

SURFACE PROTECTION OF GRAPHITE FABRIC/PMR-15
COMPOSITES SUBJECTED TO THERMAL OXIDATION

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Graphite fabric/PMR-15 laminates develop matrix cracks during long-term exposure in air at temperatures in the range of 500 to 600 °F. This study was performed to demonstrate the effectiveness of incorporating graphite mat surface plies as a means of reducing the development of matrix cracks. Celion 3000 graphite fabric/PMR-15 laminates were fabricated with graphite or graphite mat/-325-mesh boron powder surface plies. Laminates without mat surface plies were also fabricated for control purposes. Composite flexural strength, flexural modulus, and interlaminar shear strength were determined at 288 °C before and after long-term exposure (up to 1500 hr) in air at 316 °C. The results of this study showed that the incorporation of graphite mat surface plies reduces matrix cracking and improves the elevated temperature mechanical property retention characteristics of the composites.

INTRODUCTION

In many instances graphite fabric is being selected as the fiber reinforcement material in structural composites intended for high-performance aerospace applications. For example, a graphite fabric/PMR-15 polyimide composite material has been selected for replacement of the current bill-of-materials titanium outer duct used on the General Electric F404 engine (ref. 1). The unique bidirectional properties of graphite fabric laminates enable designers to design composite structures having simplified laminate configurations which not only meet design requirements but are also less costly to fabricate than structural components made from unidirectional tape.

All polymer matrix composites subjected to long-term exposure in air at elevated temperatures, even those employing the so-called high-temperature polymers, exhibit weight loss and degradation of mechanical properties. Composite weight loss and concomitant property degradation have been attributed to diffusion-controlled oxidative degradation of the matrix (ref. 2). However, a recent study (ref. 3) on the effects of long-term, elevated-temperature exposure on the properties of T300/PMR-15 fabric laminates also identified matrix cracking as a contributing factor to weight loss and property degradation. Crack initiation is likely due to stresses in the matrix resulting from the local, nonuniform fiber distribution in woven fabrics.

Recently developed graphite mat (ref. 4) has potential for providing a more uniform fiber distribution. Thus, it was postulated that incorporation of a ply of graphite mat on the surface of fabric laminates would minimize cracking and thereby improve the property retention characteristics of graphite fabric laminates exposed to an elevated temperature oxidative environment.

The results of a study to improve the char-forming characteristics of matrix resins (ref. 5) suggested that boron powder might be an effective antioxidant for high-temperature resins. It was further postulated that a surface layer consisting

of both graphite mat and boron powder would significantly improve the elevated-temperature performance of graphite fabric/PMR-15 laminates.

The purpose of this investigation was to determine the effectiveness of surface plies of either graphite mat or graphite mat with boron powder as a means of protecting graphite fabric/PMR-15 laminates exposed to thermo-oxidative environments. Celion 3000 graphite fabric laminates with and without mat or mat/boron powder surface plies were fabricated using PMR-15 polyimide. Composite flexural strength, flexural modulus, and interlaminar shear strength were determined at 288 °C before and after long-term exposure (up to 1500 hr) in air at 316 °C. Composite weight loss at 316 °C was also determined.

EXPERIMENTAL PROCEDURE

Materials

Style W1133 8 harness satin-woven fabric from Celion 3000 graphite yarn was used as the primary reinforcing material. The yarn was sized with an epoxy compatible sizing. The mat material was a commercial product consisting of 1.9-cm-long Celion carbon fibers with a polyester binder. The mat weight was 112 gm/m². The boron additive used was an amorphous -325-mesh powder.

The polyimide resin used in this investigation was the high-temperature polyimide designated as PMR-15. The monomers used to formulate PMR-15 are shown in table 1. The monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE) and 4,4'-methylenedianiline (MDA) were obtained from commercial sources. The dimethyl ester of 3,3', 4,4'-benzophenonetetracarboxylic acid (BTDE) was prepared as a 50 weight percent solution by refluxing a suspension of the corresponding dianhydride in anhydrous methanol for ~2.75 hr. The monomer stoichiometry for the PMR-15 solution was 2 NE/3.087 MDA/2.087 BTDE. The PMR-15 solution was prepared by dissolving the monomers in a calculated amount of anhydrous methanol to yield a 50 weight percent solution.

Composite Fabrication and Specimen Preparation

The woven fabric was impregnated with a predetermined quantity of the PMR-15 resin solution to provide cured laminates having a fiber content of ~55 volume percent. The prepregs were air dried to reduce the volatile content to ~10 percent prior to cutting into plies.

Prior to impregnating the mat material, the polyester binder was burned-off by placing the as-received mat between perforated steel sheets and heating the steel/mat sandwich at 450 °C in an air-convection oven for 2 hr. The binder-free mat was allowed to cool to room temperature, placed between 0.625 cm mesh screens, and then impregnated with the PMR-15 resin solution. The mat containing the boron additive was impregnated with a PMR-15 solution to which 5-percent-by-weight boron powder had been added. Both mat preparations were air dried to reduce the volatile content to ~10 percent prior to cutting into plies. The impregnated fabric and mat materials were cut into 7.6 by 20.3 cm plies. The warp yarns of the fabric plies were parallel to the 20.3 cm dimension. The basic laminate consisted of a 6-ply layup of the woven fabric; laminates with mat surfaces consisted of the basic laminate with 1 ply of mat on each side. All of the fabric plies were stacked with their warp yarns in the 0° direction. Each layup was then stacked between a porous release fabric in a preforming mold and imidized at 204 °C for 1 hr under a pressure of ~0.07 N/cm². Compression molding was accomplished by placing the

staged layup into a matched metal die and heating to 232 °C at essentially zero pressure. A pressure of 345 N/cm² was applied and the mold temperature was increased to 316 °C at a rate of 5.6 °C/min. Pressure and temperature were maintained for 2 hr followed by cooling to 204 °C before releasing the pressure and removing the laminate for the mold. The cured laminates were postcured in an air-circulating oven in which the temperature was raised from ambient temperature to 316 °C at a rate of 2.2 °C/min and then held at 316 °C for 16 hr.

Composite Environmental Exposure

Coupons (approximately half of a 7.6 by 20.3 cm laminate) were subjected to thermo-oxidative exposure. All of the coupons were cut from essentially void-free laminates as assessed by ultrasonic C-scan. The thermo-oxidative environments were provided by an air circulating oven. Air was metered into the oven at a rate of 100 cm³/min. Coupons were periodically removed from the oven and allowed to cool to room temperature in a desiccator before reweighing to determine weight loss.

Composite Testing

Flexural tests conformed essentially to the ASTM standard method D790. Tests were made on a 3-point loading fixture with a variable span. Tests were performed using a span-to-thickness ratio of ~32. The rate of center loading for flexural testing was 0.127 cm/min. Interlaminar shear strength tests were conducted in accordance to ASTM D2344 using a constant span-to-thickness ratio of 4. For the elevated temperature tests, the load was applied to the specimens after the chamber had equilibrated at the test temperature for 10 min.

RESULTS AND DISCUSSION

Figure 1 shows the variation of 316 °C weight loss with exposure time in air at 316 °C for all of the Celion 3000 graphite fabric/PMR-15 composites investigated in this study. Also shown in the figure is the 316 °C weight loss of unidirectional Celion 6000 (unsized)/PMR-15 composites (ref. 6). As can be seen in the figure, all of the composites exhibited about the same level of thermo-oxidative stability. These results indicate the surface plies of mat or mat/boron powder had neither a beneficial or adverse effect on composite thermo-oxidative stability (TOS) as assessed by weight-loss measurements. The data also show that the presence of the epoxy sizing, used in weaving the fabric, did not cause increased degradation of the fabric composites. While an improvement in thermo-oxidative stability would have been desirable, the absence of a detrimental effect encouraged further investigation of the concept of using surface plies of mat material to reduce internal cracking.

Retention of composite mechanical properties after prolonged exposure at elevated temperature is a more meaningful assessment of composite TOS than composite weight loss. Figure 2 shows the 288 °C flexural property retention characteristics of the various laminates exposed at 316 °C as a function of exposure time in air at 316 °C. It can be seen that the property retention of the all-fabric laminates is lower than the property retention of laminates surface protected with mat or mat/boron. After 1500 hr of exposure at 316 °C, the unprotected fabric composite flexural strength retention was 56 percent, compared to ~74 percent retention of flexural strength for both the mat and mat/boron protected materials. The retention of modulus was 66 percent for unprotected fabric composites as compared to 88 and 104 percent retention for mat and mat/boron protected fabric/PMR-15 composites,

respectively. These results show that the surface protection is effective and that the improved retention of modulus is particularly significant.

The foregoing flexural strength comparisons were based on the ultimate properties of the laminates tested. However, the load-deflection characteristics of the isothermally-exposed, unprotected fabric/PMR-15 laminates revealed severely degraded structural integrity. Figure 3 shows typical flexural load-deflection curves for unprotected laminates tested after postcure (fig. 3(a)) and after 624 hr of isothermal exposure at 316 °C (fig. 3(b)). It can be seen that the postcured, but not exposed, laminate (fig. 3(a)) exhibited a load-deflection curve that is essentially linear to the ultimate load. In contrast, exposed, unprotected composites showed a quasi-yield point, or discontinuity, in the load-deflection curve (fig. 3(b)) that occurred at a relatively low load depending upon the duration of exposure. The average retention level as a function of time at which the yield occurred is indicated by the tailed symbols in figure 2. In marked contrast, the load-deflection characteristics of either graphite mat or graphite mat/boron surface plies had load-deflection characteristics similar to that of the postcured, but not exposed, fabric laminates. Using the discontinuity in the load-deflection curve instead of ultimate properties as the basis for flexural strength retention, the useful flexural strength retention is 45 percent after 624 hr and 22 percent after 1500 hr.

Figure 4 shows the 288 °C interlaminar shear strength retention of the laminates as a function of exposure time in air at 316 °C. It can be seen that the shear strength retention after long-term exposure has been improved by the mat and mat/boron surface plies. After 624 hr of exposure the shear strength retention varied ~5 percent among the three laminate constructions. After 1500 hr of exposure the interlaminar shear strength retention was 69 and 73 percent for the all-fabric laminates and mat-protected laminates, respectively. The mat/boron surface-modified laminates exhibited 87 percent retention of interlaminar shear strength after 1500 hr exposure in air at 316 °C. As is known, interlaminar shear specimens fail close to the specimen neutral plane. Thus, the higher interlaminar shear strength retention level for the mat/boron protected laminates suggests that the addition of boron to the mat increased the effectiveness of the mat in preventing interior cracking.

To ascertain the changes in structural features which might have resulted from elevated temperature exposure, cross sections of as-fabricated (postcured) laminates and exposed laminates were examined metallographically. Figure 5 shows representative photomicrographs of specimens from graphite fabric/PMR-15 as-fabricated laminates and from laminates that had been exposed for 624 hr at 316 °C. Figure 5(a) shows that the as-fabricated laminates were defect free. In figure 5(b) it can be seen that numerous through-the-surface-ply cracks had developed after 624 hr of exposure. Because specimens subjected to flexural testing fail at one of the surfaces by either a tensile or compressive failure mode, the presence of numerous surface cracks in the exposed composites accounts for the severe reduction in the flexural strength retention of the unprotected laminates (fig. 3).

Figure 6 shows representative photomicrographs of graphite fabric laminates with graphite mat surface plies. As can be seen in figure 6(a), the as-fabricated laminate was essentially defect free. Figure 6(b) shows the same laminate after 624 hr at 316 °C. It can be seen that the thermal-oxidative exposure has caused some internal cracking. Also, the surface cracking of the protected laminate was negligible compared to the surface cracking of the unprotected laminate (compare figs. 5(b) and 6(b)).

Figure 7 shows representative photomicrographs of graphite fabric laminates with graphite mat impregnated with PMR-15 and boron powder. It can be seen that the as-fabricated laminate (fig. 7(a)) as well as the exposed laminate (fig. 7(b)) were essentially free of surface and interior cracking. The absence of interior cracks in the mat/boron protected laminates accounts for their higher interlaminar shear strength retention compared to the other two laminate constructions. The important point to be noted, however, is that the incorporation of a surface ply of mat material was essential for the achievement of improved properties after elevated temperature exposure.

Although no attempt was made in this investigation to optimize the physical performance of the mat as a surface protection for graphite fabric/PMR-15 composites, variables such as mat thickness and density undoubtedly influence properties. If optimized, these variables would lead to significantly enhanced performance.

CONCLUSIONS

Based on the results obtained in this investigation, the following conclusions can be drawn:

(1) Isothermally exposed Celion-3000 graphite fabric/PMR-15 composites with graphite mat surface protection have greater flexural strength, flexural modulus, and interlaminar shear strength retention than fabric laminates without mat protection.

(2) Isothermally exposed graphite composites with mat surface protection exhibit essentially a linear flexural load-deflection relationship to failure whereas composites without mat protection exhibit a pronounced quasi-yield significantly below the failure load.

(3) Adding boron powder to the mat had essentially no effect on the flexural strength retention. However, flexural modulus and interlaminar shear strength retention were significantly improved.

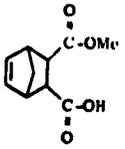
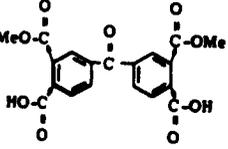
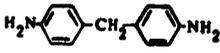
(4) Mat protected composites did not exhibit improved thermo-oxidative stability in isothermal weight loss as compared to unprotected graphite fabric composites.

REFERENCES

1. Serafini, Tito T.: PMR Polyimide Composites for Aerospace Applications. NASA TM-83047, 1982.
2. Alston, William B.: Characterization of PMR-15 Polyimide Resin Composition in Thermo-Oxidatively Exposed Graphite Fiber Composites. NASA TM-81565, 1980.
3. Serafini, T. T. and Hanson, M. P.: Environmental Effects on Graphite Fiber Reinforced PMR-15 Polyimide. Composites for Extreme Environments. ASTM STP 768, N. P. Adsit, ed., American Society for Testing and Materials, 1982, pp. 5-19.
4. New Nonwoven Fiber Mats Finding Multiple Uses In Plastics. Plastics Design Forum, Sept./Oct. 1980, pp. 82, 84, 86.

5. Gluyas, R. E. and Bowles, K. J.: Improved Fiber Retention by the Use of Fillers in Graphite Fiber/Resin Matrix Composites. NASA TM-79288, 1980.
6. Vannucci, Raymond D.: Properties of PMR Polyimide Composites Made with Improved High Strength Graphite Fibers. NASA TM-81557, 1980.

TABLE 1. - MONOMERS USED FOR PMR 15 POLYIMIDE

STRUCTURE	NAME	ABBREVIATION
	MONOMETHYL ESTER OF 5-NORBORNENE-2,3-DICARBOXYLIC ACID	NE
	DIMETHYL ESTER OF 3,3',4,4'-BENZOPHENONETETRACARBOXYLIC ACID	BTDE
	4,4'-METHYLENEDIANILINE	MDA

CS-71803

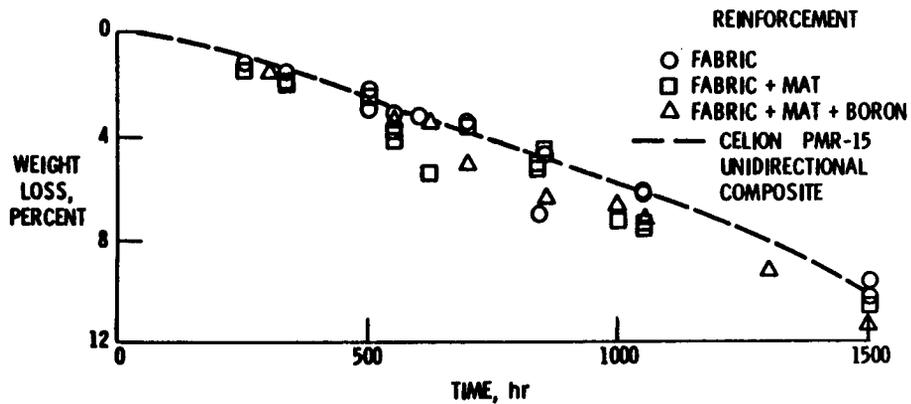


Figure 1. - Weight loss of Celion 3000 graphite fabric/PMR-15 laminates exposed in air at 316 °C.

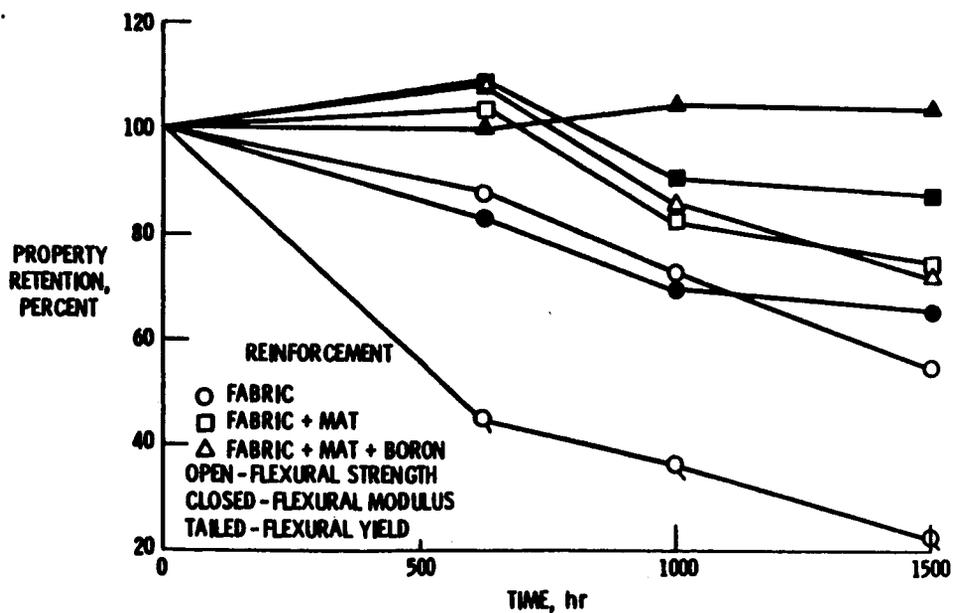


Figure 2. - Flexural properties of Celion 3000 graphite fabric/PMR-15 laminates exposed in air at 316 °C and tested at 288 °C.

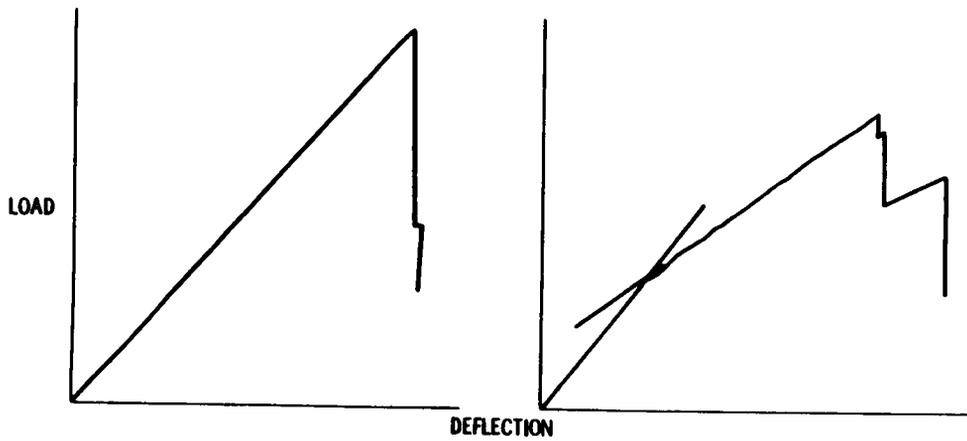


Figure 3. - Typical flexural load - deflection curves of Cellion 3000 graphite fabric/PMR-15 laminates; (a) tested at 288 °C after postcure (b) tested at 288 °C after 624 hr exposure in air at 316 °C.

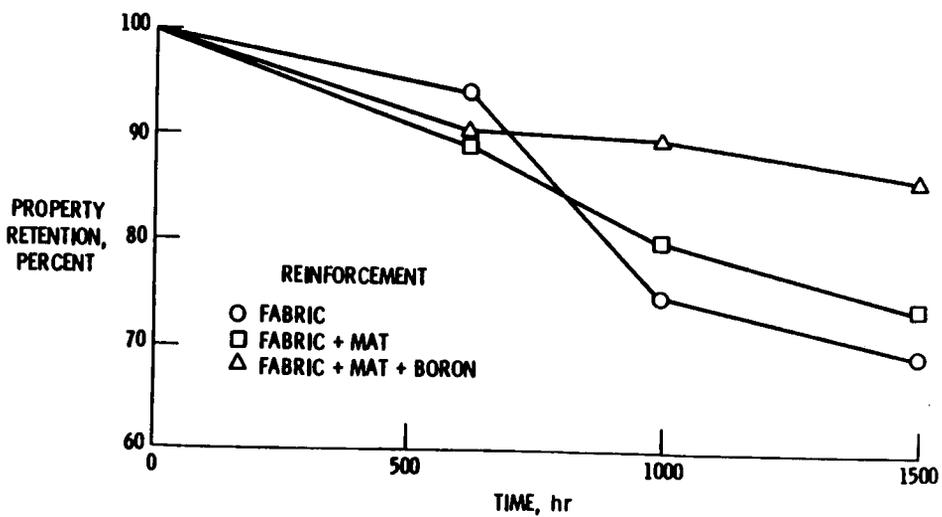
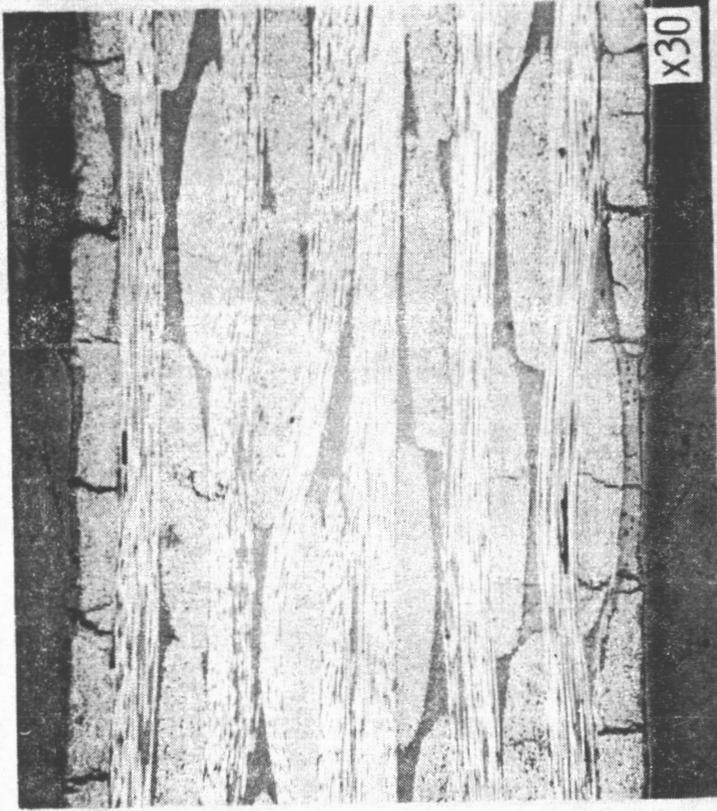


Figure 4. - Shear property retention of Cellion 3000 graphite fabric/PMR-15 laminates exposed in air at 316 °C and tested at 288 °C.



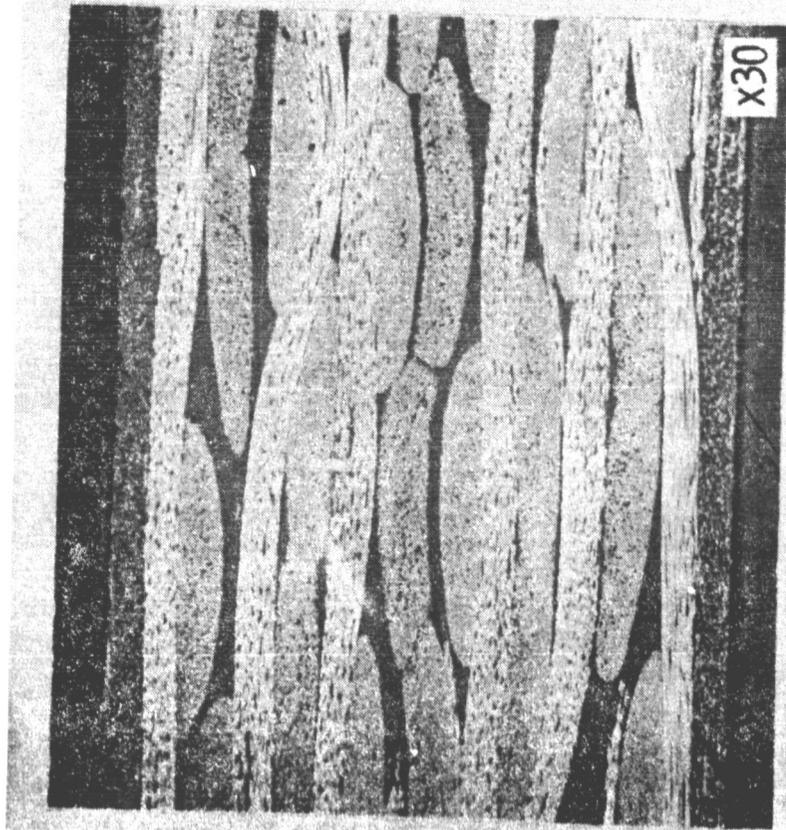
624 hr AT 316° C (600° F)

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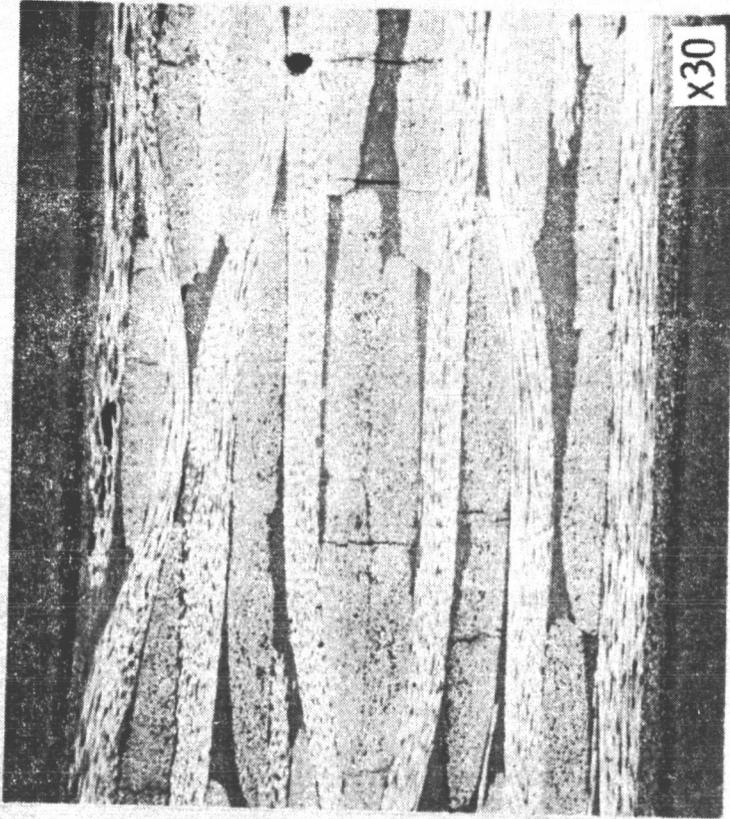


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Figure 5. - Typical photomicrographs of Celion 3000 graphite fabric/PMR-15 laminates before and after elevated temperature exposure in air.



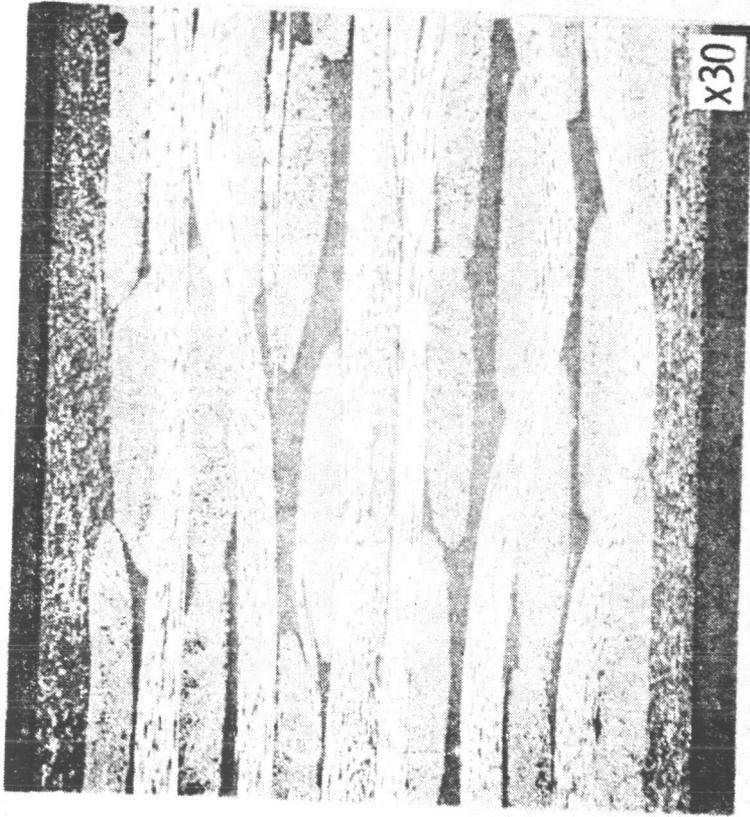
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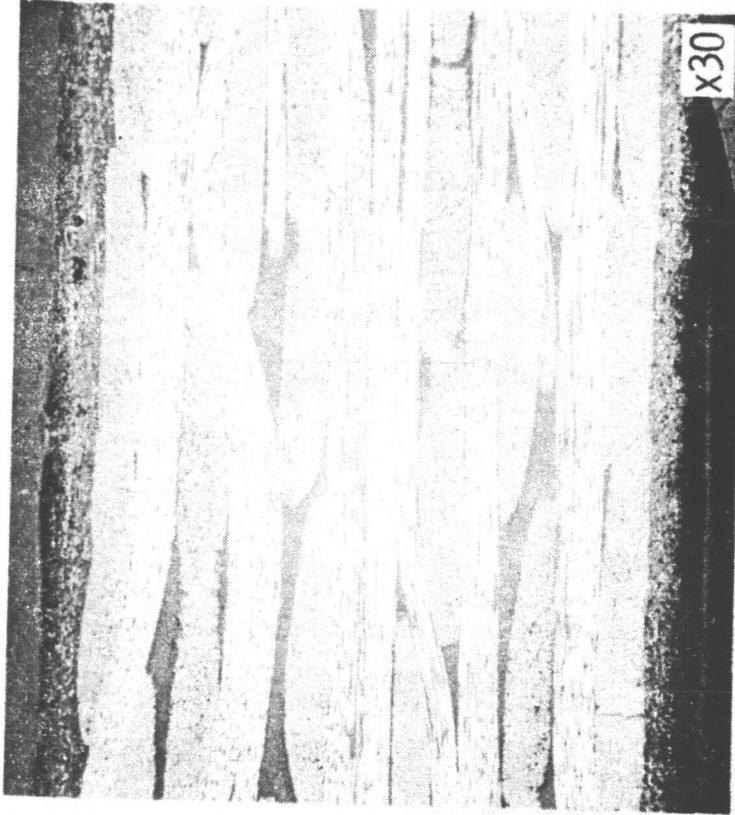
624 hr AT 316° C (600° F)

CS-83-0609

Figure 6. - Typical photomicrographs of Cellon 3000 graphite fabric/PMR-15 laminates made with graphite mat surface plies, before and after elevated temperature exposure in air.



AS FABRICATED



624 hr AT 316° C (600° F)

CS-83-0611

Figure 7. - Typical photomicrographs of Cellon 3000 graphite fabric/PMR-15 laminates, made with graphite mat/boron powder surface plies, before and after elevated temperature exposure in air.