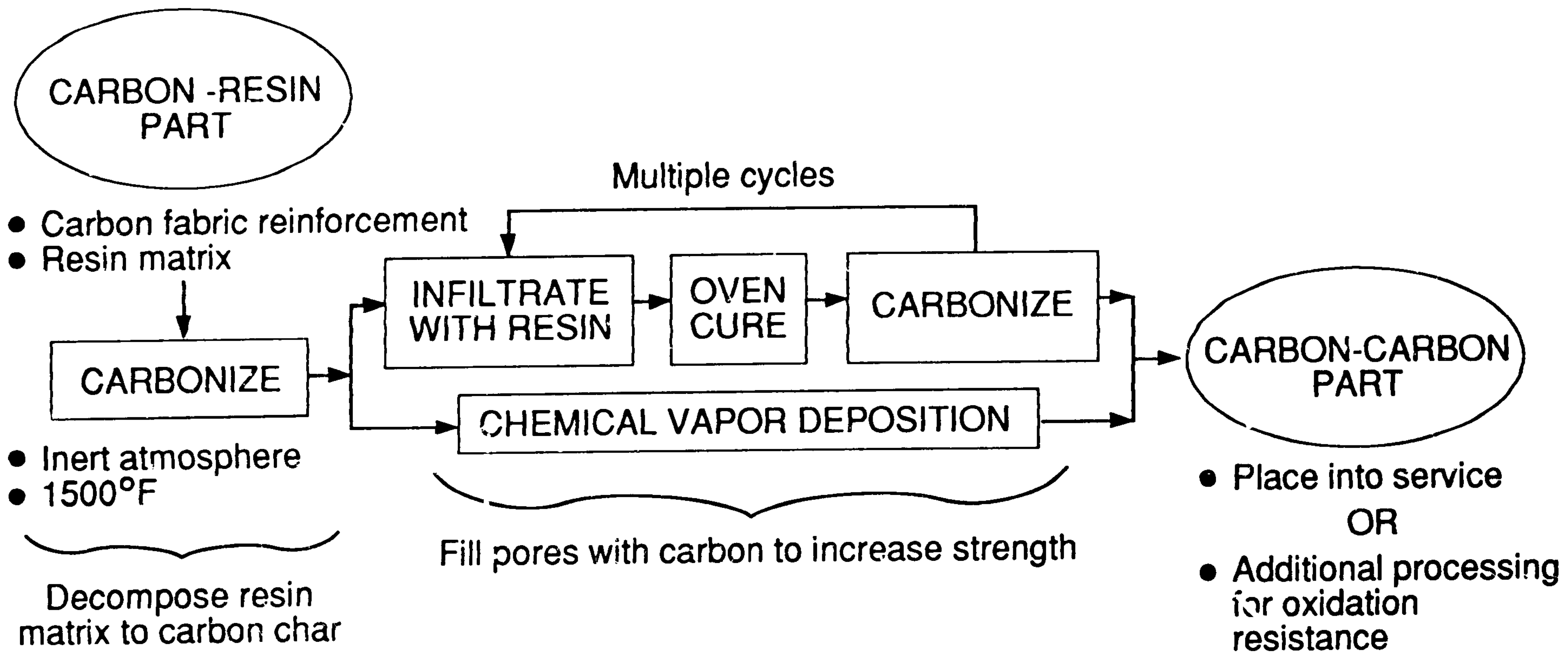
2

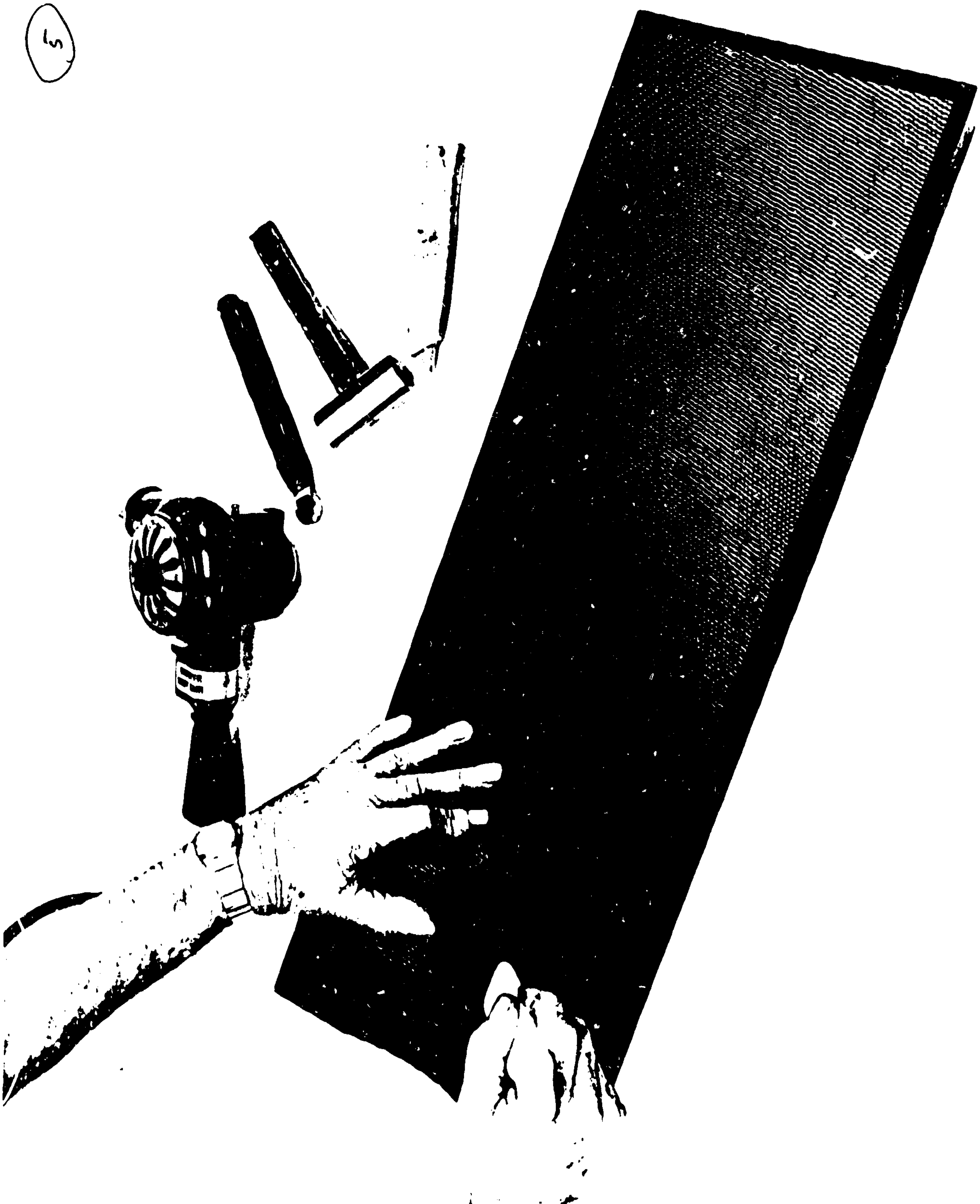

3,260°
2,000°
1,800°
1,600°
1,400°
2,650°
1,800°
1,600°
2,650°
1,800°
1,600°
1,800°
2,000°
3,250°

3

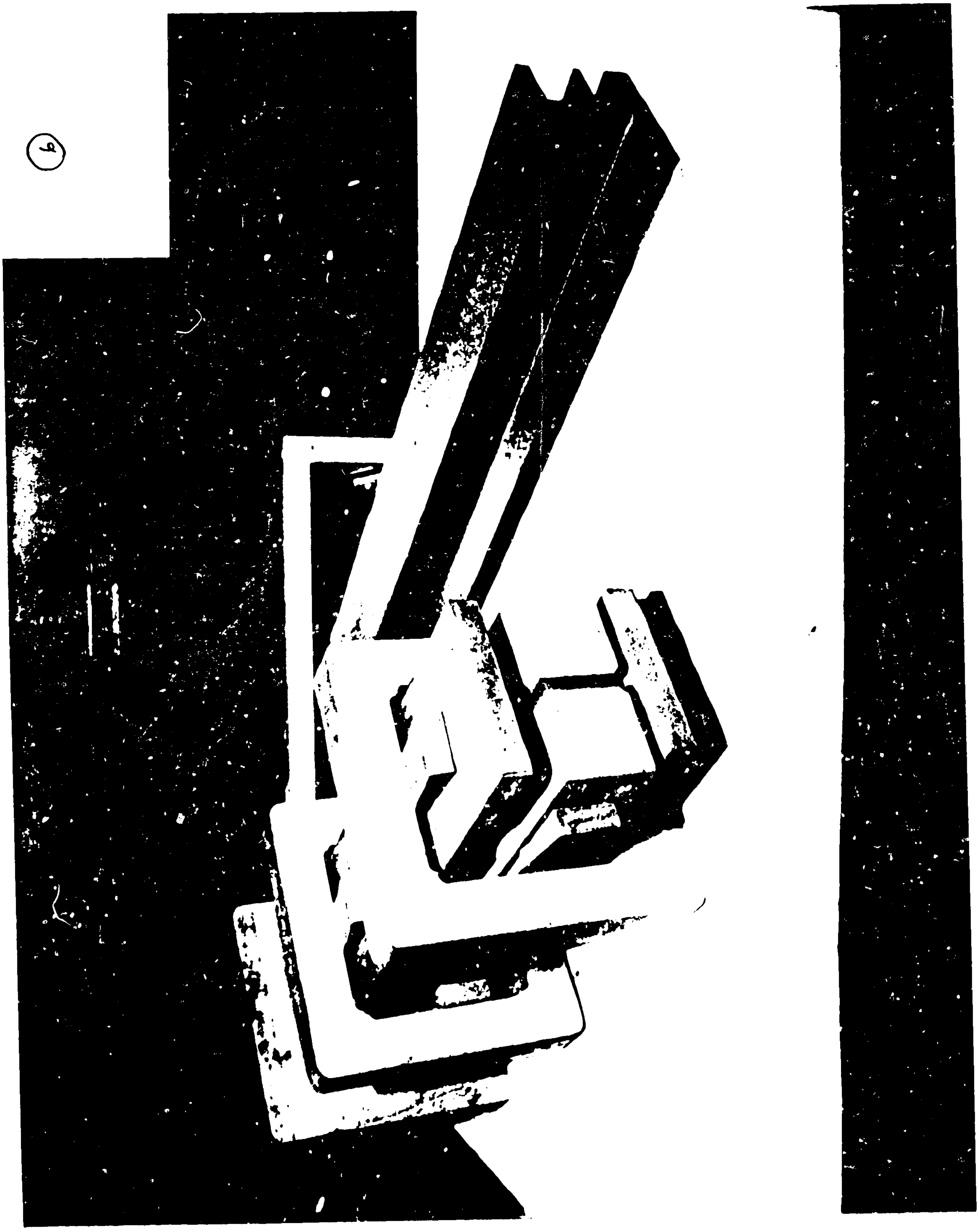

x 10^6
2.0
1.5
1.0
0.5
0
Strength/Density, psi/lb/in.^3
Advanced metal-matrix composites
Carbon-carbon composites
Other high-temperature materials
1000
2000
3000
4000
Temperature, °F

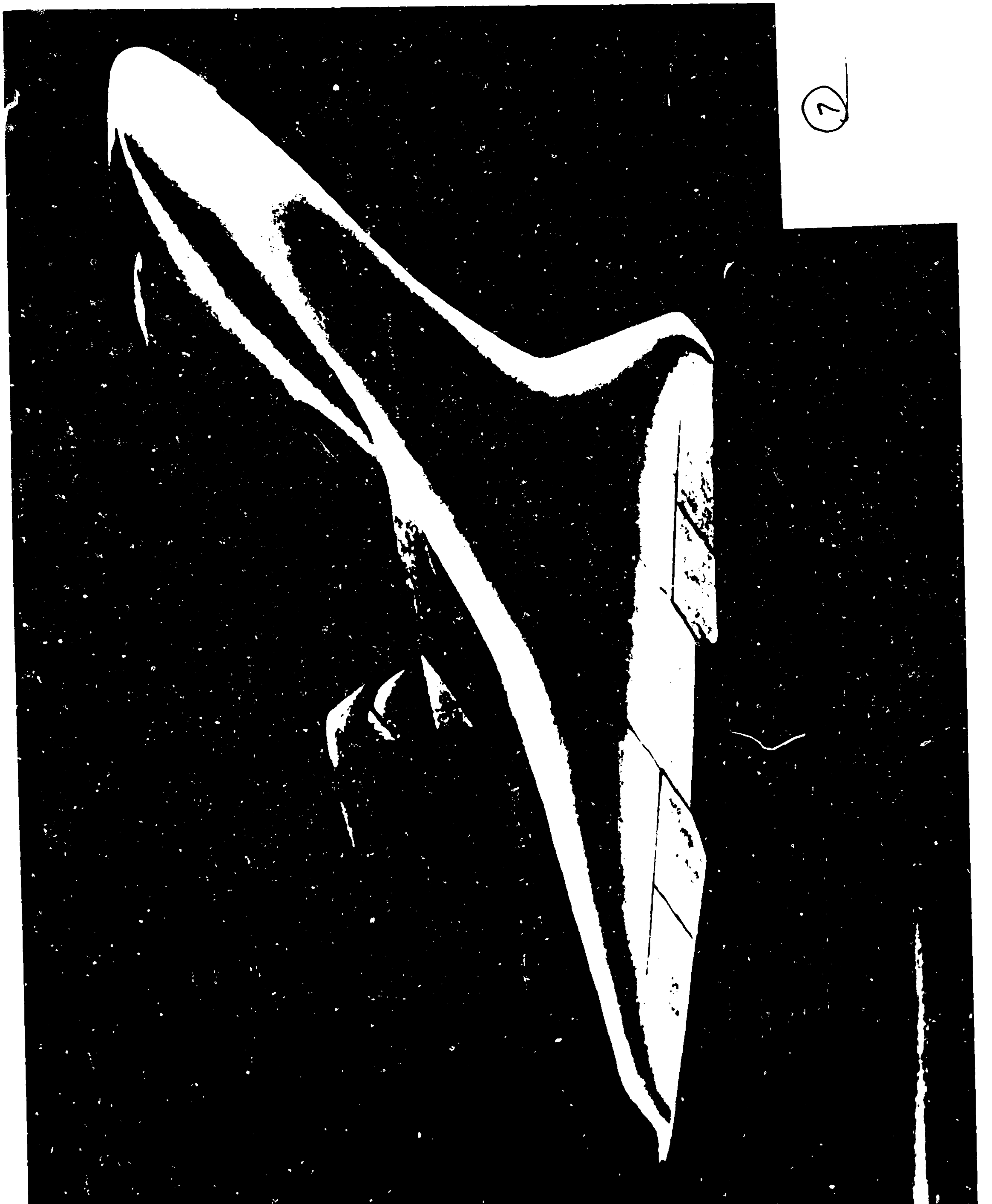
4


CARBON -RESIN PART
• Carbon fabric reinforcement
• Resin matrix
CARBONIZE
• Inert atmosphere
• 1500°F
Decompose resin matrix to carbon char
Multiple cycles
INFILTRATE WITH RESIN
OVEN CURE
CARBONIZE
CHEMICAL VAPOR DEPOSITION
Fill pores with carbon to increase strength
CARBON-CARBON PART
• Place into service
OR
• Additional processing for oxidation resistance

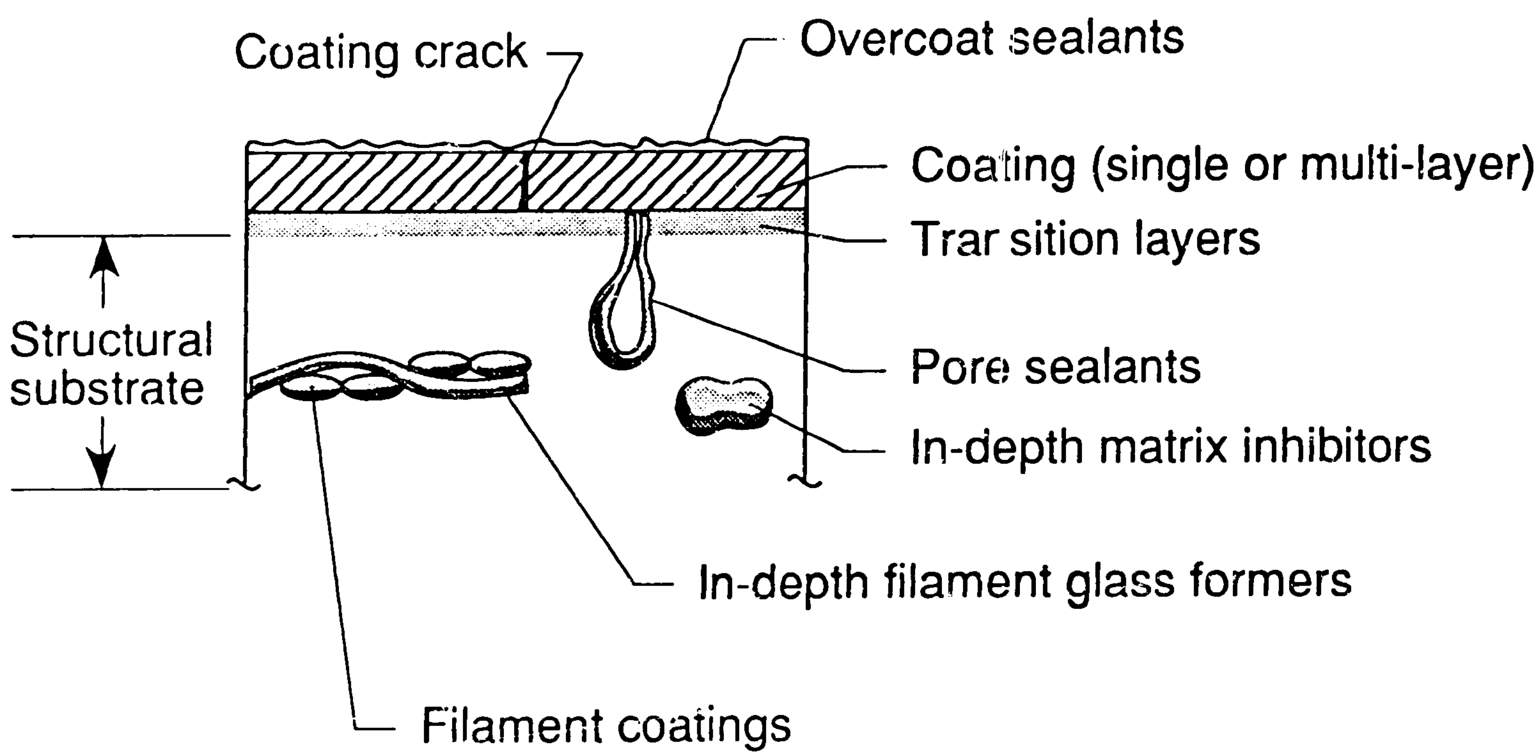


9

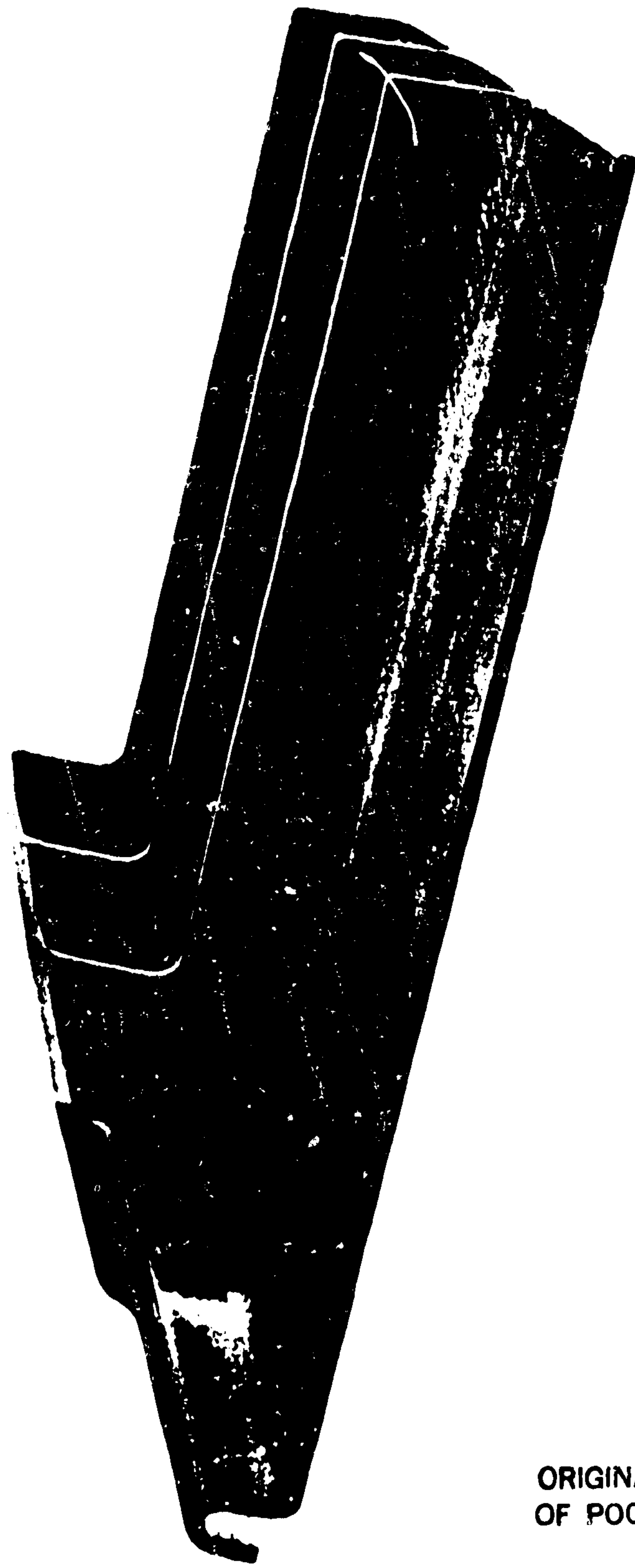




8


Coating crack
Overcoat sealants
Coating (single or multi-layer)
Transition layers
Structural substrate
Pore sealants
In-depth matrix inhibitors
In-depth filament glass formers
Filament coatings

10



END

DATE

FILMED

SEP 21 1990