RECENT ADVANCES IN CARBON-CARBON MATERIALS SYSTEMS

Donald R. Rummler
NASA Langley Research Center
Hampton, Virginia

INTRODUCTION

The development and/or improvement of materials systems for application to aerospace vehicles is a continuing research activity within NASA. The evolution of aerospace materials (figure 1) has been coupled with the development of faster vehicles and more efficient engines since the beginning of flight. In many cases the development of new or improved materials enabled the vehicle or engine advances. This continuing evolution has always pointed toward stronger, stiffer, lighter, and higher use temperature materials.

One of the most recent materials systems to evolve for aerospace application is reinforced carbon-carbon (RCC). This class of materials will have application to thermal protection systems, hot structures, and engines that may operate at temperatures in excess of 4000°F.

This paper will briefly discuss carbon-carbon materials and new oxidation-resistant coating developments for carbon-carbon and will highlight potential areas of application. A short bibliography of selected references is included that describe carbon-carbon materials and related technology in detail.

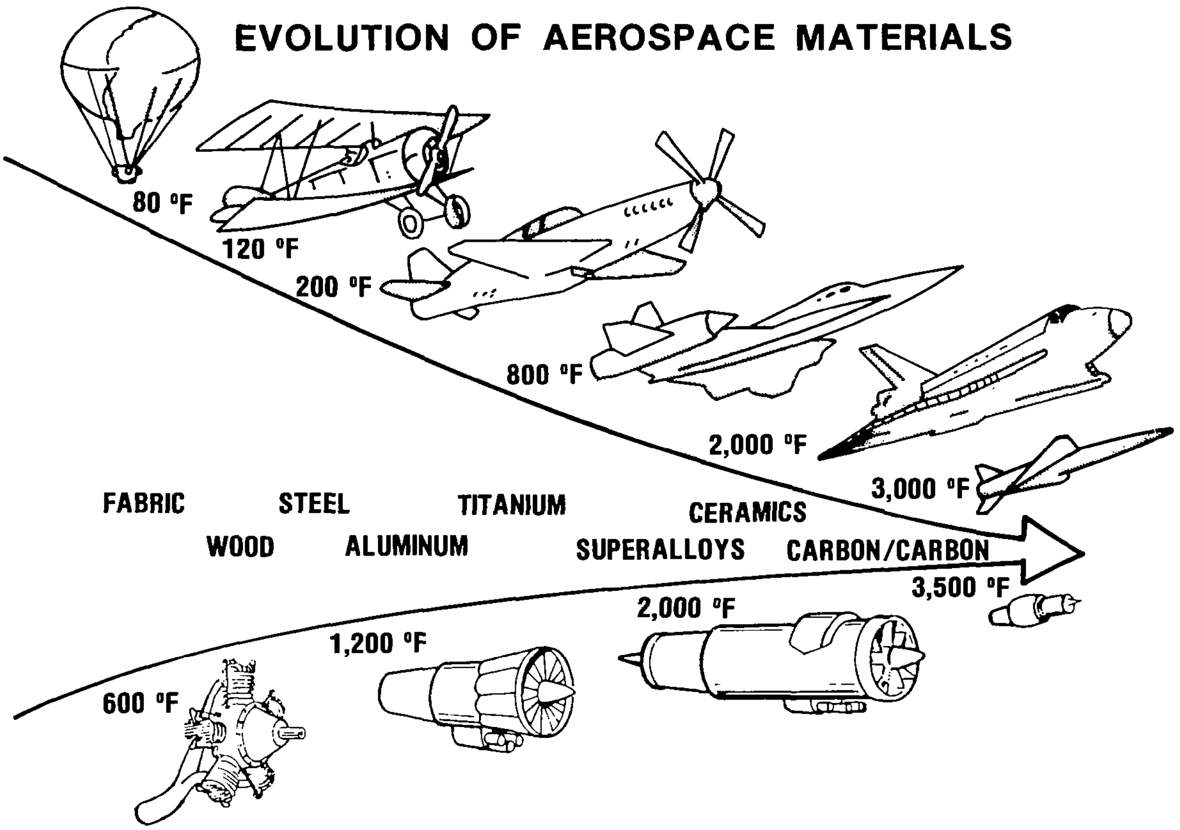


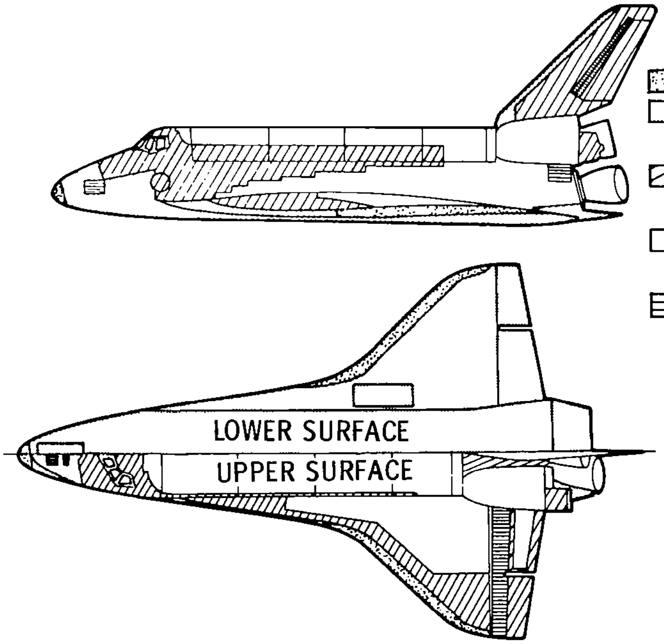
Figure 1

SHUTTLE THERMAL PROTECTION SYSTEM

The materials systems used for the Shuttle Orbiter thermal protection system (TPS) are shown in figure 2. Most of the Orbiter surface is covered with silica-based ceramic tiles. However, a small percentage of the surface (the nose cap and leading edges) is exposed to temperatures up to 3000°F. This environment is beyond the capabilities of the silica tiles. Candidate materials for these areas included oxide ceramics, coated refractory metals, bulk graphite, and carbon-carbon. The material selected was reinforced carbon-carbon (RCC), one member of the growing family of carbon-carbon materials. For this application, the RCC is coated with silicon carbide and then impregnated with silica to provide oxidation protection to the carbon-carbon substrate.

The selection of RCC was based upon the following requirements: (1) maintenance of reproducible strength levels to 3000°F, (2) sufficient stiffness to resist flight loads and large thermal gradients, (3) low coefficient of thermal expansion to minimize induced thermal stresses, (4) oxidation resistance sufficient to limit strength reduction, (5) tolerance to impact damage, and (6) manufacturing processes within the state of the art.

It is this rare combination of properties that makes the emergence of carbon-carbon materials such a rich area for materials research and development. When they are fully developed carbon-carbon materials may represent the same kind of breakthrough in high-temperature materials as was provided by the development of nickel- and cobalt-based superalloys.



░ REINFORCED CARBON-CARBON (RCC)
▭ HIGH-TEMPERATURE, REUSABLE SURFACE INSULATION (HRSI)
▨ LOW-TEMPERATURE, REUSABLE SURFACE INSULATION (LRSI)
□ COATED NOMEX FELT REUSABLE SURFACE INSULATION (FRSI)
☰ METAL OR GLASS

ELEMENT*	AREA, sq ft	WEIGHT, lb
FRSI	3851	1173
LRSI	2741	2236
HRSI	5164	9728
RCC	409	3742
MISCELLANEOUS		2025
TOTAL	11895	18 904

*INCLUDES BULK INSULATION, THERMAL BARRIERS, AND CLOSEOUTS

Figure 2

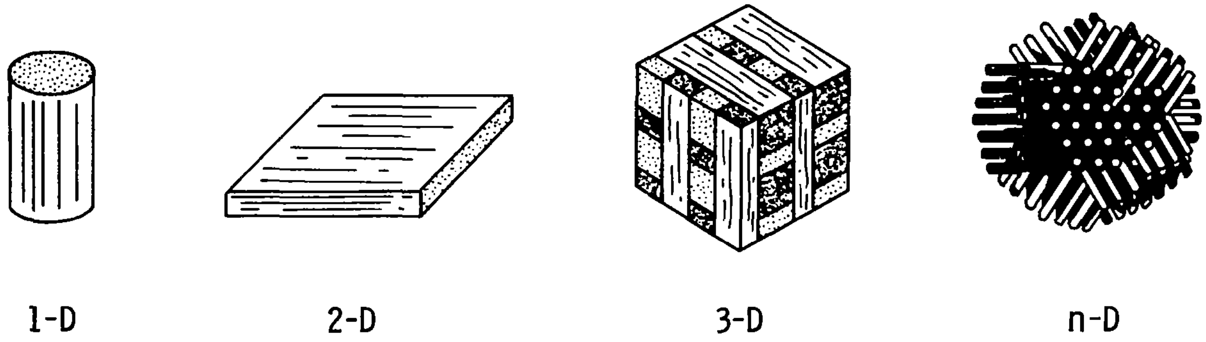
CARBON-CARBON ATTRIBUTES

Carbon-carbon materials are a generic class of composites much like the graphite/epoxy family of polymer matrix composites (figure 3). They can be made in a wide variety of forms, from one-dimensional to n-dimensional, using unidirectional tows, tapes, or woven cloth. Because of this multiformity their mechanical properties can be readily tailored. Currently our primary research interest is in two-dimensional (2-D) carbon-carbon materials that use woven carbon cloth as a precursor. The properties and applications discussed in this paper will concentrate on 2-D carbon-carbon materials.

Carbon materials have high strength and stiffness potential as well as high thermal and chemical stability in inert environments. They must, however, be protected with coatings and/or surface sealants when used in an oxidizing environment.

Carbon-carbon materials have high thermal conductivity and low thermal expansion. These two properties combine to make carbon-carbon materials very resistant to thermal shock. Low density (about 70 percent of that of aluminum alloys) is an additional desirable property of this class of materials.

- MULTIFORMITY



- HIGH STRENGTH POTENTIAL
  $\sigma_{ULT} > 40\ 000$ psi $E > 10^7$ psi
- HIGH THERMAL AND CHEMICAL STABILITY
  $T_{MP} > 7400\ ^{\circ}F$ $K \sim 60$ BTU - in/hr - ft^2 - $^{\circ}F$ $\alpha \sim 2 \times 10^{-6}\ ^{\circ}F^{-1}$
- LOW DENSITY
  $\rho < 0.07$ lbm/in^3

Figure 3

STRENGTH EFFICIENCY OF VARIOUS MATERIALS

The effect of temperature on the ratio of tensile strength to density for several classes of high-temperature materials is shown in figure 4. The major advantage of carbon-carbon materials for high-temperature applications is that they do not lose strength as the use temperature is increased. This is in contrast to other structural materials such as superalloys and ceramics.

This figure shows three levels of carbon-carbon strength efficiency. The first, labeled Shuttle material, is the strength level of the RCC material used in the Shuttle thermal protection system. Even though this material is made with low-strength carbon fibers, its strength efficiency is superior to both superalloys and ceramics at temperatures above 1800°F. Recent research has led to the development of an advanced carbon-carbon (ACC) that is twice as strong as the RCC. This material is currently being evaluated by a number of laboratories. The ACC material is made up using woven carbon cloth. If unidirectional carbon fiber tapes are interplied with woven cloth to create a hybrid ACC, its strength in at least one direction can be increased to 50,000 psi or more. Research on hybrid ACC is just beginning.

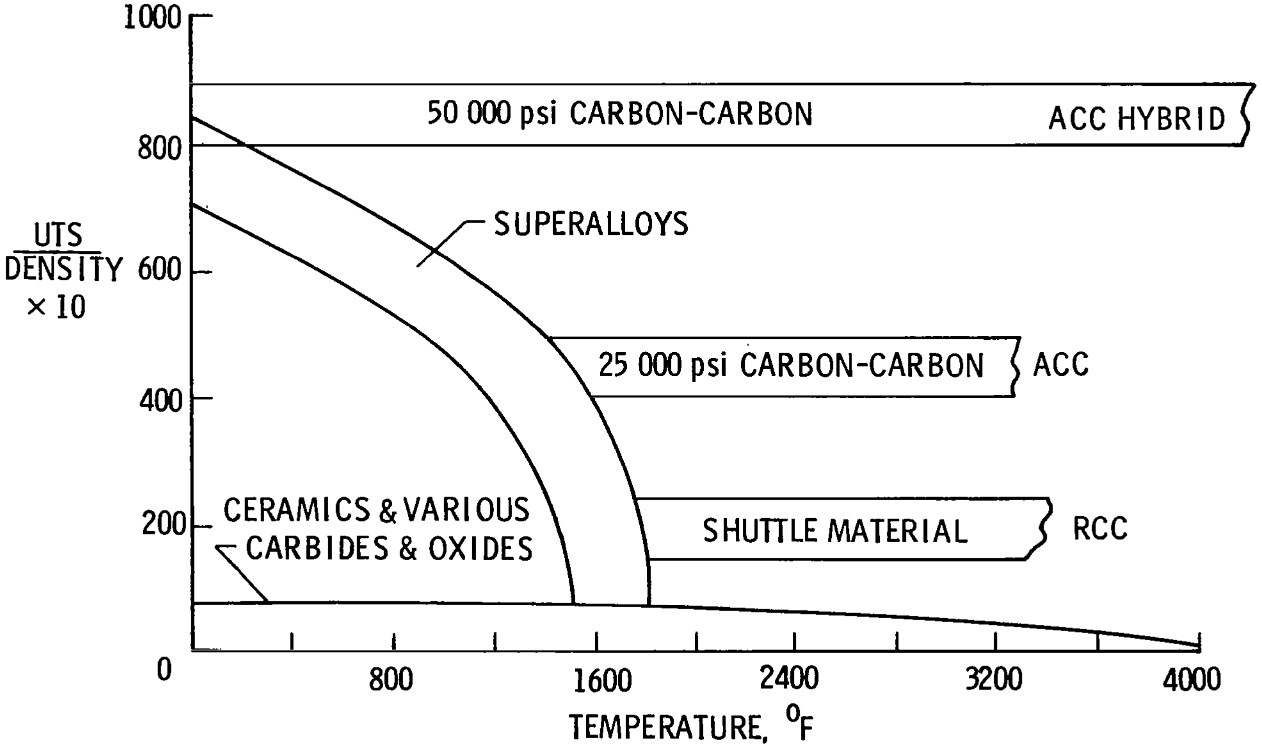


Figure 4

TYPICAL MANUFACTURING CYCLE OF 2-D Carbon-Carbon

A summary of the fabrication steps involved in the manufacture of a 2-D carbon-carbon part is shown in figure 5. First the woven graphite fabric, which is preimpregnated with phenolic resin, is laid up as a phenolic-graphite laminate in a mold and is autoclave cured. Once cured, the part is pyrolyzed to form a carbon matrix surrounding the graphite fibers. The part is then densified by multiple furfural alcohol reimpregnations and pyrolyzations. The resulting carbon-carbon part is ready for use in inert environments. The process is very time consuming. For instance, a single pyrolysis step may take more than 70 hours in a low-temperature inert-atmosphere furnace. Research is currently under way to reduce the processing time and consequent cost of carbon-carbon parts.

For application in oxidizing environments, such as on the Shuttle, the carbon-carbon parts must be coated and sealed to protect them. For the Shuttle application the outer surfaces of the parts are converted to silicon carbide in a high-temperature diffusion coating process. Because of differences in thermal expansion between the silicon carbide and the carbon-carbon part, the coating develops microcracks when the part is cooled from the coating temperature. For the Shuttle these cracks are impregnated with tetraethyl orthosilicate (TEOS). The TEOS process leaves silica (SiO_2) in all of the microcracks, greatly enhancing the oxidation protection of the carbon-carbon substrate. Recent research has been concentrating on the application of surface sealants to further improve oxidation resistance. These improvements will be discussed later in this paper.

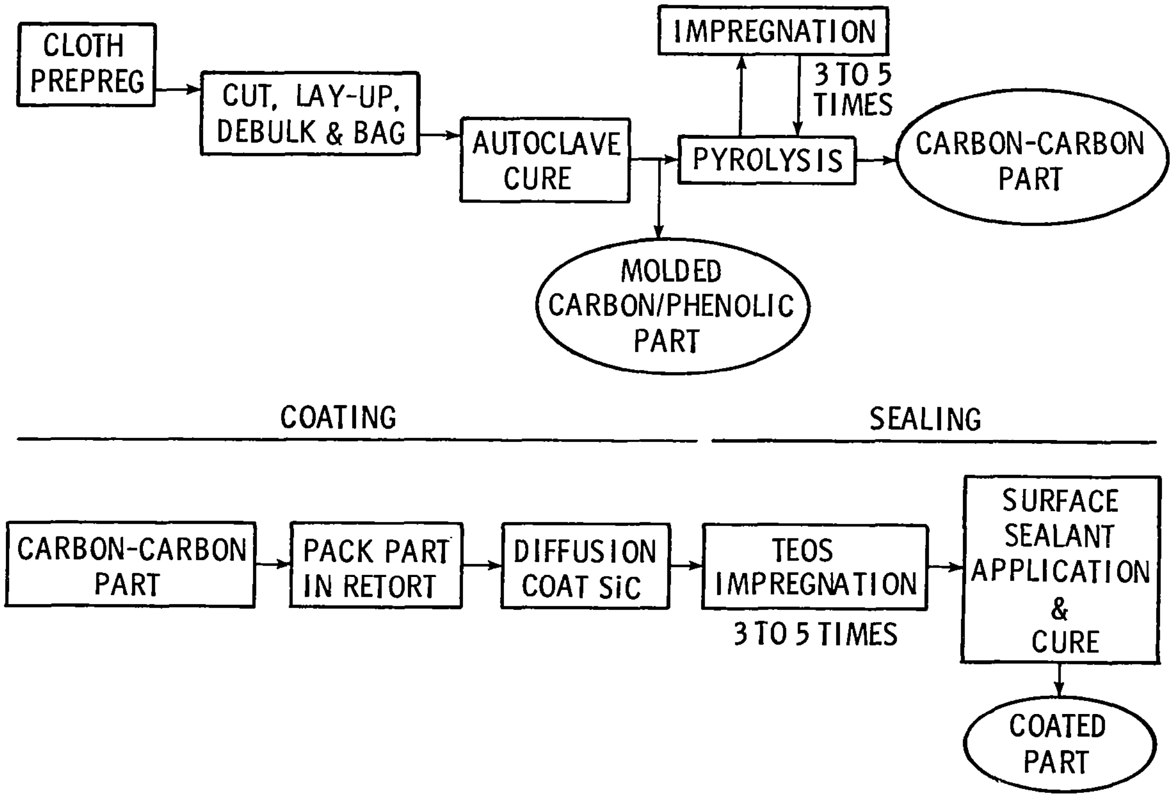


Figure 5

MICROSTRUCTURE OF TEOS-SEALED RCC

Details of the TEOS-impregnated coated RCC microstructure are presented in figure 6. The top photomicrograph shows the woven and layered nature of the carbon-carbon as well as the integral silicon carbide coating. The enlargement of the silicon carbide coating shows traces of the outer layer of the carbon-carbon, was converted to silicon carbide during the coating process. A microcrack is also visible in the coating. The cracks are due to the differences in thermal expansion between the coating and the carbon-carbon matrix.

The close-up of the carbon-carbon microstructure shows the individual graphite fibers imbedded in the carbon matrix. Minor porosity in the matrix is also evident. A pore-free microstructure may not be desirable since pores probably act as crack stoppers and improve impact resistance.

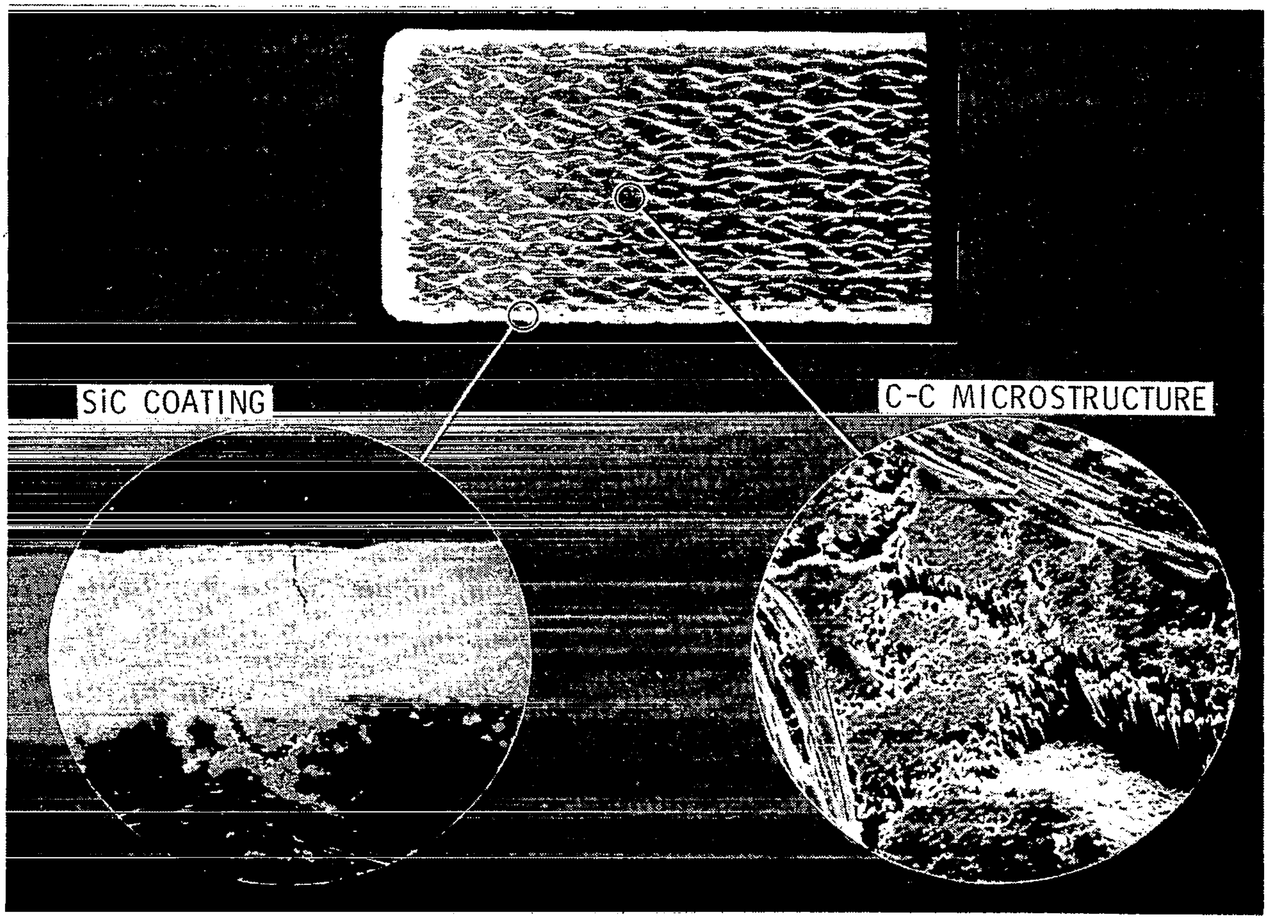


Figure 6

TYPICAL 2-D CARBON-CARBON STRESS-STRAIN BEHAVIOR

Typical stress-strain behavior for a 2-D carbon-carbon material is shown in figure 7. The material in this case is the advanced carbon-carbon (ACC) with 20 plies of woven graphite fabric. The warp of all plies is in the same direction. The stress-strain behavior is linear up to a stress level of about 16 ksi. Above 16 ksi the material is nonlinear and the differences in behavior in tension and compression and in the warp and fill directions become evident.

The behavior of the material depends on both the type and direction of loading. This was not unexpected since most composites show a similar sensitivity to the type and direction of loading. What is somewhat surprising is that the material is not completely brittle; it exhibits some nonlinearity prior to failure. A typical ceramic would not be expected to exhibit this nonlinear behavior and would fail in a completely brittle manner.

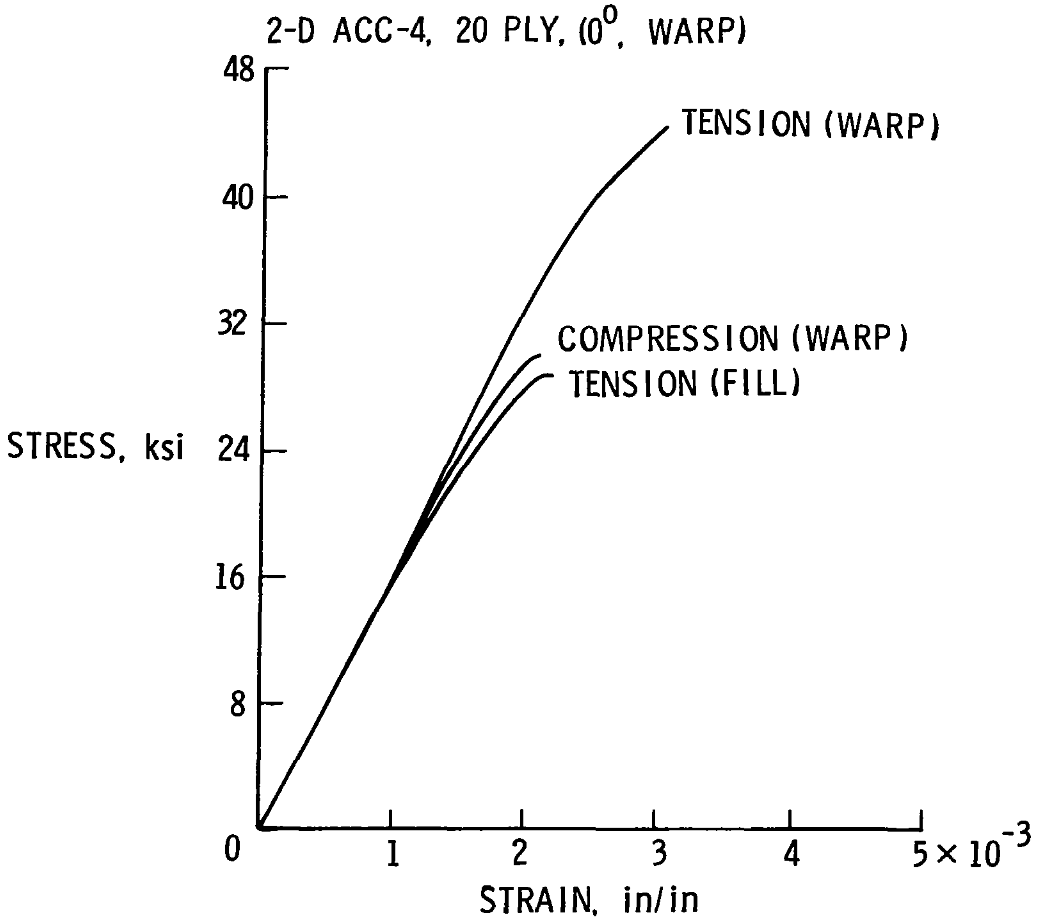


Figure 7

COMPARISON OF 2-D CARBON-CARBON PROPERTIES

The wide range of mechanical properties currently available in carbon-carbon is illustrated in figure 8. These data are from room-temperature tests. However, since strength properties do not degrade with increasing temperature these data are also typical of data generated at temperatures up to 4000°F. The fiber, the weave, the lay-up, and the number of densification steps can be changed to tailor the mechanical properties. Tensile strength can be higher or lower than compressive strength. Elastic modulus can be the same in tension and compression or it can be different. So far we have not been very successful with our attempts to improve in-plane shear or out-of-plane tensile properties.

We will continue our research efforts to characterize, understand, and improve the properties of carbon-carbon materials. Emphasis is being placed on improving in-plane shear and out-of-plane tensile strength so that the full potential of these materials can be realized.

MATERIAL	RCC	ACC-3	ACC-4
FIBER	WCA (RAYON)	T300 (PAN)	T300 (PAN)
WEAVE	SQUARE	8-HARNESS	8-HARNESS
ORIENTATION	X-PLY	QUASI-ISTROPIC	0^0(WARP)
IN-PLANE			
TENSILE STRENGTH, ksi	7.5	16	44
TENSILE MODULUS, msi	2	11	16
COMPRESSIVE STRENGTH, ksi	24	16	28
COMPRESSIVE MODULUS, msi	4.4	11	16
SHEAR STRENGTH, ksi	1.8	1.0	2.0
OUT-OF-PLANE			
TENSILE STRENGTH, ksi	0.8	0.4	0.5

Figure 8

IMPROVED OXIDATION-RESISTANT COATINGS - 1000°F THERMAL CYCLES

Early work on the Shuttle program established a correlation between mass loss, temperature, air pressure, and time in order to be able to predict RCC mass loss during the complex reentry heating cycle. This was necessary to evaluate end-of-life strength of parts exposed to different thermal environments. This correlation is used to compare the expected performance of Shuttle baseline RCC with ACC-3, which has been coated, impregnated with TEOS, and sealed with a low-temperature glass former. The improvement in oxidation resistance as a result of our recent research on coating sealants is shown in figure 9. Here the 1000°F maximum temperature during the thermal cycle simulates the temperature that might be encountered in a leading-edge attachment area. At a mass loss of 0.05 lb/ft^2 the improvement in mission life is a factor of 3 for ACC compared to Shuttle baseline RCC.

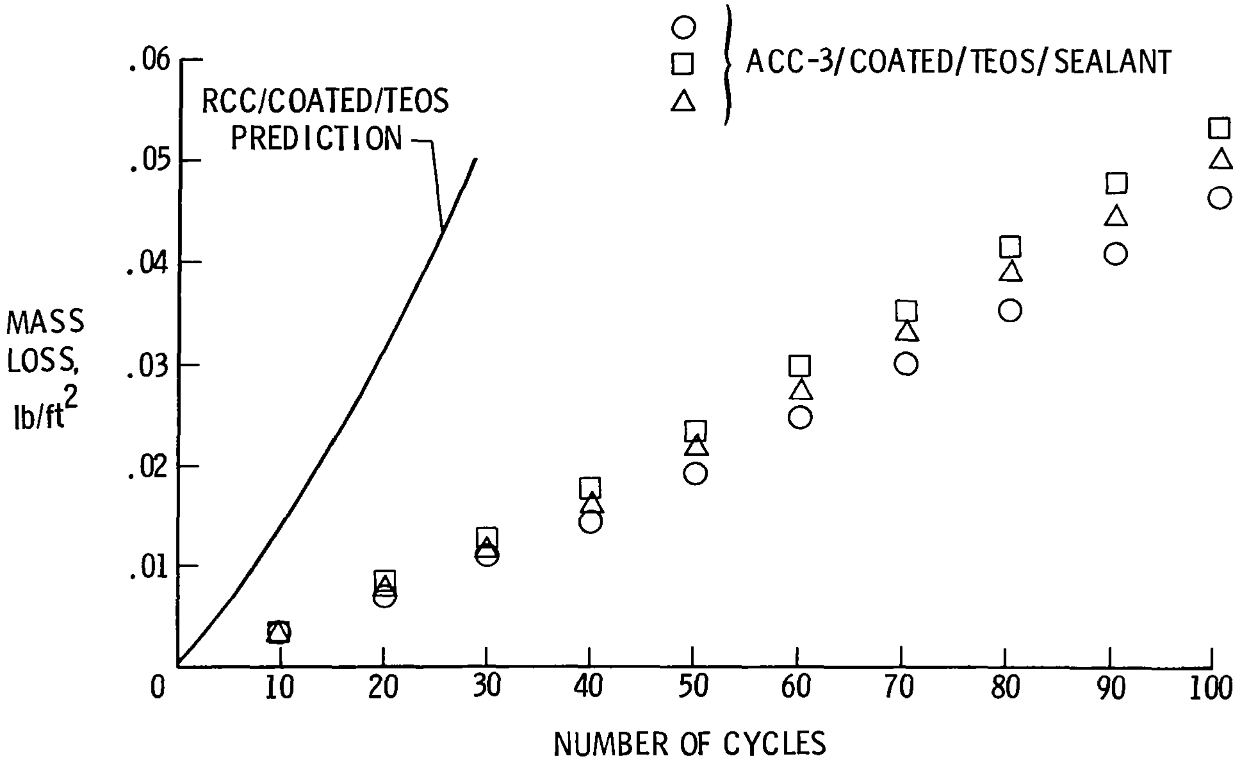


Figure 9

IMPROVED OXIDATION-RESISTANT COATING - 2450°F THERMAL CYCLES

As in the previous figure, the mass loss characteristics of coated and sealed ACC are compared to predicted RCC baseline behavior. The data in figure 10 are for a maximum-temperature thermal cycle of 2450°F. This cycle simulates the type of thermal history that would be expected on the outer surface of the Shuttle leading edge. Although the predicted mass loss for the RCC is only 0.02 lb/ft^2 after 100 simulated missions, the oxidation resistance of the coated and sealed ACC is twice as good as the baseline RCC.

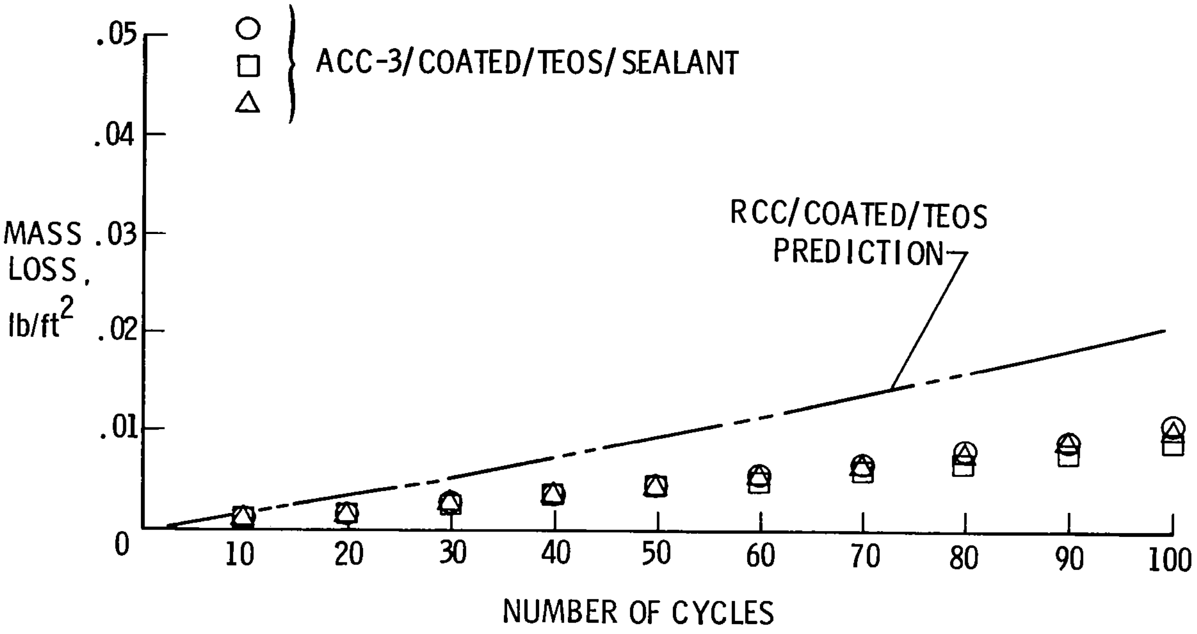


Figure 10

EFFECT OF COATING/SEALANT ON MASS LOSS

Because oxidation of the silicon carbide baseline coating will form a protective layer of glass when RCC parts are exposed to temperatures above 1600°F, we have concentrated our most recent sealant experiments below the protective oxide formation temperature. Figure 11 shows a comparison of mass loss following a 10-hour exposure to atmospheric-pressure air at 1000°F for three carbon-carbon materials systems. The RCC/SiC/TEOS represents the Shuttle baseline system. The ACC/SiC/TEOS/MAP is one of our coated and sealed advanced carbon-carbon materials. As we have seen before, the addition of a low-temperature glass former significantly reduces mass loss. Recently, we have further improved oxidation resistance by modifying the baseline silicon carbide coating (DSIC). This doped and sealed coating has 25 times the oxidation resistance of the Shuttle baseline RCC material.

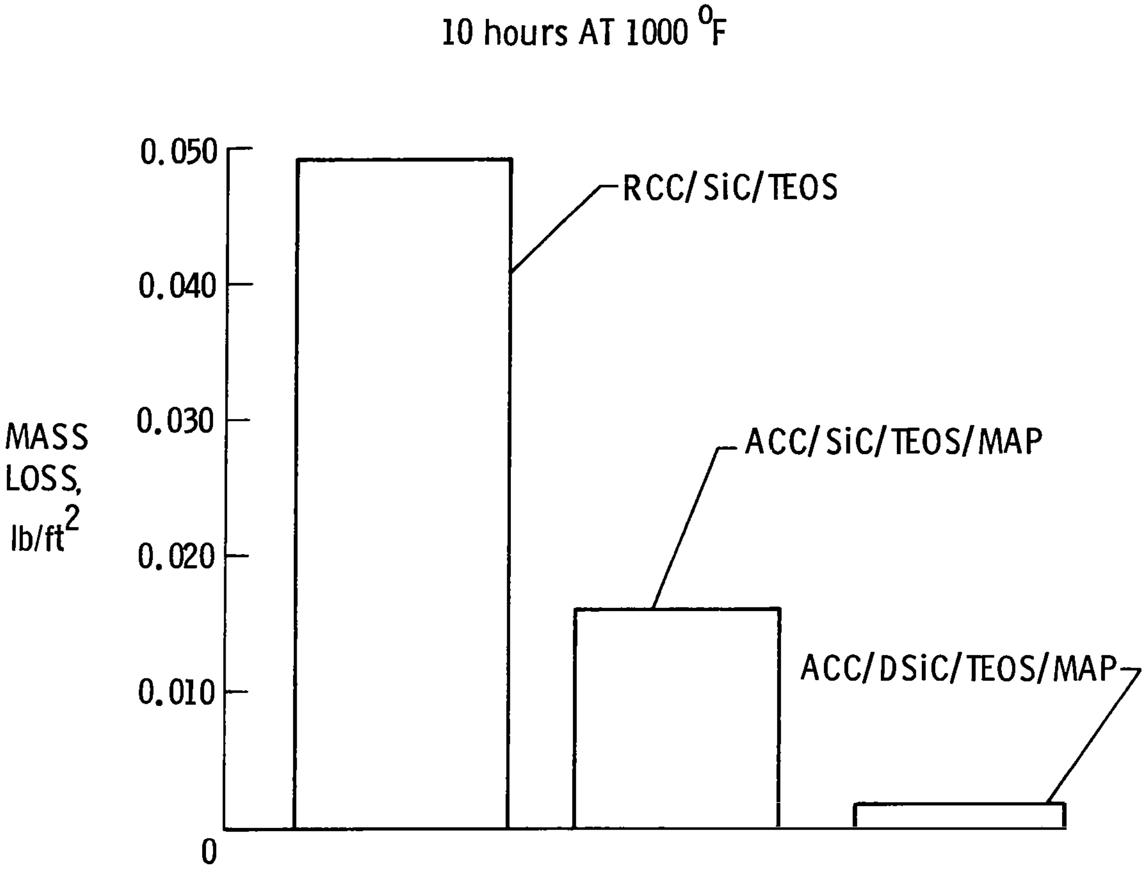


Figure 11

CARBON-CARBON COMPOSITES

A brief summary of the present state of carbon-carbon technology is presented in figure 12. Carbon-carbon composites offer a unique combination of properties. In nonoxidizing environments they retain room-temperature mechanical properties up to temperatures in excess of 4000°F. For application in oxidizing environments, current coatings limit maximum use temperatures to about 2900°F. Their high thermal conductivity and low thermal expansion make carbon-carbon composites excellent candidates for applications involving thermal shock.

Because of the variety of fibers, weaving patterns, and lay-up procedures that can be used for carbon-carbon composites, their mechanical properties can be tailored over a wide range to fit the application.

A strong research activity in carbon-carbon materials is building in this country. Major emphasis is being placed on understanding materials behavior. These research activities should lead to improved matrix properties (particularly in-plane shear and out-of-plane tensile strengths), improved oxidation-resistant coatings with higher use temperatures, longer lifetimes, and less costly fabrication methods.

The first generation of this new class of structural materials is available today. The rest of this paper will briefly discuss some of the aerospace applications for carbon-carbon that are currently being explored.

- UNIQUE COMBINATION OF PROPERTIES
- PROPERTIES CAN BE TAILORED
- STRONG RESEARCH BASE TO IMPROVE PERFORMANCE
- FIRST GENERATION AVAILABLE TODAY

Figure 12

MULTIPOST PANEL CONCEPT

The development of advanced carbon-carbon (ACC) was instigated by the desire to make available to the Shuttle program a thermal protection system that would be more durable and impact resistant than the current reusable surface insulation (RSI). As the mechanical properties of the ACC and the oxidation resistance of the new coating systems improved, it became apparent that an ACC-based TPS might be feasible. We have recently completed an assessment of alternate thermal protection systems for the Space Shuttle Orbiter. This study demonstrated that ACC-based TPS is both feasible and weight competitive with the current RSI-based TPS. ACC is a particularly attractive candidate for TPS locations that experience surface temperatures above 1800°F.

One of the ACC-based TPS concepts to emerge from this study is shown in figure 13. The multipost panel concept utilizes a series of 36-inch-by-36-inch ACC cover plates (outer surface) to bridge airloads to the aluminum substructure and to reradiate reentry thermal energy just as do the current RSI tiles. Since the RSI tiles are, on the average, 6 inches by 6 inches on the surface, these ACC panels would each replace 36 Orbiter tiles. The outer panel is suppported by multiple posts that separate the cover plate from the substructure. The posts are configured to minimize induced thermal stresses as the ACC panel thermally expands. Fibrous insulation packages are used between the outer panel and the aluminum to insulate the substructure from the entry thermal energy that is not rejected by reradiation.

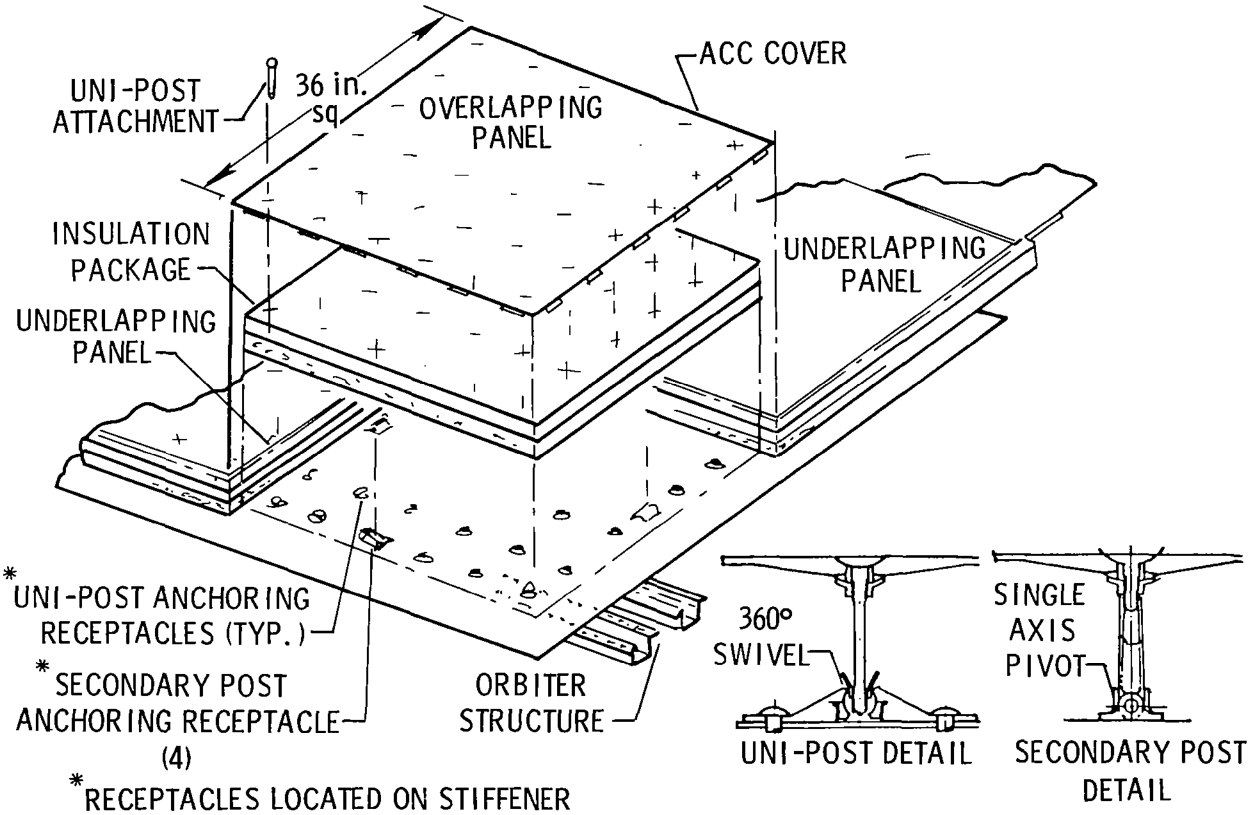


Figure 13

CARBON-CARBON HOT STRUCTURE FOR SPACE SHUTTLE

The current use of RCC for the nose cap and leading edges of the Shuttle can be considered a hot-structure application of carbon-carbon. These parts must transmit thermomechanical loads to the aluminum substructure. They are also similar to the previously discussed panel TPS in that insulation packages must be used behind them to protect the substructure from overheating.

Recently we have begun to look at "true" hot-structure applications of ACC. Such an application is shown in figure 14. Potential Orbiter carbon-carbon hot structures are the rudders, speed brakes, ailerons, and the body flap. For these applications carbon-carbon would perform the dual role of primary structure and thermal protection system. Since the primary structure can operate at high temperature, no insulation would be required. If ACC hot structure can be developed for these retrofittable control surfaces, a potential weight saving of 2500 pounds exists for conventional two-skin construction. If an open-face aileron (only a single aerodynamic skin) can be developed, the potential weight saving is 5000 pounds per vehicle.

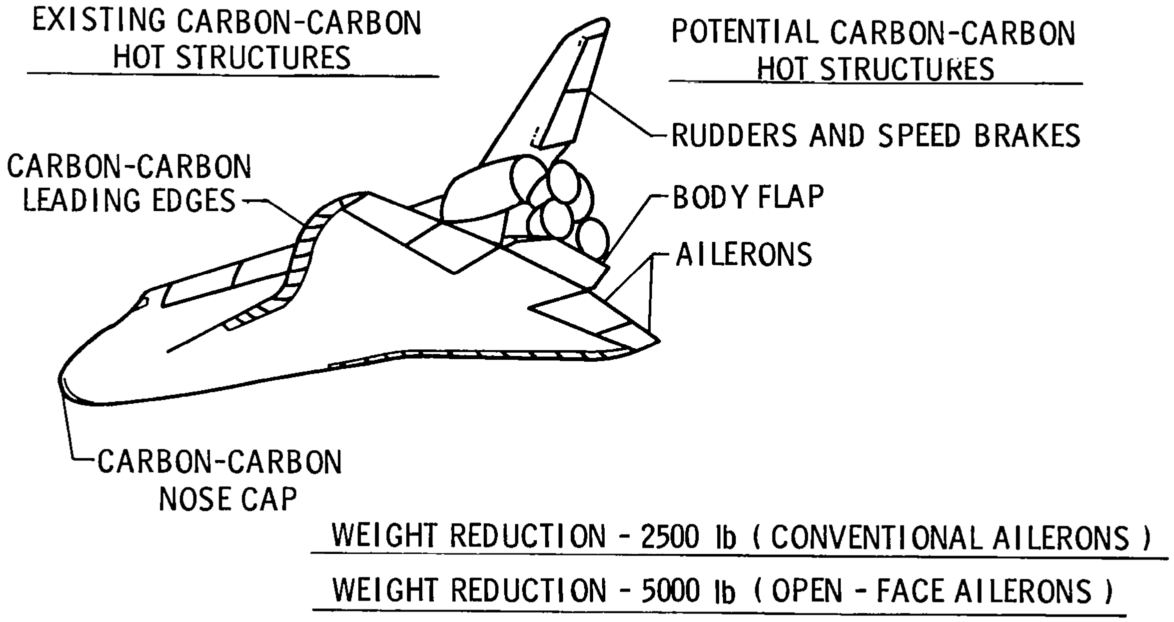


Figure 14

ACC OPEN-FACE HOT-STRUCTURE SHUTTLE CONTROL SURFACES

A concept for an ACC open-face hot-structure Shuttle control surface is presented in figure 15. In this case we show the body flap. The ACC torque tube would use the existing aft body cove. The single aerodynamic surface would be stiffened with ACC ribs. The feasibility of eliminating the top aerodynamic surface will be investigated in wind tunnel tests.

Our preliminary structural studies of this concept indicate that mechanical fastners would be required to operate at high temperatures. This poses potential structural design problems because of the large difference in thermal expansion between carbon-carbon and any metallic fastener. To minimize these potential problems we are currently developing a fastener concept called DAZE (differential &, zero strain).

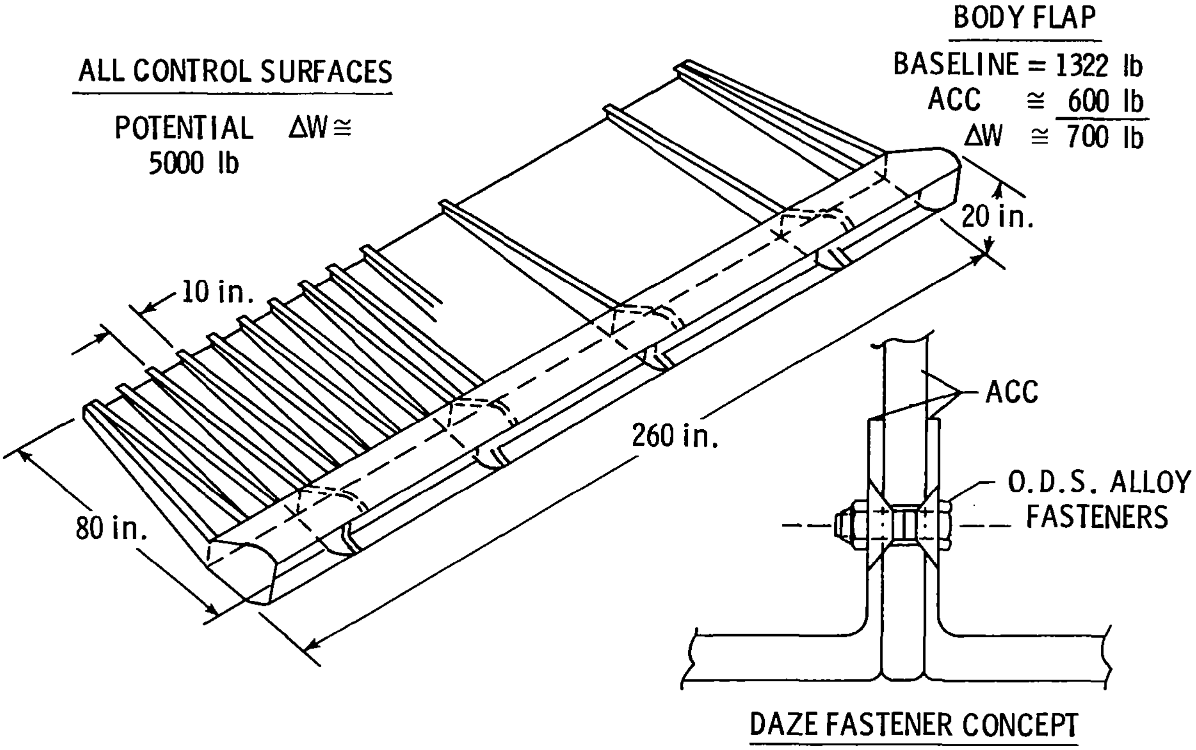


Figure 15

FASTENER CONCEPT FOR LARGE CARBON-CARBON HOT STRUCTURES

The thermal expansion mismatch between high-temperature metallic fasteners and carbon-carbon causes many potential structural design problems. The DAZE fastener concept is illustrated in figure 16. This concept utilizes a conventional metallic bolt surrounded by two intersecting cones. The joint is tightened at room temperature sufficiently to prevent relative motion between the carbon-carbon parts under the expected design loads. During service at high temperature the joint does not loosen up because the cones expand and slide along the conical surfaces of the carbon-carbon parts. This expansion of the cones prevents the bolt from losing tension. Sufficient radial clearance between the bolt and the carbon-carbon parts is established during assembly to avoid introduction of tensile loads into the carbon-carbon when the joint is hot. The feasibility of this concept has been demonstrated by thermally cycling two pieces of graphite that had been joined using two DAZE fasteners. After four cycles to 1600°F the joints were still snug with no apparent damage to the graphite parts. A snug-fitting conventional fastener failed the graphite in tension during a single thermal cycle. The tensile loads were introduced by the radial expansion of the metallic bolt.

We are continuing to evaluate the DAZE concept both in house and on contract. This concept may represent a breakthrough in high-temperature mechanical fastening.

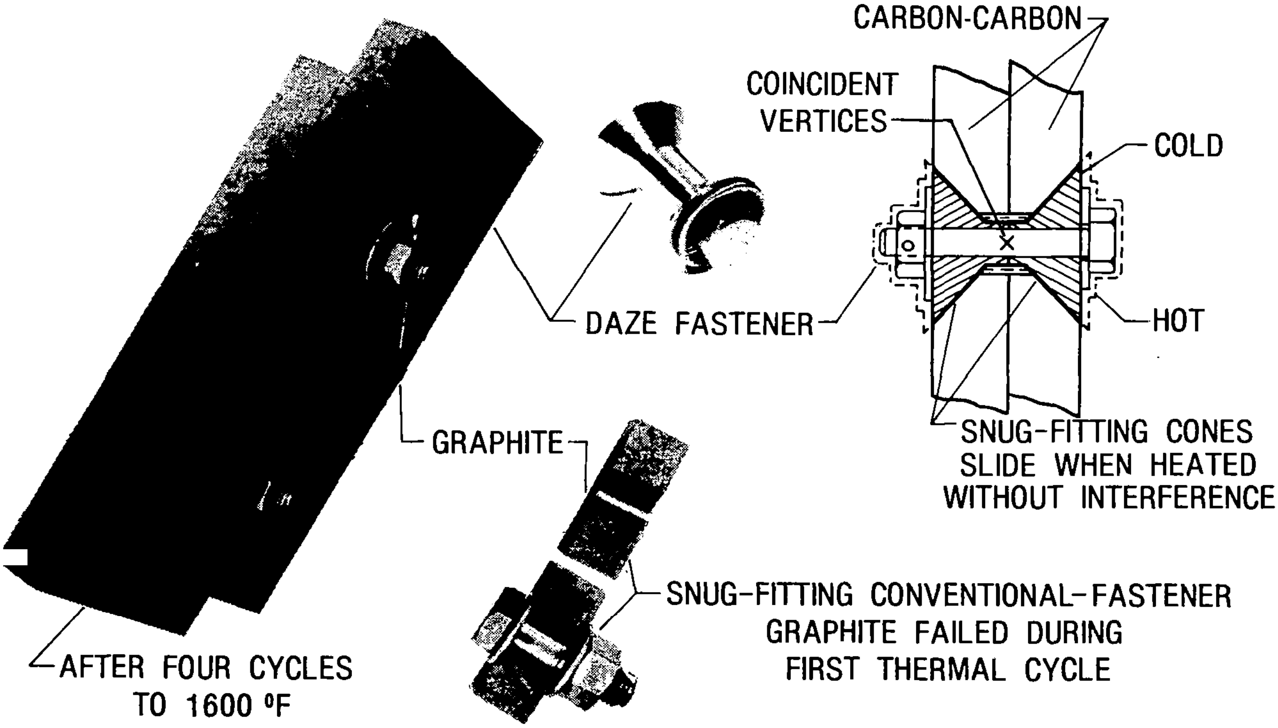


Figure 16

ACC TRUSS CORE PANEL

Initial studies for some carbon-carbon applications indicate that a monolithic carbon-carbon structure, such as the one proposed for the Orbiter body flap, will not be weight/cost competitive with current structures. It will be necessary to use internally reinforced or lightweight carbon-carbon constructions such as rib-stiffened sheet or truss core panels.

An initial effort to fabricate a truss core advanced carbon-carbon part is illustrated in figure 17. In this figure the panel has been cut in half to reveal the truss core. This part uses thin-gage face sheets and core. In addition, the fabrication procedures yielded a part with built-in panel closeouts. The integral panel closeout makes feasible the possibility of coating only the outside surfaces of the part for use in oxidizing environments. Research will continue in the development of lightweight carbon-carbon configurations.

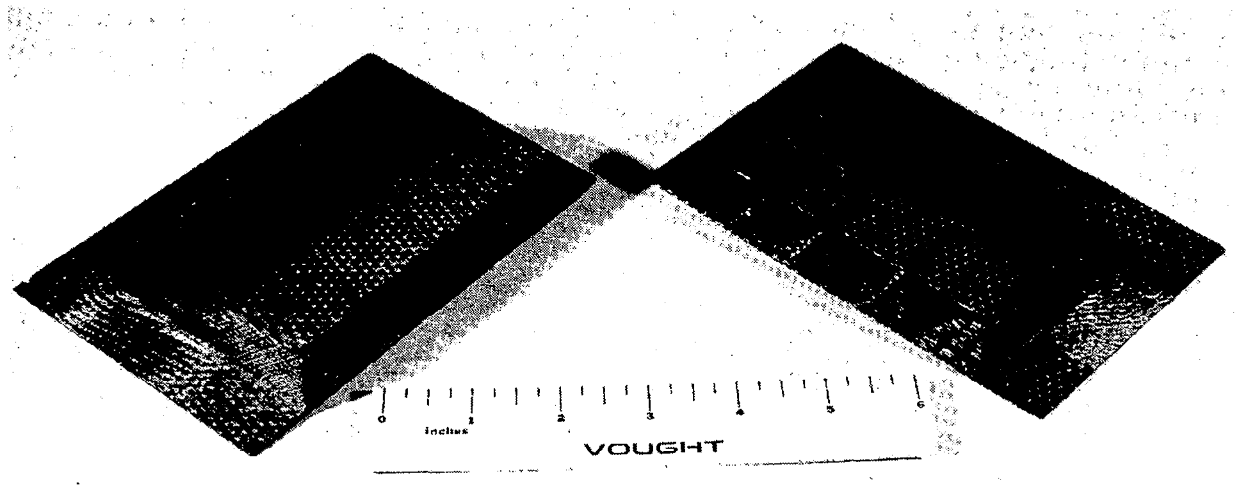


Figure 17

SUMMARY

A summary of the recent advances and expected future improvements in advanced carbon-carbon materials systems is presented in figure 18. The ACC family of carbon-carbon materials represents a significant improvement in strength and stiffness over the baseline RCC material. In the future, hybrid ACC constructions offer the possibility of additional improvements in strength and stiffness. Methods will have to be found to increase in-plane shear and out-of-plane tensile strengths so that the full potential of the ACC matrix materials can be realized.

The concurrent ACC and coating research activities have led to significant improvements in the oxidation resistance of coatings for ACC. Matrix strength retention after exposure to the expected use environment will continue to be an important criterion for coating improvements. Continued research on doped silicon carbide coatings and advanced coating sealants is expected to yield additional improvements in matrix oxidation protection and increase maximum use temperatures.

In the area of ACC applications, our initial efforts show that ACC is both a feasible and attractive candidate material class for both TPS and hot-structure applications. We will continue to pursue these application areas both analytically and experimentally. Particular emphasis will be placed on continued development of the DAZE fastener concept for mechanical joints.

- MATRIX
  - IMPROVED STRENGTH AND STIFFNESS
  - HYBRID CONSTRUCTIONS
  - SHEAR PROPERTIES
- COATINGS
  - IMPROVED OXIDATION RESISTANCE
  - STRENGTH RETENTION
  - DOPED SiC
  - IMPROVED SEALANTS
- APPLICATIONS
  - TPS
  - HOT STRUCTURE

Figure 18

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