TIME-TEMPERATURE-STRESS CAPABILITIES OF COMPOSITES FOR SUPERSONIC CRUISE AIRCRAFT APPLICATIONS*

J. F. Haskins and J. R. Kerr
General Dynamics Corporation
Convair Division

B. A. Stein
NASA-Langley Research Center

ABSTRACT

Advanced composite materials have the potential of reducing the weight of future supersonic cruise aircraft structures. However, information on the effects of long-time, cyclic exposure to environments, and loadings representative of long-time supersonic cruise aircraft service for the composite materials of interest is not available. A program to generate such information was initiated in 1973. A range of baseline properties was determined for representatives of 5 composite materials systems: B/Ep, Gr/Ep, B/PI, Gr/PI, and B/Al. Long-term exposures are underway in static thermal environments and in ones which simultaneously combine programmed thermal histories and mechanical loading histories. Material behavior during these exposures and post exposure residual property tests will provide exposure effects and reveal material degradation mechanisms.

Much of the baseline property data including tensile, notched tensile, shear, fatigue and creep that have been obtained on this program have been published previously. This paper presents selected results from the environmental exposure studies with emphasis placed on the 10,000-hour thermal aging data. Results of residual strength determinations and changes in physical and chemical properties during high temperature aging are discussed and illustrated using metallographic, fractographic and thermomechanical analyses. Some initial results of the long-term flight simulation tests are also included.

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INTRODUCTION

In the materials portion of the SCAR program, NASA's goal is to advance the technology and establish a data base so that sound technical decisions may be made in the future regarding the use of advanced composite materials in supersonic cruise aircraft structures. This paper reviews the objectives and status of the on-going study to determine the time-temperature-stress characteristics of five classes of composite materials: boron/epoxy, graphite/epoxy, boron/polyimide, graphite/polyimide, and boron/aluminum.

This is the fourth in a series of papers (ref. 1, 2, 3) presenting data developed during this study at General Dynamics Convair under NASA Contract NAS1-12308. The general objective of this study is to assess the suitability of these advanced filamentary reinforced composite materials for future supersonic cruise aircraft structures. The study has two phases. The first includes all material property determinations and aging and simulation exposures up through 10,000 hours. The second continues these tests up to 50,000 hours.

Figure 1 is a schematic diagram of the study. The changes in baseline tensile, notched tensile, shear, fatigue, and fracture properties that occur during times out to 50,000 hours are being measured for ambient and thermal aging conditions, as well as random cyclic loading with cyclic temperature variations. These latter tests are intended to simulate the conditions experienced during supersonic flight. In the previous reports some data have been presented on the effects of thermal aging and ambient aging on mechanical properties. These reports contain extensive baseline data and some of the preliminary results of the fatigue and creep portions of the study. The design and construction of the flight simulation equipment have also been discussed in a previous paper (ref. 3).

This paper updates the results of residual mechanical property tests and discusses in some detail the analysis to date on the graphite/epoxy thermal aging specimens and provides some explanation for their loss in strength after 10,000 hours of elevated temperature exposure at ambient and reduced pressures. Some preliminary results of the flight simulation tests are also included.

MATERIALS

Of the multitude of advanced composite material systems that have been developed and evaluated, five have generally been accepted as the most promising for aerospace structural design applications: boron/epoxy (B/E), graphite/epoxy (G/E), boron/polyimide (B/PI), graphite/polyimide (B/PI), and boron/aluminum (B/Al). Within each of these five classes there are several types of matrix materials and different types of filaments. Table I lists the specific advanced composite systems evaluated in this program. The selection of these particular composite systems was based on cost, current availability and manufacturing maturity, existing data base, fabrication history, good thermomechanical and physical properties, and material suppliers' continuing interest in producing a particular system.

The organic matrix composites were fabricated by Convair from vendor supplied prepreg material using conventional autoclave processing methods. The B/Al, which was purchased in the form of finished sheet material, was fabricated by diffusion bonding at approximately 800 K (975°F) using a single-step hot pressing technique. Both unidirectional and $[0° \pm 45°]$ laminates were evaluated for each system. Six-ply laminates were used for all tests except flexure, short beam shear, transverse tensile, and R = -1 fatigue for which 12-ply panels were required. Diamond impregnated saws were used for specimen cutting, and all holes and notches were prepared by rotary ultrasonic drilling, electrical discharge machining, or ultrasonic impact grinding.

Since the beginning of this contract, many new advanced composite systems have been developed, and of these several are now commercially available. One of the goals of the overall program was to follow this progress and to add new materials if sufficiently promising ones appeared. This will be done by choosing a material from the group of recently developed high temperature graphite fiber reinforced polyimide systems listed in table II. In order to select the best materials system of these emerging graphite reinforced polyimides, a preliminary screening test will be conducted. The criteria for selecting the best system will include:

a. Availability and cost of prepreg material.

b. Ability to fabricate both full-size 12-ply panels and a simple structural shape.

c. Moisture resistance.

d. High temperature thermal stability and oxidation resistance.

PROGRAM STATUS AND INTERIM RESULTS

Because of the length of this contract, it was thought to be desirable to provide periodic reports on the program status. In this way, results can be presented as they become available rather than waiting until the end of the study for a complete presentation of the data. The program is currently nearing the end of Phase 1, the 10,000-hour portion, and considerable data have been obtained. Table III summarizes the type and number of tests included and also shows the number of tests that have been completed at this time. Customary units rather than the International System of Units (SI) were used as the working units of measurement for all tests. The following sections describe these tests and test procedures and, in addition, present and discuss some of the recently obtained results. Much of the earlier data has been presented in previous papers, and these references have been noted.

Quality Assurance

Quality assurance testing was conducted on the epoxy and polyimide prepregs and on all fabricated panels of all materials. These acceptance tests included ultrasonic C-scans, volume percentage determinations, mechanical property testing, and for the organic matrix composites flexural testing before and after 24-hour water boil.

While all five materials passed the acceptance tests, one, B/PI, was later dropped from the program because of extensive thermal degradation observed during thermal aging and short term flight simulation testing at 505 K (450F). Later tests by the resin producer, Ciba Geigy, substantiated Convair's data and reinforced the conclusion that the resin was not suitable for this application.

Baseline Testing

The purpose of the baseline tests is threefold. First, these data will serve to characterize the composite materials and add to any existing data bases. Second, the baseline tests will provide the scale and shape parameters necessary to define the statistical distribution of the ultimate tensile strengths for each of the material systems. These, in turn, are used to set the loads for the short term tests, and with the short term results, are used in a wear out analysis model to relate static and fatigue strengths. Finally, the baseline tests will provide a rational starting point against which the various environmental effects may be measured.

Tests that were conducted included: ultimate tensile, tensile modulus, Poisson's ratio, notched tensile (K_t = 3), transverse tensile (unidirectional laminates only), shear, and fracture. Testing was performed over the temperature range from 218 K (-67°F) to 450 K (350°F) for the epoxy specimens, to 616 K (650°F) for the polyimide specimens, and to 700 K (800°F) for the boron aluminum specimens. These data have been presented previously, reference 1, and are not included in this paper.

Environmental Aging

Most of the data generated to date on advanced composite materials have been initial strength data without regard to environmental conditions. The small amount that is available is generally for only relatively short periods of exposure compared to the lifetime of a commercial airliner. This portion of the program was intended to evaluate the composite systems as a function of exposure to moisture, ambient aging, and atmospheric contaminants over relatively long periods of time.

For the resin matrix composites, 24-hour water boil, 6-week humidity, and 20-week and 52-week ambient aging tests were conducted as accelerated means of simulating long-term ambient exposure. Residual strength testing (flexure) of these specimens was performed to determine the effects of exposure. The results are summarized in table IV. For the epoxy systems the room temperature flexural strengths were nearly unaffected, while those at 450 K (350°F) were, in general, severely degraded. The effects of the moisture exposures on the polyimide specimens were generally less damaging than for the epoxy systems. Some decreases in flexural strength of the crossplied material were observed at

450 K (350°F) after the 24-hour water boil and 6-week humidity tests, but no significant effects were observed as a result of the 20- and 52-week ambient ages. Absorption of moisture is the primary cause for the deterioration in high temperature properties. The water plasticizes the resin which subsequently lowers the glass transition temperature of the resin and, thereby, decreases the high temperature mechanical properties. Complete results for the epoxy and polyimide systems can be found in reference 2.

Significant efforts exist at several laboratories in this country to determine moisture effects on mechanical properties of polymer matrix composites. Many results have been recently presented at U.S. Air Force Materials Laboratory and Society of Aerospace Materials and Process Engineers workshops, while some initial data have been published (see, for example, references 4 and 5). A general conclusion based on this information is that epoxy matrix composites should generally be limited to less than 394 K (250°F) for supersonic cruise aircraft applications.

Another environmental study is being conducted to determine the effects of corrosion and atmospheric contaminants on the four composite systems. Tensile specimens of the epoxy and polyimide systems and tensile and shear specimens of coated and bare B/Al have been placed in an outdoor industrial-seacoast atmosphere corrosion test facility maintained by Convair in San Diego, California. A high temperature coating with a maximum use temperature of about 589 K (600°F) was applied to one-half of the B/Al specimens. The coating consisted of a chemical conversion coating followed by an epoxy primer and a polyimide topcoat. No coatings were used on any of the organic matrix composites. The specimens are tested after 10,000 and 50,000 hours of exposure for the B/Al and 50,000 hours for the epoxy and polyimide specimens.

To date, the 10,000-hour B/Al exposure tests have been completed with the remaining specimens having approximately 25,000 hours of exposure. For the 10,000-hour B/Al exposure, the coated specimens have shown no change in either appearance or mechanical properties. The uncoated specimens, on the other hand, have experienced significant surface corrosion and decreases in matrix controlled properties, i.e, transverse tensile and shear strength. Results of the 10,000-hour exposures are available in reference 3.

Thermal Aging

All of the composite materials are being thermally aged for periods up to 50,000 hours. At various times during the 50,000 hours, specimens are removed for examination and determination of residual tensile strength. Both unidirectional and $[0° \pm 45°]$ crossply materials are included. The aging temperatures are: epoxy, 394 K (250°F) and 450 K (350°F); polyimide, 505 K (450°F) and 561 K (550°F); and B/Al 450 K (350°F), 561 K (550°F) and 700 K (800°F). The organic matrix composites are aged at one atmosphere (101 kN/m^2) and at a reduced pressure of 13.8 kN/m^2 (2 psi) to simulate high altitude flight conditions. Previous work has shown a direct correlation of thermal aging and oxygen pressure on residual strength of resin matrix composites (reference 6). The B/Al system is aged at atmospheric pressure (101 kN/m^2) only.

Exposures were conducted as described in reference 1. The effects of moisture were eliminated from all tests by carefully baking-out each of the specimens before test. Thermal aging tests are currently in progress with exposure times of just under 25,000 hours for several of the systems. Residual strength data are available for all of the composites out to at least 10,000 hours. Table V and figure 2 show the thermal aging data for A-S/3501 graphite/epoxy. Those specimens aged at 394 K (250°F) and one atmosphere and those aged at 450 K (350°F) and 13.8 kN/m^2 (2 psi) show no loss in strength out to 10,000 hours for either the unidirectional or $[0° \pm 45°]$ crossply materials. The G/E aged at 450 K (350°F) and one atmosphere showed a 20 percent loss in strength for the unidirectional materials, and a 60 percent loss in strength for the $[0° \pm 45°]$ crossply material after 10,000 hours. Photomicrographs and fractographs of this material during thermal aging will be discussed later in the paper. The data shown in table VI are for B/5505 boron/epoxy and are very similar to the graphite/epoxy data except for the 30 percent loss in strength of the crossply material after 10,000 hours exposure at 450 K (350°F), and 13.8 kN/m^2 (2 psi). In summary of these data, A-S/3501 graphite/epoxy and B/5505 boron/epoxy should be limited to 394 K (250°F) for exposures greater than 10,000 hours because of loss of residual tensile strength during thermal aging.

Table VII and figure 3 show the data for HT-S/710 graphite/polyimide after aging at 505 K (450°F) and 561 K (550°F). The results are analogous to those for boron/ and graphite/epoxies in that the lower temperature exposures had little effect, while the high temperature aging caused a considerable decrease in tensile strength. It should be noted that the aging temperatures for the polyimide system were 111 K (200°F) higher than those used for the epoxies. In like manner to the crossply boron/epoxy, the reduced pressure

aging of unidirectional graphite/polyimide at the higher temperature also lowered the tensile strength significantly. In summary of these data, HT-S/710 graphite/polyimide should be limited to 505 K (450°F) for exposures greater than 10,000 hours because of loss of residual tensile strength during thermal aging.

In general, strength degradation during aging in all organic matrix composites tested appears to be matrix related. Subsequent sections will discuss organic matrix degradation in more detail.

Table VIII and figure 4 show the thermal aging results for boron/aluminum at three aging temperatures and times out to 10,000 hours. The 5,000-hour data were presented and discussed previously in reference 3. The 10,000-hour data show a further decrease in tensile properties at all aging temperatures for both unidirectional and crossply material and substantiate the results described in reference 3. Based on transverse tensile and shear data (not shown) for boron/aluminum specimens, the decrease in properties appears to be primarily fiber related. Boron filaments have apparently become embrittled and weakened as a result of interdiffusion between the boron and 6061 aluminum alloy at the fiber matrix interface during thermal exposure. In summary of these data, B/6061 boron/aluminum should be limited to 450 K (350°F) for supersonic cruise aircraft cumulative exposures greater than 10,000 hours because of loss of residual tensile strength during thermal aging.

Microscopic Examination of the Thermal Aging Specimens - After tensile testing, many of the thermal aging specimens were sectioned and mounted for study using both an optical microscope (metallograph) and scanning electron microscope (SEM).* These studies were intended to detect changes which occurred in the composites during exposure in order to assist in identifying degradation mechanisms. Additional examinations were conducted of the fractured surfaces (primarily with the SEM) to determine failure modes and to further study the degradation processes. As these investigations have been completed for only the graphite/epoxy, the following discussion will be limited to this system.

Figure 5 shows photomicrographs using a metallograph and a SEM at 100X and 500X magnifications. These pictures are for 10,000 hours exposure at 450 K (350°F) and 13.8 kN/m^2 (2 psi) pressure. Close examination of these photomicrographs shows only surface changes in the resin and some

* The photomicrographs used in this paper were provided by M. Featherby of General Dynamics.

cracking which probably occurred during post exposure tensile testing. Some of the cracks are located at boundaries between lamina and others within a particular lamina, as shown in the upper two photomicrographs. The lighter cast at the specimen edges in the SEM pictures will be shown later to be oxidation. In this case, it has only occurred at the surfaces exposed to oxygen.

The pictures in figure 6 taken at 100X with the metallograph show good examples of how oxidation of the epoxy resin can proceed inward as a function of time and temperature. The upper pictures show that there is little difference between the as-received material and that aged for 10,000 hours at 394 K (250°F) in one atmosphere air. The lower pictures, on the other hand, show extensive degradation in the outside plies after 5,000 hours at 450 K (350°F), and considerable degradation in both the inner and outer layers after 10,000 hours. The SEM pictures in figure 7 taken from the same specimens show the identical effects, but even more clearly than the metallographic pictures. For example, the slight amount of surface oxidation after 10,000 hours at 394 K (250°F) is easily distinguished in the SEM photograph in figure 7, while scarcely visible in figure 6.

The changes from light to dark for pictures taken using the metallograph and dark to light using the SEM are explained by the amount of relief polishing around the individual fibers that increases with the degree of oxidation. When the epoxy resin oxidizes, it is more prone to crumble and differences in the amounts of oxidation in the polished mounts can easily be detected using the SEM at higher magnifications.

Figure 8 shows typically how this occurs. The as-received specimen has little and uniform relief for all plies as shown at 2500X using the SEM to examine a typical polished surface. The inner plies of a specimen aged for 10,000 hours at 394 K (250°F) look much the same except for the filaments being oriented at 45° to the surface. If one moves to the outer ply, the relief has increased as shown at the lower right of figure 8. This effect becomes more pronounced for specimens aged at 450 K (350°F) and 10,000 hours as shown in the lower left picture. The magnification was lowered to a 1,000X for clarity.

Fractographs - In addition to the metallographic cross sectional examinations, a study was also made of the fracture surfaces of several of the specimens. Examples are presented in figures 9 and 10. Typical fractographs of graphite/epoxy unaged and aged at 394 K (250°F) for 10,000 hours are shown in the upper portion of figure 9. As might be predicted from the tensile results, the appearance of the fracture surfaces are very similar for the two specimens. The matrix is relatively intact and there is little fiber pull out. For specimens aged at 450 K (350°F) for either 5,000 or 10,000 hours, it was not possible to

get a good SEM picture of the fracture. The very brittle resin had crumbled away from the filaments in the area of the fracture so that only a few filament ends would have appeared in the field of view.

The pictures in the lower portion of figure 9 show some of the filaments near the fracture locations in specimens aged at 450 K (350°F). The filaments are quite different in appearance than those in the upper two photographs in the amount of resin adhering to the surface. The presence of this much resin on the graphite filaments indicates a severe degradation of the epoxy matrix which accounts for the failure within the matrix rather than at the fiber/resin interface.

An interesting example of the gradient of oxidation into the specimens is illustrated in the fractographs of figure 10. These pictures were taken from areas near the surface of specimens aged at 394 K (250°F) and ambient pressure and at 450 K (350°F) and reduced pressure. As shown in figures 5 and 7, only a slight amount of oxidation (only at the outer surfaces) had occurred in these specimens in 10,000 hours. In figure 10 the depth to which the oxidation had progressed is readily visible. The resin near the outer surface has been embrittled by oxidation and has broken away from the filaments during tensile testing. Deeper into the specimen the fracture surface more closely resembles that of an unaged specimen.

Glass Transition Temperature Studies - Further studies of the changes in the epoxy resin were made by measuring the glass transition temperature (Tg) of small samples cut from the thermal aging specimens. These tests were performed using a DuPont 942 Thermomechanical Analyzer module in conjunction with a DuPont 990 Thermal Analyzer. The results are tabulated in table IX. For aging at 394 K (250°F) no change was observed for aging times out to 10,000 hours, in agreement with the tensile results. For the reduced pressure, 13.8 kN/m^2 (2 psi), exposures at 450 K (350°F), however, significant increases in Tg were found. These changes in the resin were not detected by either the mechanical property tests or microscopic examinations. No measurements could be made on the 5,000-hour and 10,000-hour specimens aged at ambient pressure and 450 K (350°F) because of the damage which occurred during tensile testing. The full significance of the changes in the Tg values and their relationship to the changes in the resin systems during aging are not clearly understood at this time. It is hoped, however, that this analytical technique will assist in the study of the processes which take place during elevated temperature exposure.

The last entry in table IX is for a flight simulation specimen (aging plus random fatigue loading) which failed in approximately 4,500 hours. The rather large increase in Tg obtained from this specimen is the first indication that the combined effects of heat and load may be much larger than one would predict.

Creep and Fatigue

The creep and constant amplitude fatigue testing portions of Phase I have recently been completed. Creep tests were conducted at two temperatures for each system for exposure times of 100 and 1,000 hours. The fatigue tests were performed at room and one elevated temperature at stress ratios of 0.1 and -1. Both flawed and unflawed fatigue specimens were included in the study. Details of the test procedures for both creep and fatigue have been described in reference 1. Data reduction, curve plotting, and analysis of the results of both the creep and fatigue tests are currently in progress. Because these tasks are unfinished at this time, only a small portion of the data is included in this paper. The completed results will be presented in a later publication.

Creep data for graphite/polyimide tested at 561 K (550°F) are shown in figure 11 for both unidirectional and $[0° \pm 45°]$ crossply specimens. The amount of creep (plastic strain) after 100 hours was less than 0.1 percent. This small amount of creep is typical of composites with unidirectional plies. Figure 12 compares the results of fatigue testing $[0° \pm 45°]$ graphite/polyimide at 505 K (450°F) at stress ratios of R = 0.1 and R = -1. The data show the fatigue life for a stress ratio of R = -1 to be much lower than for R = .1. Similar results have been observed for the other composite systems at room and elevated temperatures and for both unnotched and notched specimens. The fatigue properties of unnotched and notched $[0° \pm 45°]$ B/Al tested at 297 K (75°F) and 561 K (550°F) are compared in figure 13. The effect of raising the test temperature from 297 K (75°F) to 561 K (550°F) is to significantly reduce the fatigue strength at 10^7 cycles. For fatigue lives of 10^5 cycles or less, however, the effect of temperature is not very great.

Examination of the B/Al specimens that were fatigue tested at 561 K (550°F) has revealed severe degradation of the aluminum matrix material, as shown in figure 14. The surface of the specimen showed multiple cracks and roughness caused by localized deformation. The surface appearance suggests that the degradation may have been caused by grain growth and embrittlement at the grain boundaries. Specimens tested at 505 K (450°F) showed none of this surface degradation. Tests at 561 K (550°F) in either argon or nitrogen atmospheres gave significant decreases in surface degradation, an indication that environment plays an important role in the degradation process. In view of these results, boron/aluminum should be limited to 505 K (450°F) applications where it will be subjected to fatigue loading in air.

Flight Simulation

The major task of this program, the flight simulation tests, is the one for which the least amount of data are available at this time. These tests involve evaluation of the composite materials after they have been subjected to simulated supersonic flight environments for 10,000, 25,000 and 50,000 hours. The 50,000 hours are composed of 25,000 flight cycles similar to the one presented in figure 15. Exposures are performed in the General Dynamics Convair flight simulator shown in figure 16. This apparatus is capable of long time automatic testing using random loading and realistic flight temperature profiles. Both load level and maximum temperature are adjusted to suit the particular capabilities of each composite system. Following exposure residual tensile, notched tensile, fatigue, and notched fatigue strength will be determined. Details of(a) the design, construction, and checkout of the flight simulator, (b) the specimen configuration, and (c) the test plan have been covered extensively in references 2 and 3.

The flight simulation tests are in progress, but no residual strength results will be available until the first 10,000 hours have been completed. At the time of this writing, the boron epoxy and graphite epoxy systems have completed 7,500 hours of exposure and the graphite polyimide and boron aluminum systems 4,500 hours.

There have been, however, four unnotched graphite epoxy specimens that have failed in less than 5,000 hours, a rate well in excess of that predicted from the wearout theory used to set the test load levels and temperature. Three of these specimens are shown in figure 17. Fracture has occurred in the 5 cm (2 inch) long heated zone located at each end of the specimen. The fourth fractured in a manner which suggested an equipment problem rather than a material failure. A study is now in progress to determine the degradation mechanisms responsible for these early failures. Preliminary results indicate that the compression load which occurs once per flight cycle may be an important factor in the failure of the specimens. This is shown by the delaminations visible in the edge view in figure 18. The photograph is of the heated zone of a specimen which has not failed. Another mechanism which may be important is the accelerated oxidation that occurs as filaments in the outer plies fail, thereby exposing the underlying resin to the oxidizing environment. This is clearly shown in figure 19. SEM and optical examinations, residual compression and tensile strength, and chemical and thermomechanical analyses are currently in progress to resolve the difference between predicted and experimental failure for the graphite epoxy system. If compression continues to be the failure mode of these long term flight simulation specimens,

then wearout model predictions of failure (based on short term flight simulation specimens which failed in tension) are not applicable. Analyses based on more complex wearout plus oxidation mechanisms will need to be developed to predict long term flight simulation test failures.

CONCLUDING REMARKS

This paper describes a long term study to characterize the properties of several types of advanced filamentary reinforced composite material systems and to determine the effects of long time supersonic flight simulation on these properties. A status report on the progress to date has been presented along with some detailed results and analysis of the thermal aging phase of the program. While the investigation is still in progress, interim conclusions have been drawn on the basis of the data generated to date concerning the capabilities of these composite materials for supersonic cruise aircraft applications. These conclusions are in the form of exposure time and temperature limits; stress limits cannot be suggested until more results of simulated flight service testing are available. The interim conclusions are:

Graphite/epoxy (A-S/3501) and boron/epoxy (B/5505) should be limited to temperatures lower than 394 K (250°F) for cumulative exposures greater than 10,000 hours because of:

1. Moisture effects on elevated temperature strength (due to matrix degradation).

2. Loss of residual tensile strength during thermal aging (due to oxidation induced matrix degradation).

3. Early flight simulation test failures (due to compression loading combined with oxidation induced matrix degradation).

Boron/aluminum (B/6061) should be limited to 450 K (350°F) for exposures greater than 10,000 hours because of:

1. Loss of residual tensile strength during thermal aging (due to interface diffusion induced fiber degradation).

2. High temperature fatigue effects (matrix surface cracking and oxidation).

Boron/polyimide (B/P105AC) is not suitable for this application (because of lack of thermal exposure stability for 1000 hours at 505 K (450°F)).

Graphite/polyimide (HT-S/700) should be limited to 505 K (450°F) for exposures greater than 10,000 hours because of loss of residual tensile strength during thermal aging (due to oxidation induced matrix degradation).

REFERENCES

1. Kerr, J. R., Haskins, J. F. and Stein, B. A.: Program Definition and Preliminary Results of a Long-Term Evaluation Program of Advanced Composites for Supersonic Cruise Aircraft Applications. Environmental Effects on Advanced Composite Materials, Spec. Tech. Publ. 602, American Soc. Testing and Materials., 1976, pp. 3-22.

2. Haskins, J. F. Wilkins, D. J. and Stein, B. A.: Flight Simulation Testing Equipment for Composite Material Systems. Environmental Effects on Advanced Composite Materials, Spec. Tech. Publ. 602, American Soc. Testing and Materials, 1976, pp. 23-36.

3. Haskins, J. F. and Kerr, J. R., Time-Temperature-Stress Capabilities of Composite Materials for Advanced Supersonic Technology Applications, Third Conference on Fibrous Composites in Flight Vehicle Design, November 4-6, 1975, NASA TMX-3377, April 1976.

4. McKague, E. L.; Reynolds, J. D. and Halkias, J. E.: Life Assurance of Composite Structures, Vol. I - Moisture Effects, AFML-TR-75-51, May 1975.

5. Hertz, J.: Investigation Into The High Temperature Strength Degradation of Fiber-Reinforced Resin Composites During Ambient Aging, NASA CR-124290, June 1973.

6. Chase, V. and Beeler, D., Manufacturing Methods for Large High-Temperature Sandwich Structures, Technical Report AFML-TR-70-211, Air Force Materials Laboratory, Dayton, Ohio 1970.

TABLE I. LIST OF ADVANCED COMPOSITE SYSTEMS.

MATERIAL SYSTEM	TYPE	VENDOR	NOMINAL FIBER VOLUME (%)	SPECIFIC GRAVITY
BORON/EPOXY	RIGIDITE 5505 4.0-MIL BORON	Avco	58	2.0
GRAPHITE/EPOXY	A-S/3501	HERCULES	60	1.6
BORON/POLYIMIDE	B/P105AC 4.0-MIL BORON	Avco	50	2.0
GRAPHITE/POLYIMIDE	HT-S/710	HERCULES	63	1.5
BORON/ALUMINUM	DIFFUSION BONDED 5.6-MIL BORON; 6061 ALUMINUM	Avco	50	2.6

TABLE II. SCREENING EVALUATION CANDIDATES.

MATERIAL SYSTEM	POTENTIAL VENDORS
HT-S/NR-150B2	NARMCO, FIBERITE, U.S. POLYMERIC
HT-S/PMR-15	U.S. POLYMERIC, FERRO
HT-S/HR-600	FIBERITE
HT-S/5230	NARMCO
HT-S/F-178	HEXCEL
HT-S/4397	HERCULES

TABLE III. SUMMARY OF PHASE I TEST PROGRAM.

TEST TYPE	TOTAL TESTS	TESTS COMPLETED	PERCENT COMPLETED
QUALITY ASSURANCE	356	356	100
TENSILE	558	558	100
SHEAR	56	56	100
FRACTURE	24	8	33
ENVIRONMENTAL AGING	189	189	100
THERMAL AGING	297	297	100
CREEP	90	90	100
FATIGUE	495	495	100
FLIGHT SIMULATION	200	160	80
A. RESIDUAL TENSILE	550	160	29
B. RESIDUAL FATIGUE	160	0	0
C. RESIDUAL SHEAR	20	0	0
	2,995	2,369	79

TABLE IV. SUMMARY OF EFFECTS OF MOISTURE AND AMBIENT AGING ON RESIN-MATRIX COMPOSITES

Retention of Flexural Strength (Percent) after Indicated Exposure*					
Orient	Temp Deg K (Deg F)	24 Hour H_2O Boil	6 Week Humidity	20 Week Ambient	52 Week Ambient
B/5505 Boron/Epoxy					
[0]	297 (75)	94	103	105	110
[0]	450 (350)	23	39	59	53
[0 ± 45]	450 (350)	63	74	102	94
A-S/3501 Graphite/Epoxy					
[0]	297 (75)	100	100	110	96
[0]	450 (350)	34	30	54	46
[0 ± 45]	450 (350)	54	41	81	57
HT-S/710 Graphite/Polyimide					
[0]	297 (75)	85	85	103	100
[0]	450 (350)	105	106	85	107
[0 ± 45]	450 (350)	75	81	111	93

*Average of 3 Tests

TABLE V-A. THERMAL AGING DATA FOR UNIDIRECTIONAL A-S/3501 GRAPHITE/EPOXY.

Aging Temp K (F)	Pressure kN/m^2 (psi)	Test Temp K (F)	Aging Time (HR)	Tensile Strength MN/m^2	(ksi)
394 (250)	101 (14.7)	450 (350)	0	1,590	(230)
			100	1,520	(220)
				1,590	(230)
				1,540	(224)
				Avg 1,550	(225)
			500	1,260	(182)
				1,270	(184)
				1,470	(213)
				Avg 1,330	(193)
			1,000	1,480	(214)
				1,560	(227)
				1,450	(210)
				Avg 1,500	(217)
			5,000	1,630	(236)
				1,600	(232)
				1,440	(209)
				Avg 1,560	(226)
			10,000	1,650	(240)
				1,650	(239)
				1,850	(268)
				Avg 1,720	(249)
450 (350)	101 (14.7)	450 (350)	100	1,500	(218)
				1,650	(239)
				1,460	(212)
				Avg 1,540	(223)
			500	1,630	(236)
				1,620	(235)
				1,550	(225)
				Avg 1,600	(232)
			1,000	1,260	(182)
				1,500	(218)
				1,540	(223)
				Avg 1,430	(208)
			5,000	1,210	(175)
				1,370	(199)
				1,300	(188)
				Avg 1,290	(188)
			10,000	1,360	(198)
				1,270	(184)
				1,210	(176)
				Avg 1,280	(186)
450 (350)	13.8 (2)	450 (350)	5,000	1,730	(251)
				1,740	(252)
				1,560	(227)
				Avg 1,680	(243)
			10,000	1,770	(257)
				1,870	(271)
				1,760	(255)
				Avg 1,800	(261)

TABLE V-B. THERMAL AGING DATA FOR [0° ± 45°] CROSSPLY A-S/3501 GRAHPITE/ EPOXY.

Aging Temp K (F)	Pressure kN/m^2 (psi)	Test Temp K (F)	Aging Time (HR)	Tensile Strength MN/m^2	(ksi)
394 (250)	101 (14.7)	450 (350)	0	500	(72.5)
			100	496	(72.0)
				542	(78.6)
				483	(70.0)
				Avg 507	(73.5)
			500	475	(68.9)
				492	(71.4)
				494	(71.7)
				Avg 487	(70.7)
			1,000	494	(71.6)
				552	(80.0)
				626	(90.8)
				Avg 557	(80.8)
			5,000	589	(85.4)
				559	(81.1)
				536	(77.7)
				Avg 561	(81.4)
			10,000	559	(81.1)
				593	(86.0)
				585	(84.9)
				Avg 579	(84.0)
450 (350)	101 (14.7)	450 (350)	500	494	(71.6)
				608	(88.2)
				559	(81.1)
				Avg 554	(80.3)
			1,000	552	(80.0)
				501	(72.6)
				563	(81.6)
				Avg 539	(78.1)
			5,000	485	(70.3)
				440	(63.8)
				474	(68.7)
				Avg 466	(67.6)
			10,000	265	(38.5)
				60	(8.7)
				238	(34.5)
				Avg 188	(27.2)
450 (350)	13.8 (2)	450 (350)	5,000	584	(84.7)
				596	(86.4)
				571	(82.8)
				Avg 584	(84.6)
			10,000	535	(77.6)
				498	(72.3)
				548	(79.5)
				Avg 527	(76.5)

TABLE VI-A. THERMAL AGING DATA FOR UNIDIRECTIONAL B/5505 BORON/EPOXY.

Aging Temp K (F)	Pressure kN/m^2 (psi)	Test Temp K (F)	Aging Time (HR)	Tensile Strength MN/m^2	(ksi)
394 (250)	101 (14.7)	450 (350)	0	1,380	(200)
			100	1,390	(202)
				1,350	(196)
				1,370	(198)
				Avg 1,370	(199)
			500	1,460	(212)
				1,360	(197)
				1,340	(194)
				Avg 1,390	(201)
			1,000	1,330	(193)
				1,390	(201)
				1,380	(200)
				Avg 1,370	(198)
			5,000	1,480	(214)
				1,450	(210)
				1,520	(220)
				Avg 1,480	(215)
			10,000	1,410	(204)
				1,430	(208)
				1,450	(211)
				Avg 1,430	(208)
450 (350)	101 (14.7)	450 (350)	5,000	1,230	(179)
				1,240	(180)
				1,250	(182)
				Avg 1,240	(180)
			10,000	1,010	(146)
				1,010	(147)
				1,080	(156)
				Avg 1,030	(150)
450 (350)	13.8 (2)	450 (350)	5,000	1,520	(220)
				1,290	(187)
				1,400	(203)
				Avg 1,400	(203)
			10,000	1,390	(201)
				1,340	(195)
				1,400	(203)
				Avg 1,380	(200)

TABLE VI-B. THERMAL AGING DATA FOR [0° ± 45°] CROSSPLY B/5505 BORON/EPOXY.

Aging Temp K (F)	Pressure kN/m^2 (psi)	Test Temp K (F)	Aging Time (HR)	Tensile Strength MN/m^2	(ksi)
394 (250)	101 (14.7)	450 (350)	0	550	(79.8)
			100	510	(73.9)
				496	(71.9)
				493	(71.5)
				Avg 500	(72.4)
			500	478	(69.4)
				428	(62.1)
				474	(68.7)
				Avg 460	(66.7)
			1,000	512	(74.2)
				504	(73.1)
				539	(78.2)
				Avg 518	(75.2)
			5,000	535	(77.6)
				527	(76.4)
				533	(77.3)
				Avg 532	(77.1)
			10,000	538	(78.1)
				534	(77.4)
				522	(75.7)
				Avg 531	(77.1)
450 (350)	101 (14.7)	450 (350)	500	544	78.9
				461	66.9
				517	75.0
				Avg 507	73.6
			1,000	581	84.2
				508	73.7
				493	71.5
				Avg 527	76.5
			5,000	310	(44.9)
				319	(46.3)
				309	(44.8)
				Avg 313	(45.3)
			10,000	339	(49.2)
				342	(49.6)
				314	(45.6)
				Avg 332	(48.1)
450 (350)	13.8 (2)	450 (350)	5,000	519	(75.3)
				529	(76.7)
				590	(85.6)
				Avg 546	(79.2)
			10,000	379	(54.9)
				367	(53.2)
				381	(55.3)
				Avg 376	(54.5)

TABLE VII-A. THERMAL AGING DATA FOR UNIDIRECTIONAL HT-S/710 GRAPHITE/ POLYIMIDE.

Aging Temp K (F)	Pressure kN/m^2 (psi)	Test Temp K (F)	Aging Time (HR)	Tensile Strength MN/m^2	(ksi)
505 (450)	101 (14.7)	505 (450)	0	1,210	(176)
			500	827	(120)
				752	(109)
				758	(110)
				Avg 779	(113)
			1,000	1,210	(175)
				990	(144)
				1,370	(198)
				Avg 1,190	(172)
			5,000	1,190	(173)
				1,420	(206)
				1,240	(180)
				Avg 1,280	(186)
			10,000	1,280	(185)
				1,390	(201)
				1,350	(196)
				Avg 1,340	(194)
505 (450	13.8 (2)	505 (450)	5,000	1,370	(198)
				1,210	(175)
				1,480	(215)
				Avg 1,350	(196)
			10,000	1,280	(185)
				1,140	(166)
				1,180	(171)
				Avg 1,200	(174)
561 (550)	101 (14.7)	561 (550)	0	1,320	(191)
			200	1,290	(187)
				1,280	(185)
				1,350	(196)
				Avg 1,310	(189)
			500	1,170	(170)
				1,300	(189)
				1,200	(174)
				Avg 1,220	(178)
			1,000	1,100	(159)
				1,170	(169)
				1,190	(173)
				Avg 1,150	(167)
			5,000	1,170	(169)
				1,070	(155)
				1,010	(147)
				Avg 1,080	(157)
			10,000	1,117	(162)
				876	(127)
				807	(117)
				Avg 933	(135)
561 (550)	13.8 (2)	561 (550)	5,000	1,300	(188)
				980	(142)
				1,300	(188)
				Avg 1,190	(173)
			10,000	1,060	(154)
				1,010	(146)
				970	(140)
				Avg 1,010	(147)

TABLE VII-B. THERMAL AGING DATA FOR [0° ± 45°] CROSSPLY HT-S/710 GRAPHITE/ EPOXY.

Aging Temp K (F)	Pressure kN/m^2 (psi)	Test Temp K (F)	Aging Time (HR)	Tensile Strength MN/m^2	(ksi)
505 (450)	101 (14.7)	505 (450)	0	470	(68.2)
			1,000	521	(75.5)
				443	(64.3)
				328	(47.5)
				Avg 431	(62.4)
			5,000	435	(63.1)
				501	(72.6)
				576	(83.5)
				Avg 504	(73.1)
			10,000	335	(48.6)
				525	(76.2)
				454	(65.9)
				Avg 438	(63.6)
561 (550)	101 (14.7)	561 (550)	0	434	(63.0)
			1,000	443	(64.2)
				474	(68.7)
				394	(57.1)
				Avg 437	(63.3)
			5,000	276	(40.0)
				276	(40.0)
				258	(37.4)
				Avg 270	(39.1)
			10,000	192	(27.8)
				211	(30.6)
				274	(39.7)
				Avg 226	(32.7)

TABLE VIII-A. THERMAL AGING DATA FOR UNIDIRECTIONAL BORON/ALUMINUM.

Aging Temp K (F)	Pressure kN/m^2 (psi)	Test Temp K (F)	Aging Time (HR)	Tensile Strength MN/m^2	(ksi)
450 (350)	101 (14.7)	297 (75)	0	1,430	(208)
			5,000	1,320	(191)
				1,230	(179)
				1,070	(155)
				Avg 1,210	(175)
			10,000	1,007	(146)
				986	(143)
				869	(126)
				Avg 954	(138)
561 (550)	101 (14.7)	297 (75)	5,000	841	(122)
				855	(124)
				889	(129)
				Avg 862	(125)
			10,000	855	(124)
				703	(102)
				786	(114)
				Avg 781	(113)
700 (800)	101 (14.7)	297 (75)	5,000	327	(47.4)
				631	(91.5)
				315	(45.7)
				Avg 424	(61.5)
			10,000	263	(38.1)
				320	(46.4)
				318	(46.1)
				Avg 300	(43.5)

TABLE VIII-B. THERMAL AGING DATA FOR [0° ± 45°] CROSSPLY BORON/ALUMINUM.

Aging Temp K (F)	Pressure kN/m^2 (psi)	Test Temp K (F)	Aging Time (HR)	Tensile Strength MN/m^2	(ksi)
450 (350)	101 (14.7)	297 (75)	0	516	74.8
			5,000	430	62.3
				467	67.7
				535	77.6
				Avg 477	69.2
			10,000	459	66.6
				444	64.4
				428	62.1
				Avg 444	64.4
561 (550)	101 (14.7)	297 (75)	5,000	276	40.1
				251	36.4
				257	37.3
				Avg 261	37.9
			10.000	184	26.7
				214	31.1
				210	30.4
				Avg 203	29.4
700 (800)	101 (14.7)	297 (75)	5,000	168	24.4
				185	26.8
				198	28.7
				Avg 184	26.6
			10,000	142	20.6
				143	20.7
				154	22.3
				Avg 146	21.2

TABLE IX. GLASS TRANSITION TEMPERATURE, TG, DATA FOR [0°± 45°] A-S/3501 GRAPHITE/ EPOXY.

CONDITION	Tg, K (F)
AS-RECEIVED	463 (374)
AGED 5, 000 HR. AT 394K, 101 kN/m^2	463 (374)
AGED 10, 000 HR. AT 394K, 101 kN/m^2	464 (375)
AGED 5, 000 HR. AT 450K, 13. 8 kN/m^2	490 (422)
AGED 10, 000 HR. AT 450K, 13. 8 kN/m^2	505 (449)
AGED 5, 000 HR. AT 450K, 101 kN/m^2	*
AGED 10, 000 HR. AT 450K, 101 kN/m^2	*
FLIGHT SIMULATION, 4, 5000 HR. AT 408K	498 (436)

* SPECIMENS WERE UNSUITABLE FOR Tg DETERMINATION.

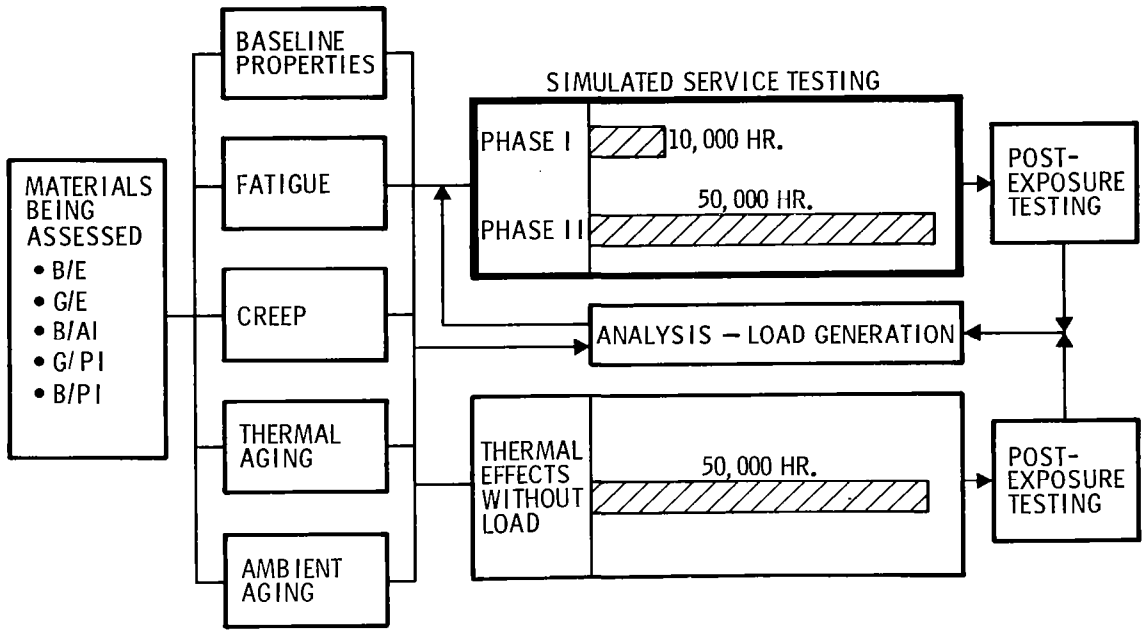


Figure 1.- Time-temperature-stress capabilities of composite materials.

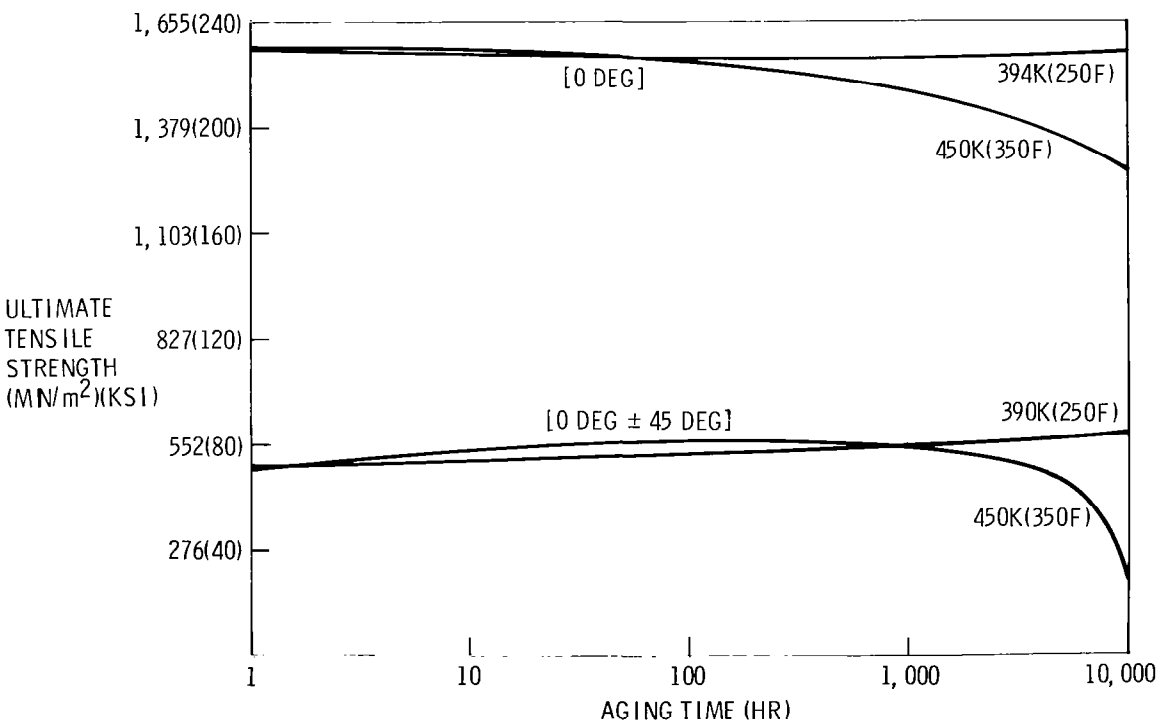


Figure 2.- Tensile strength of A-S/3501 graphite/epoxy at 450 K (350°F) after thermal aging at indicated temperature.

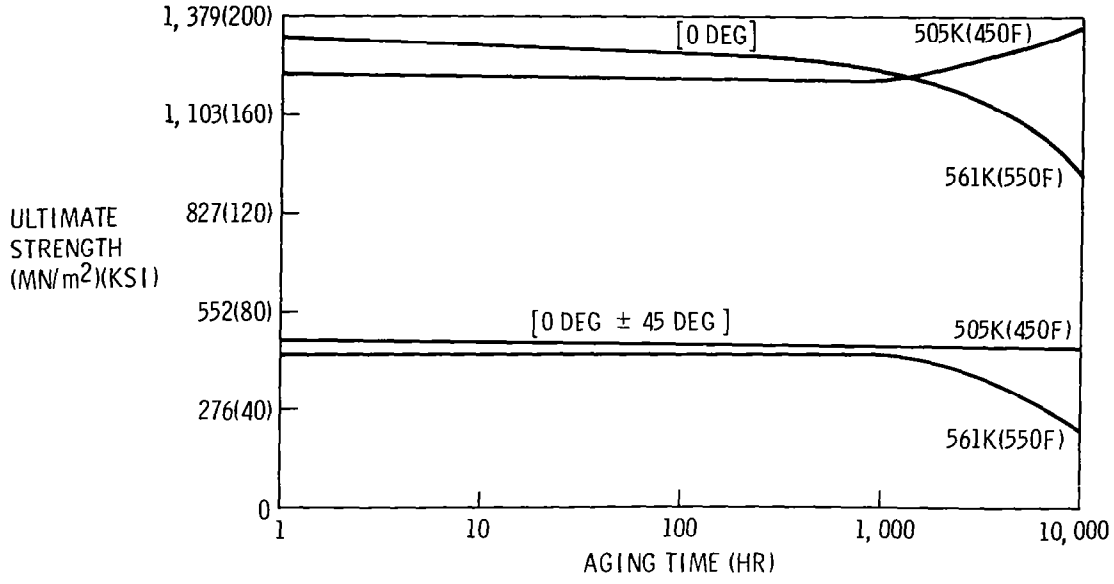


Figure 3.- Tensile strength of HT-S/710 graphite/polyimide at 505 K (450°F) and 561 K (550°F) after thermal aging at the same temperature.

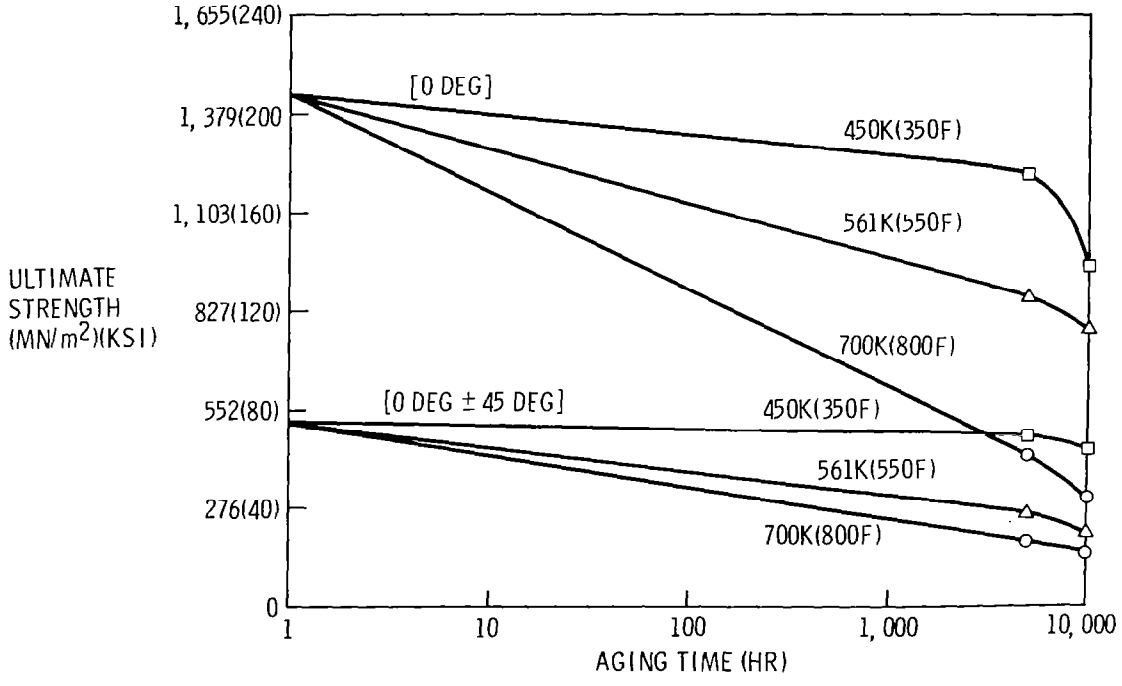


Figure 4.- Tensile strength of diffusion-bonded boron/aluminum at 297 K (75°F) after thermal aging at indicated temperature.

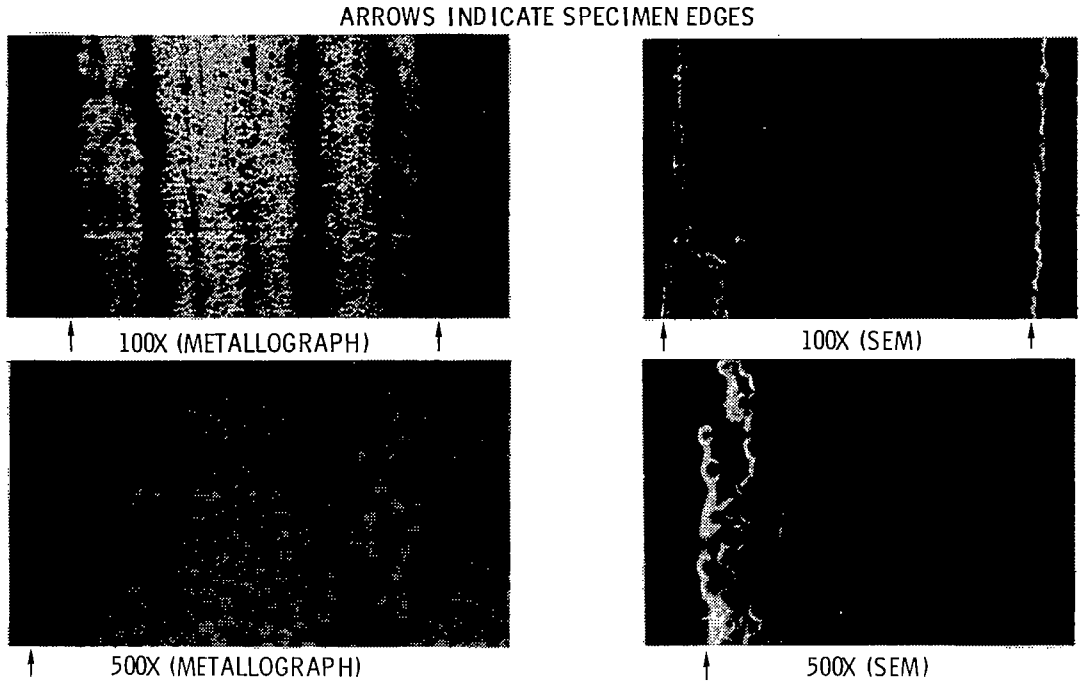


Figure 5.- Photomicrographs of A-S/3501 graphite/epoxy after thermal aging at 450 K (350°F) and 13.8 kN/m^2 (2 psi) for 10,000 hours.

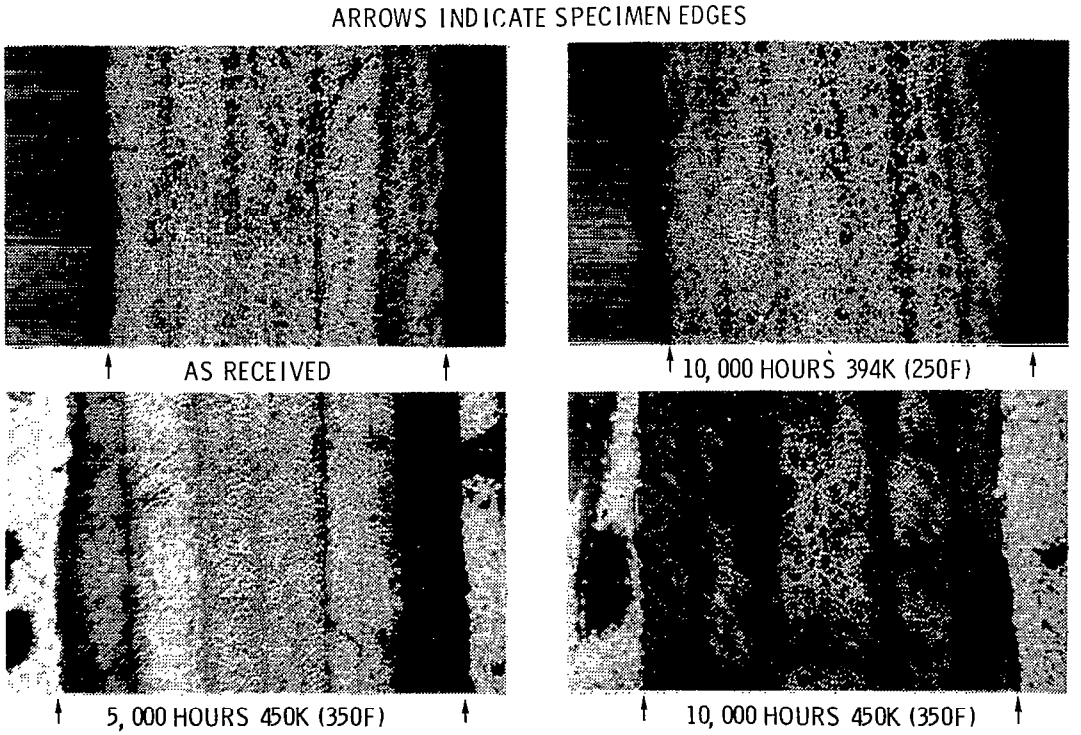


Figure 6.- Photomicrographs (metallograph) of A-S/3501 graphite/epoxy at 100X magnification.

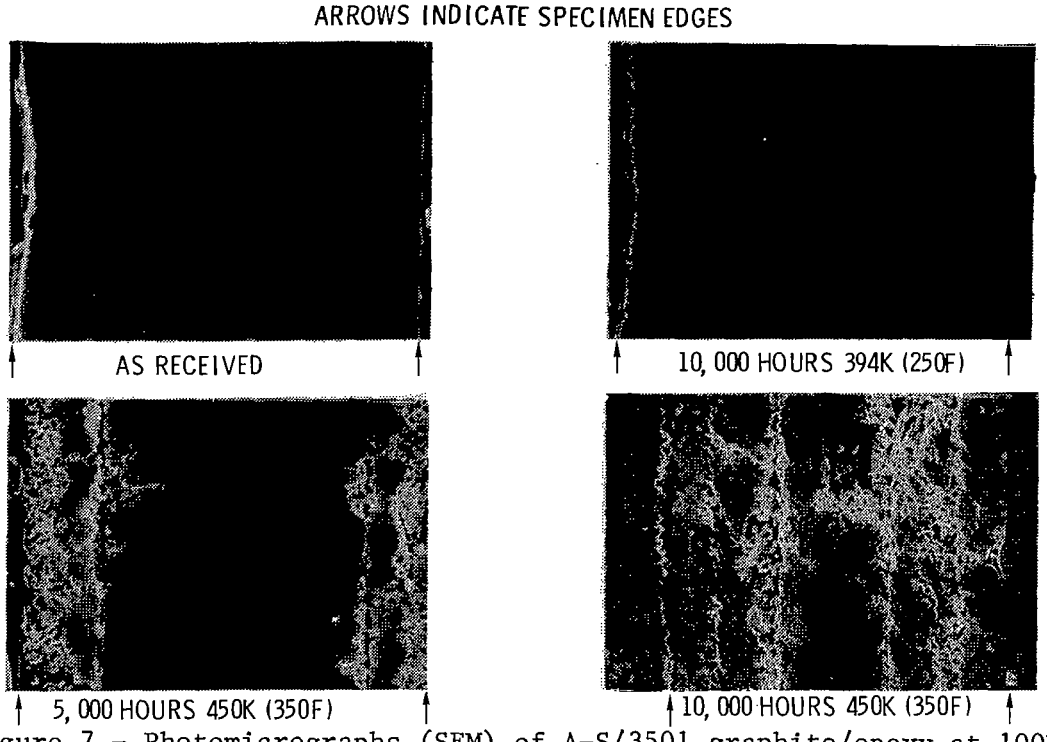


Figure 7.- Photomicrographs (SEM) of A-S/3501 graphite/epoxy at 100X magnification.

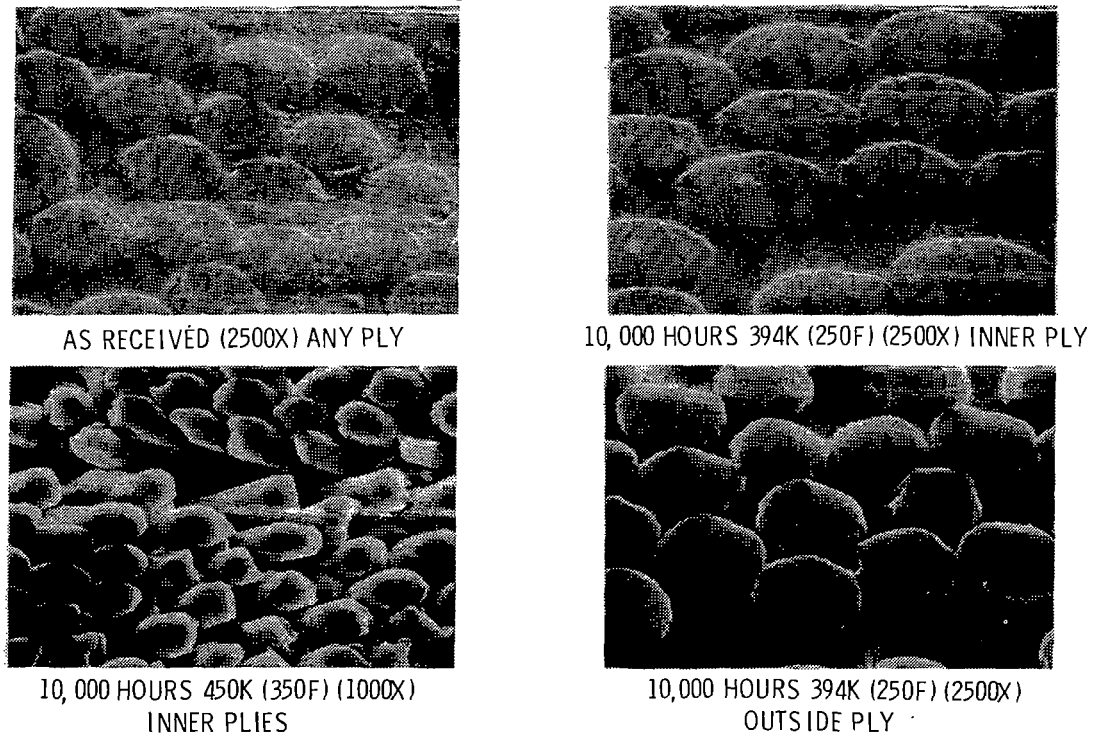
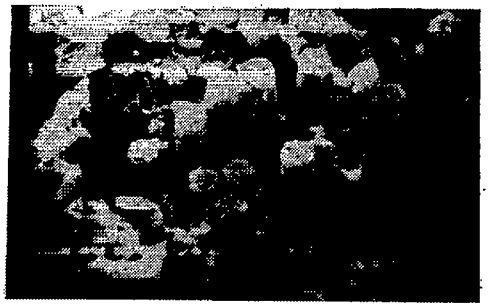
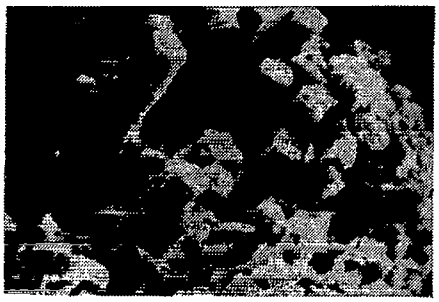


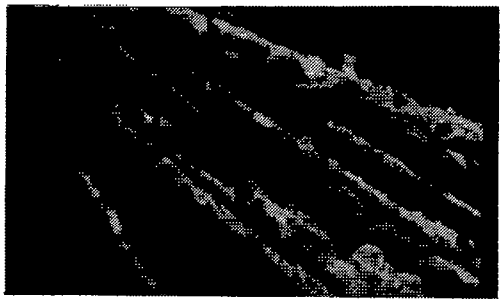
Figure 8.- Photomicrographs (SEM) of A-S/3501 graphite/epoxy.



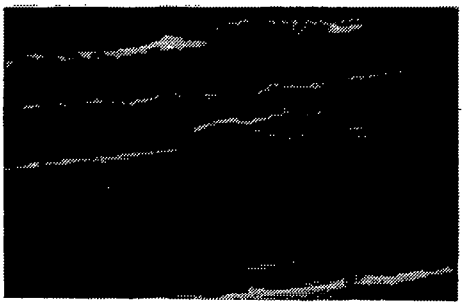
- AS RECEIVED TESTED AT 450K (350F) (900X)



10, 000 HOURS 394K (250F) (1000X)

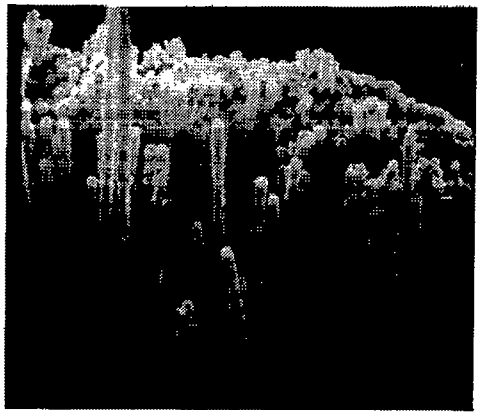


5, 000 HOURS 450K (350F) (500X)



10, 000 HOUR 450K (350F) (600X)

Figure 9.- SEM fractographs of A-S/3501 graphite/epoxy. 101 kN/m^2.



10, 000 HOURS 394K (250F), 101 kN/m^2 (14.7 psi)

10, 000 HOURS 450K (350F), 13.8 kN/m^2 (2 psi)

Figure 10.- SEM fractographs of A-S/3501 graphite/epoxy.

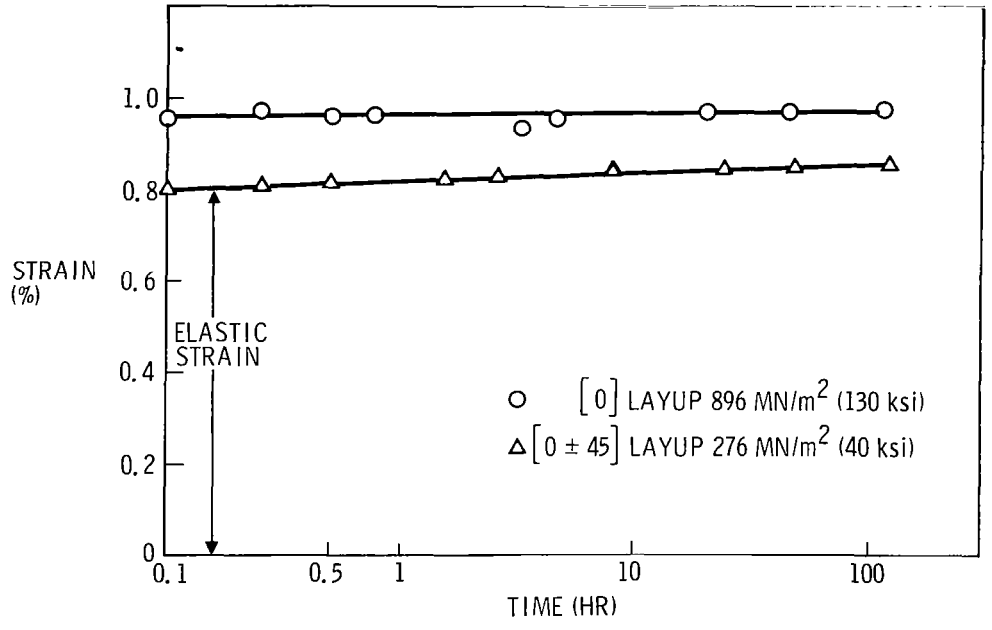


Figure 11.- Creep strain versus time for HT-S/710 graphite polyimide at 561 K (550°F).

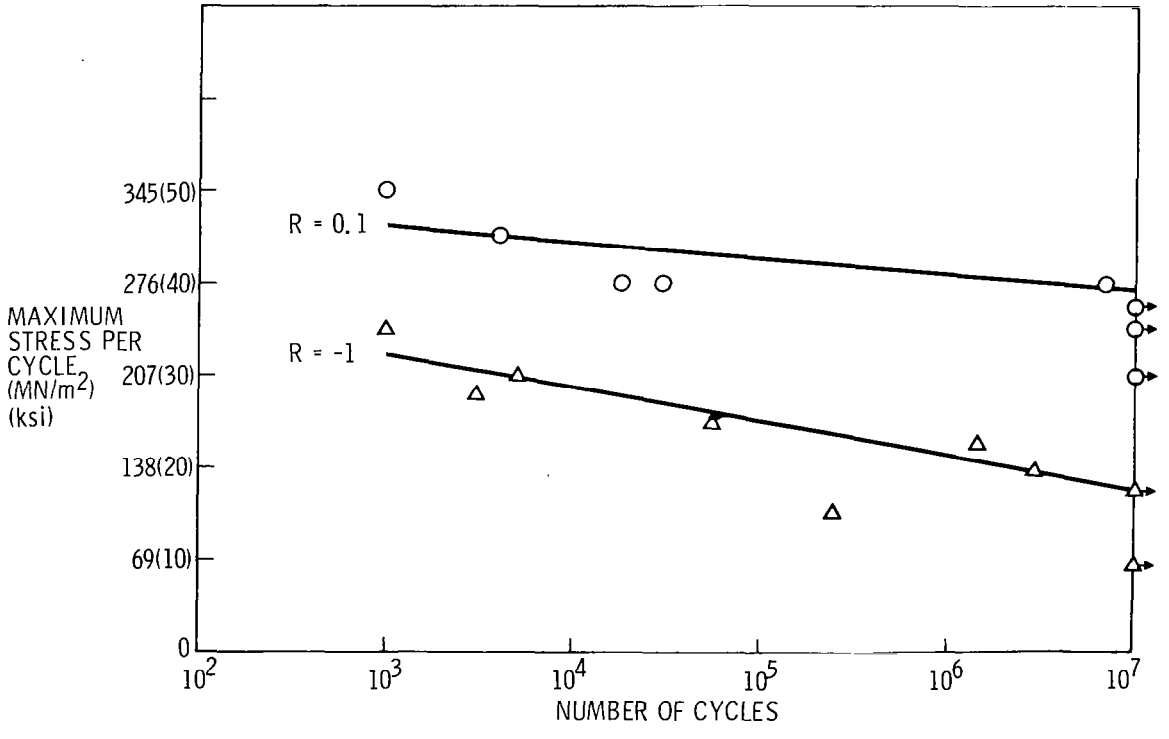


Figure 12.- Axial fatigue properties of [0 ± 45] HT-S/710 graphite polyimide at 505 K (450°F).

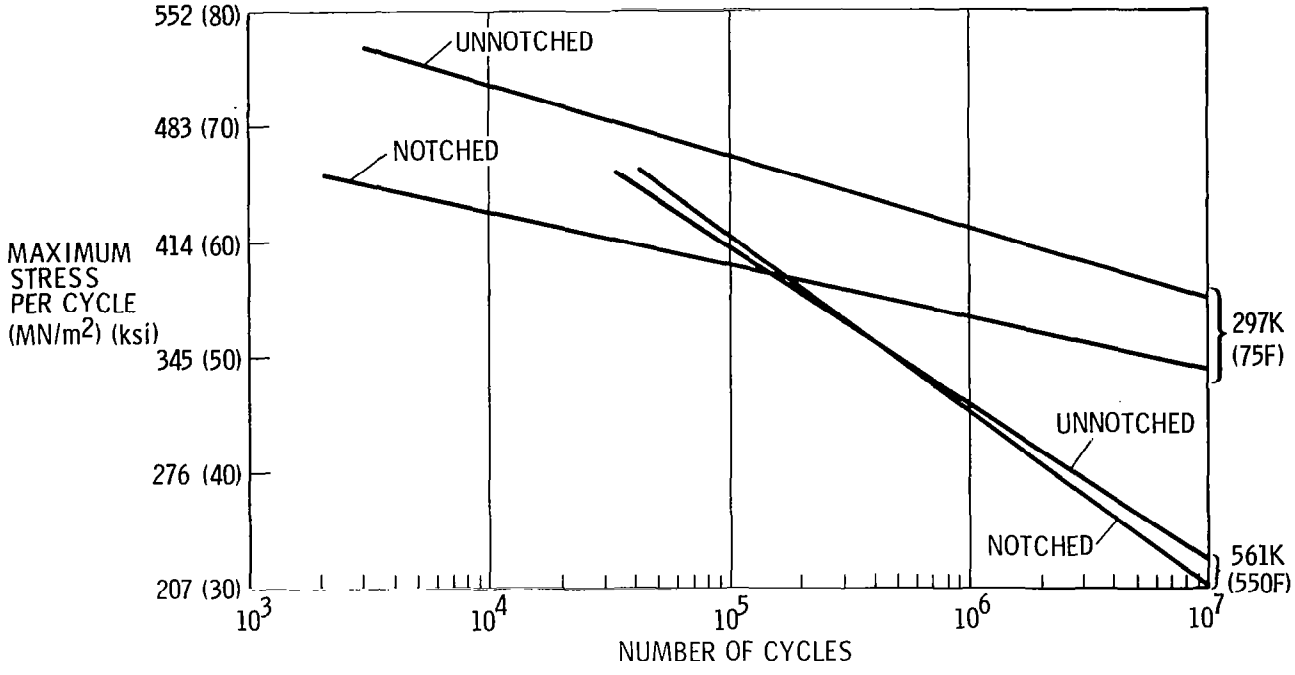


Figure 13.- Axial fatigue properties of $[0 \pm 45]_s$ boron/aluminum, for a stress ratio, R, of 0.1.

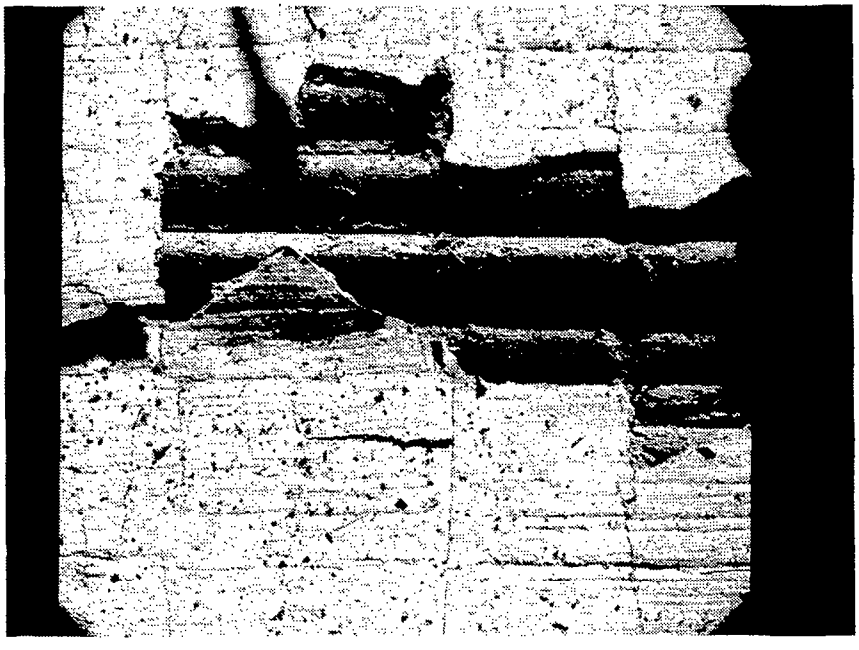


Figure 14.- Area of degraded boron aluminum surface showing reticulation and exposed boron fiber.

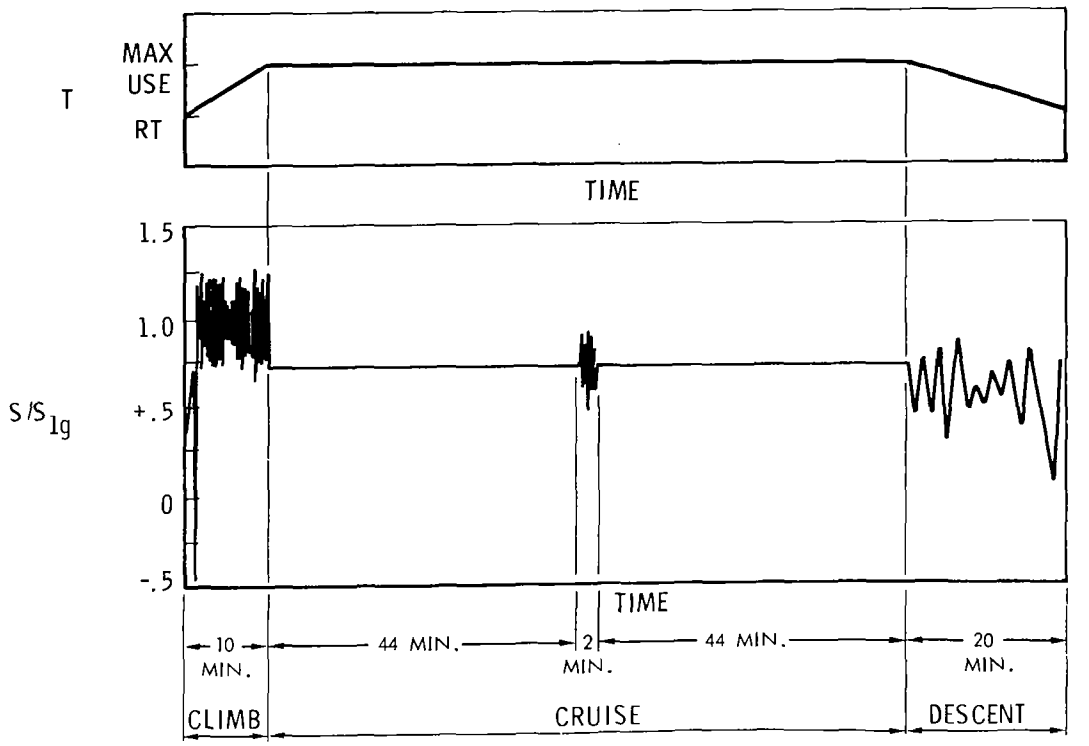


Figure 15.- Typical flight simulation cycle showing load and temperature profile.

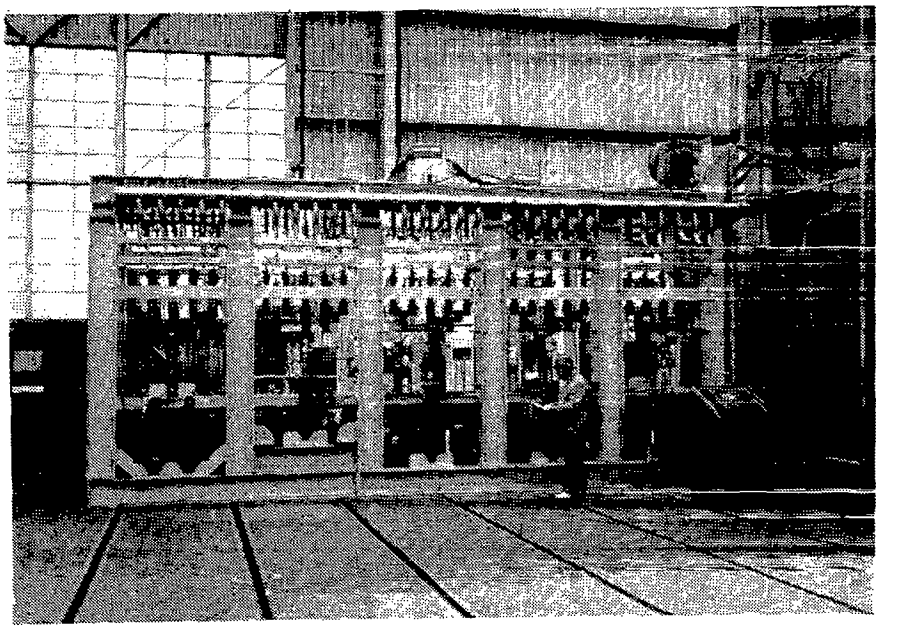


Figure 16.- Flight simulation equipment.

Figure 17.- A-S/3501 graphite/epoxy specimens after flight simulation exposure.

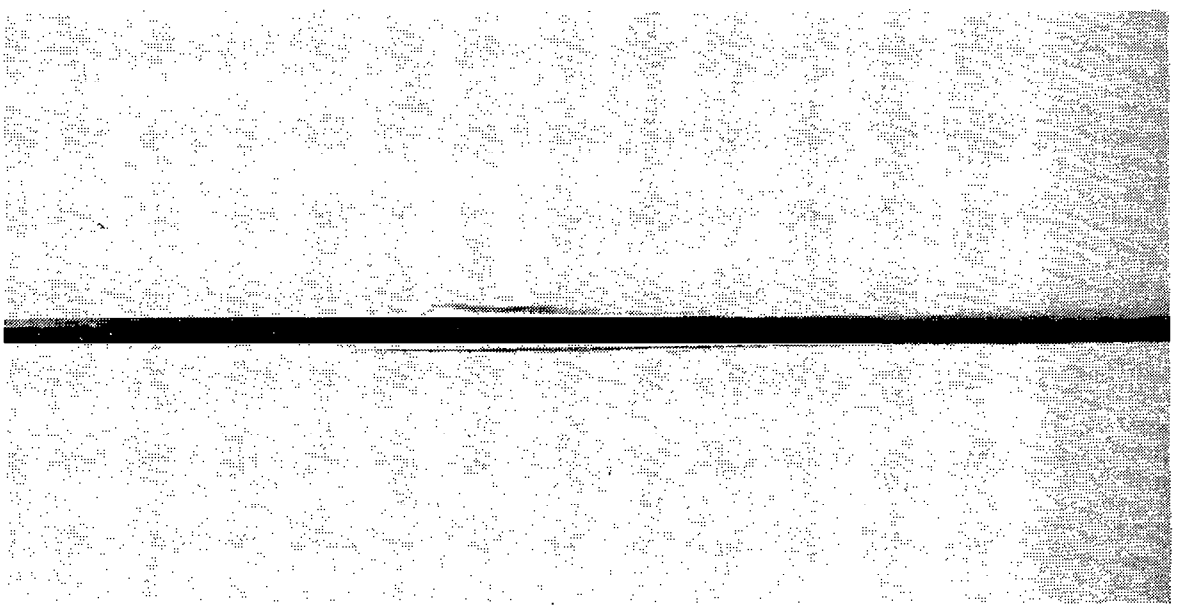


Figure 18.- A-S/3501 graphite/epoxy flight simulation specimens showing edge delaminations.

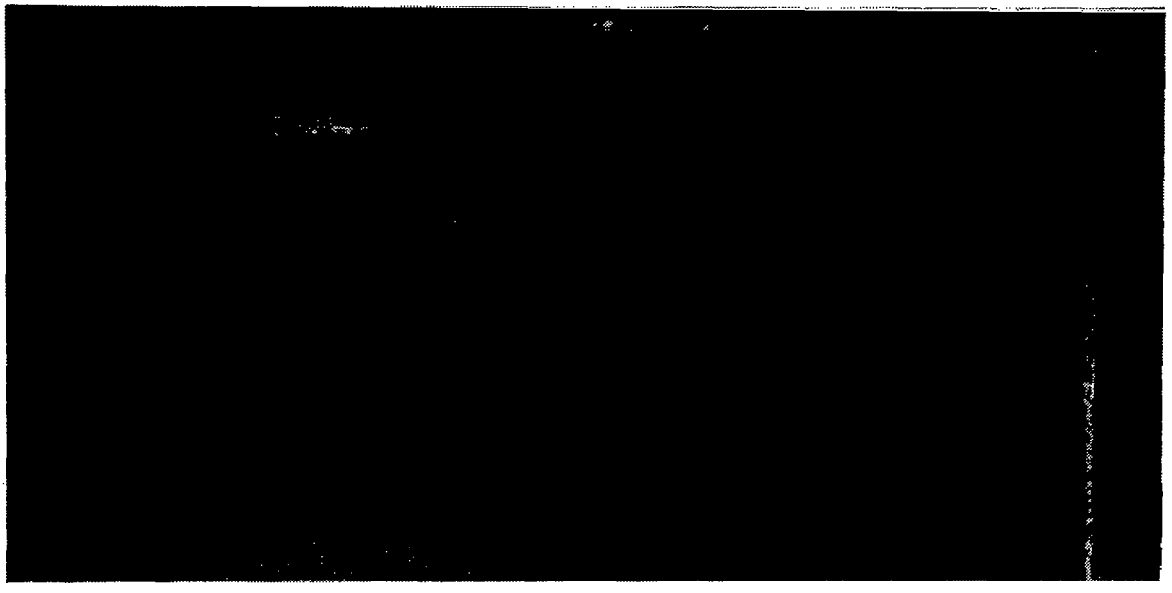


Figure 19.- A-S/3501 graphite/epoxy flight simulation specimen showing surface damage in 5 cm (2 inch) heated zone.