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ABSTRACT

We have systematically studied the variation of ultimate tensile strength with thermal treatment of B-Al composite materials and of boron fibers chemically removed from these composites in an attempt to determine the mechanism of the resulting strength degradation. This knowledge will be of value in designing to extend the use-temperature of these composites. Our findings indicate that thermally cycling B-Al represents a more severe condition than equivalent time at temperature. Degradation of composite tensile strength from about 1.3 GN/m^2 to as low as 0.34 GN/m^2 was observed after 3000 cycles to 420° C for 203 μm B-1100 Al composite. In general, the 1100 Al matrix composites degraded somewhat more than the 6061 matrix material studied. Measurement of fiber strengths confirmed a composite strength loss due to the degradation of fiber strength. Microscopy indicated a highly flawed fiber surface.

On the basis of the thermal cycling studies in air and in the absence of air and of electron diffraction analysis of the reaction zone, a mechanism is favored in which B reacts with Al, freshly exposed by cold working during cycling, to form AlB_2. The nonuniform interface reaction leads to a highly flawed and weakened B fiber.

INTRODUCTION

The upper use-temperature for a metal matrix composite is often limited not by the approach to the softening point of the matrix, but rather by factors such as thermally induced stresses and chemical reaction between the components. The source of this premature degradation of the composite strength may be due to weakening or failure of the matrix, the fiber, and/or the fiber-matrix interface.

Typical composite components display a wide disparity in thermal expansion that leads to the generation of large interfacial shear or debonding stresses. These stresses can exceed the yield stress of the matrix alloy at moderate temperatures. However, in a metal matrix composite, the resulting plastic deformation of the matrix contributes little to the composite strength. Exceptions occur where the composite is repeatedly cycled to temperature and cumulative thermal fatigue damage can result.[1] The seriousness of this effect also depends on the degree of constraint the matrix experiences; e.g., the volume fraction of fiber, the layup, etc.

Fiber-matrix interface failure may result from the thermal stresses directly or from these stresses in combination with increased chemical reaction at the interface. Interface failure will prevent the desired transfer of load between the fibers when the composite is stressed causing early failure of weaker fibers.

While the thermal stresses alone are usually insufficient to cause fiber failure in a composite such as B-Al, the fiber strength may be degraded by chemical reaction at elevated temperatures[2] leading to subsequent failure under reduced load. Previous studies, while demonstrating

that reaction occurs, have not led to a specific understanding of the thermal failure mechanism. To this purpose, we present the results of a systematic study of the effects of thermal history on the fracture strength of B-Al composites. This study was designed to elucidate the degradation and failure processes occurring. It is anticipated that the understanding developed here might well lead to approaches that would extend the use of B-Al or similar composites.

Boron-aluminum composites used in these studies were purchased from commercial fabricators and contained either 143 µm (5.6 mil) or 203 µm (8 mil) boron fibers in either a 6061 or 1100 Al matrix. Thermal treatments included cycling from near room temperature to either 320° C or 420° C for up to 3000 cycles, or annealing at 420° C for equivalent times at temperature. Fracture strengths of both the fibers and composites were measured. Physical and chemical studies were made on both fibers and composites. The findings of these studies are discussed in terms of probable failure mechanisms.

EXPERIMENTAL

The 143 µm B-Al composites used in this study were fabricated by Avco Systems, Inc., and the 203 µm B-Al composites by TRW, Inc. using Avco fibers. The composites were diffusion bonded under the manufacturers' optimum conditions. The nominal fiber content in all cases was 48 vol %. Twelve inch by twelve inch sheets were prepared having 8 fiber plies laid up uniaxially. Two matrix materials were selected for this study, 6061 Al (1% Mg, 0.6% Si, 0.25% Cu, 0.25% Co, 98% Al) and 1100 Al (99 + % Al), both in the as-fabricated condition.

Rectangular coupons 1.1 cm wide by 8 to 10 cm long were cut from the sheets with a diamond wheel. Care was taken to insure that the fiber direction was parallel to the long axis of the coupons. The cut edges were found to have a satisfactory finish without further surface preparation. The fiber ends were left exposed in all testing.

Thermal cycling was done by alternately dipping a frame supporting six specimens into a hot (320° C or 420° C) fluidized sand bath and then into a similar cold bath that equilibrated near 50° C. In one experiment, some 203 µm B-1100 Al specimens were encapsulated in a stainless steel envelope in a 99.998% argon atmosphere and cycled 2500 times to 420° C. Identical specimens were simultaneously cycled in air. This experiment was designed to determine if the strength degradation was due to oxidation in the air environment.

For the 143 µm B-Al composites (Avco), the cycle consisted of a 1.7 minute hot period and 1.2 minute cold period. With the 203 µm B-Al composites (TRW), a cycle with a 2.7 minute hot period and 1.2 minute cold period was used. In both cases, the heating and cooling profiles were essentially identical. Typical time-temperature profiles are shown in Figure 1. Some 203 µm B-Al composites, fabricated by Avco, were run using the shorter cycle but these panels were found to be incompletely bonded and the strength data will not be presented here. It might be stated, however, that these data showed qualitative agreement with the TRW specimen data as to the temperature at which strength degradation appeared.

After cycling to a predetermined number of cycles, the specimens were removed from the bath and aluminum doublers were bonded to the

coupon ends with a contact adhesive. Tensile strengths were obtained with an Instron testing machine using wedge type grips. The specimens were pulled to failure at a constant crosshead speed of 0.126 cm/min.

Similar coupon specimens were also heated at 420° C in air for times equivalent to the time at temperature for the 1000, 2000, or 3000 cycle experiments. After this treatment, doublers were attached and tensile strengths were obtained as with the cycled specimens.

Boron fibers were chemically removed from 203 μm fiber composites similarly heat treated, i.e., as-received, cycled, and annealed. This was acccmplished by simple immersion in dilute hydrochloric acid. The fibers so removed were counted and measured and their distribution with length was determined for each specimen. A number (usually six) of the unbroken fibers from each type of specimen and heat treatment were pulled to failure in an Instron testing machine. Selected fibers were examined in the scanning electron microscope.

Fragments of the fiber-matrix interface reaction zone of some cycled specimens were analyzed using transmission electron diffraction. Under the conditions used in this program, this zone is only between 0.2 to 0.4 μm thick and is soluble in most reagents which could be used to expose the layer. However, a mechanical removal method which involved gentle flexure of the composite and floatation of the resulting fragments proved successful for several 203 μm B-1100 Al specimens which had been cycled 3000 times to 420° C.

RESULTS AND DISCUSSION

The tensile strengths of the composites as a function of temperature cycles are shown in Figures 2, 3, 4 and 5. The shaded curve through the

data points is meant only to illustrate the trend of the data and not the scatter band or probable error. Curves are drawn in each figure through the data from specimens cycled to 320° C and to 420° C.

For the 143 μm B-Al composites, the strengths of specimens cycled to 320° C show no degradation from the as-received strengths (plotted at 0 cycles) even after as many as 3000 cycles. However, after 3000 cycles to 420° C, these specimens show significant loss of strength from initial values near 1.4 GN/m^2 to values near 1.0 GN/m^2 for the 6061 matrix material and near 0.75 GN/m^2 for the 1100 matrix material. The 3000 cycle data are plotted in Figures 6 and 7 against maximum cycle temperature to better illustrate the temperature dependence of the degradation. The trend curve drawn conforms with a thermally activated process.

Also shown in Figures 6 and 7 are bands which include all the strength data for similar composite specimens which have been held at 420° C for times equivalent to the time-at-temperature for the cycled specimens. The actual strengths measured for these specimens are presented in Table I. These data show little variation from those of the as-received specimens and indicate that the strength degradation depends on thermal cycling.

The strength data for cycled 203 μm B-Al composites are shown in Figures 4 and 5. For the 203 μm B-Al composites, in contrast to the 143 μm B-Al composite data, degradation appears even at 320° after 3000 cycles. As before, the 1100 matrix alloy composite showed more degradation than the 6061. The strength of the 203 μm B-1100 Al composite after 3000 cycles to 420° C was only 0.4 GN/m^2. Figures 8 and 9 show these

data plotted against maximum cycle temperature for 2000 and 3000 cycles.
The strengths for specimens cycled 3000 times to 420° C show only a lit-
tle more degradation than for those cycled 2000 times to 420° C. This
small change probably reflects the approach to a minimum value set by the
matrix strength. We have, therefore, drawn an "S" shaped trend curve for
these data. Again, the scatter band for the thermal annealed data at 420°
indicates no degradation due to heating alone.

We can gain additional insight into the degradation process from
studies fibers removed from the matrix by acid dissolution. The fiber
strengths measured for fibers removed from 203 μm B-6061 Al and from
203 μm B-1100 Al composites, as-received or cycled 2000 or 3000 times to
320° or 420° C, are plotted in Figures 10 and 11 against maximum cycle
temperature. The data for fibers from thermally annealed composites are
again shown in the scatter band at 420° C. The data indicate that ther-
mal cycling causes a degradation of B fiber strength in Al matrix com-
posites. This finding, based on actual fiber strength measurements, con-
firms indirect evidence from the degradation of composite strength to
values below the "lower bound"[3] defined by the bundle strength of aligned
composite fibers with no matrix. Using the method of Corten[4] in the
Appendix, we calculate the lower bound strengths of specimens with unde-
graded fibers from the knowledge of the distribution of individual fiber
strengths from Smith[5], the volume fraction of complete fibers in the spec-
imen, and the fiber test length to diameter ratio. The lower bound
strengths so calculated are 0.83 GN/m^2 for 143 μm B-Al specimens and
0.88 GN/m^2 for 203 μm B-Al specimens, well above some of the strengths we
measured for cycled composites.

The temperature dependence of the fiber strength degradation seen in Figures 10 and 11 correlates remarkably well with that for composite strength degradation. This correlation and temperature dependence strongly suggests a composite degradation process in which the fiber is weakened by reaction. However, the process requires more than just thermal activation. This is evident from the lack of degradation due to thermal annealing alone. The calculated thermally induced stresses due to cycling either to $320°$ or $420°$ C are insufficient to cause failure of the fibers, even those having strengths below 0.9 GN/m^2 as found in Figures 10 and 11. This fact was confirmed by counts of broken fibers in as-received and cycled composites. No statistically significant difference in the number of broken fibers was seen for cycled specimens compared with as-received. The small number of broken fibers found, (<3%), could be accounted for as surface fibers damaged during specimen fabrication.

We conclude then that the fibers in our experiments do not fail during the thermal cycling process, but rather that they fail at reduced stress during testing.

Perhaps the most revealing insight into the mechanism of degradation comes from scanning electron micrographs of the fibers removed from the matrix. Figure 12 shows 2000 X magnification of the surface of fibers from as-received composite, from composites cycled 2000 times to $320°$ C and to $420°$ C, and from composites simply heated to $420°$ C for a time equivalent to 2000 cycles. The fiber from the as-received composite is seen to be relatively smooth as is that from the $320°$ C cycled

material. In contrast, the fiber from composite cycled to 420° C shows a very roughened surface. The annealed composite fiber shows a slightly roughened surface, but apparently not sufficient to cause weakening of the fiber: of all fibers so studied, only the ones showing the highly flawed surface similar to the 420° cycled fibers were weakened. Keeping in mind that the thermal stresses alone are insufficient to roughen the boron surface, we next propose a model to account for this surface condition. This model requires that the boron undergoes a nonuniform surface reaction during thermal cycling.

Based on possible reactions of B at the temperature of the degradation, and also on the apparent need for cycling, two mechanisms are considered. Both require plastic deformation of the matrix under the thermally induced stresses during cycling. This requirement is easily met in these experiments. For example, we calculate the radial stress at the B-Al interface of a composite heated from room temperature to 300° C to be in excess of 0.4 GN/m^2. The first mechanism involves the reaction of the B fiber with air which, because of the cold working of the matrix, can now permeate the aluminum at these relatively low temperatures. Repeated cycling can, by a grain boundary sliding, produce a microporosity in the Al matrix, and even a macroporosity in the more severe cases, cf. Figure 13. The site of oxidation of the B surface would depend on the nature of the matrix porosity or grain structure. This could lead to an uneven oxidation, hence a roughened B surface.

The second mechanism involves the known reaction of B and Al

$$B + Al \rightarrow AlB_2$$
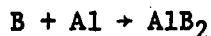
In most B-Al composites, this reaction is minimized because, during fabrication, aluminum at the B/Al interface forms a film of Al_2O_3 which does not react readily with B. However, during thermal cycling, the plastic deformation of the Al matrix would break this film and expose fresh Al to the B surface and the reaction could occur quite readily. Here again, surface roughening is due to the localized reaction determined by the plastic deformation. The boriding reaction apparently does not occur as we cycle to lower temperatures. This mechanism also would explain why reaction did not occur during thermal annealing experiments at 420° C. Here since the specimen undergoes only one thermal cycle, little fresh Al was provided.

Unfortunately, the acid solution required to remove the fibers from the matrix also dissolves both AlB_2[6] and B_2O_3 making it difficult to differentiate between these mechanisms by simple chemical analysis of the fiber surface. However, as discussed in the Experimental Section, we were able to obtain electron diffraction patterns on interface reaction zone material mechanically removed from some cycled specimens. This material was found to be predominately AlB_2. No B_2O_3 or other borates were found. Other work that supports the second mechanism (boride formation) includes several studies[7] of the degradation of strength of B-Al composites which have been held at temperatures somewhat higher (~470° C) than the temperatures at which we observe degradation after cycling. In these cases where the matrix is not highly cold worked, the likely reaction is AlB_2 formation due to the proximity of the reactants. At the higher temperature, this reaction would be enhanced.

Finally, we consider the results of the argon atmosphere experiment. If the oxidation mechanism prevailed, we might expect to see little or no degradation of the airfree composite strengths compared with the strengths of those cycled in air. This was not found to be the case. The range and average values of strengths were nearly identical for both conditions and about 30 percent below the as-received strengths. This initial experiment, while representing only a single thermal history, again favors the boride model. This result, however, seems to be in conflict with the findings of Wright and White[8] who note a difference in the strength of B-Al specimens cycled in air and in argon.

SUMMARY

A systematic study of the variation of ultimate tensile strength with thermal treatment of B-Al composite materials and of bor n fibers chemically removed from these composite. was made in an attempt to determine the mechanism of the resulting strength degradation. We found the following. (1) Thermally cycling B-Al represents a more severe condition than equivalent time at temperature. Degradation of composite tensile strength from about 1.3 GN/m^2 to as low as 0.34 GN/m^2 was observed after 3000 cycles to 420° C for 203 μm B-1100 Al composite. (2) In general, the 1100 Al matrix composites degraded somewhat more than the 6061 matrix material studied. (3) Measurement of fiber strengths confirmed a composite strength loss due to the degradation of fiber strength. (4) Microscopy indicated a highly flawed fiber surface.

On the basis of the thermal cycling studies in air and in the absence of air and of electron diffraction analysis of the reaction zone, a mechanism is favored in which B reacts with Al, freshly exposed by cold working during cycling, to form AlB_2. The nonuniform interface reaction leads to a highly flawed and weakened B fiber.

APPENDIX

The strength of a bundle of similar fibers, σ_B, can be calculated[4] from

$$\sigma_B = \sigma_0\left[(L/d)\omega e\right]^{-1/\omega} \tag{1}$$

where L/d is the fiber length to diameter ratio and σ_0 and ω are constants determined from the probability-distribution function

$$G(\sigma) = 1 - \exp\left\{- (L/d)\left[\frac{\sigma - \sigma^*}{\sigma}\right]^{\omega}\right\} \tag{2}$$

where $\left[(\sigma - \sigma^*)/\sigma_0\right]^{\omega}$ is the Weibull distribution function. Here, σ^* is lower limit of strength (assumed to be zero), σ_0 is a scale parameter, and ω is a parameter related to the scatter in the data. $G(\sigma)$ is the number of samples that have fractured at a stress σ or less. Equation (2) can be rearranged to give

$$\ln\left\{\ln\left[1/(1 - G(\sigma))\right]\right\} = \omega\left[\ln(\sigma/\sigma_0)\right] + \ln(L/d)$$

from which a plot of $\ln\left\{\ln 1/\left[1 - G(\sigma)\right]\right\}$ vs. $\ln \sigma$ will yield the parameters σ_0 and ω. Such plots of Smith's data[5] for as-received 143 µm and 203 µm Avco boron fiber are shown in Figure 14. The curves are linear, justifying the assumption of a Weibull distribution. The value of the parameters, σ_0 and ω, are also shown in the figures.

Using these parameters and appropriate values of (L/d) from our tests ($L = 4.45$ cm) and Smith's value for the average fiber diameters ($d = .0141$ and 0.0201 cm) we can calculate σ_B for either 143 µm or 203 µm fiber bundles.

The lower bound of strength is given by σ_B multiplied by the volume fraction of fibers in the composite. The volume fraction measured was corrected for the small number of surface fibers which were split by the cut-off wheel in specimen preparation (~2%). The lower bounds of strength thus measured were for the 143 μm composites,

$$\sigma_{LB} = 0.83 \text{ GN/m}^2$$

and for the 203 μm composites,

$$\sigma_{LB} = 0.88 \text{ GN/m}^2$$

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TABLE I. – TENSILE STRENGTHS OF COMPOSITES AFTER HEATING

IN AIR AT 420° C FOR TIMES INDICATED

	45 Hr	90 Hr	135 Hr
203 μm B – 1100 Al	1.26 GN/m^2	1.25 GN/m^2	1.25 GN/m^2
	1.31	1.30	1.17 .
203 μm B – 6061 Al	1.12	1.12	1.05
	1.15	.94	1.11
	28 Hr	56 Hr	85 Hr
143 μm B – 1100 Al	1.20	1.22	0.99
	1.33	1.04	1.05
143 μm B – 6061 Al	1.26	1.41	1.37
	1.43	1.28	1.25
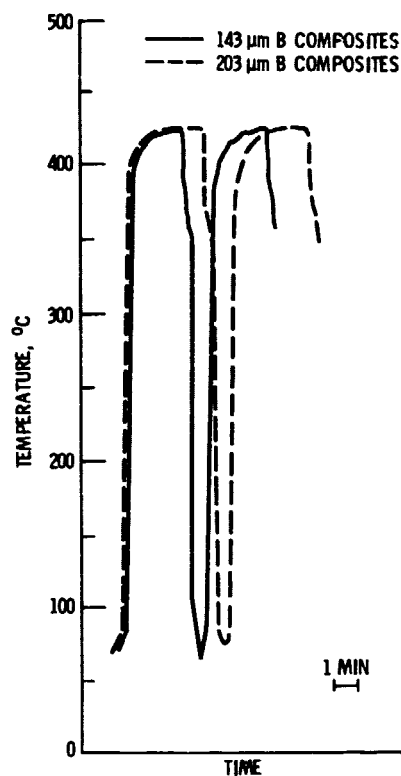
Figure 1. - Typical thermal cycle time-temperature profiles.
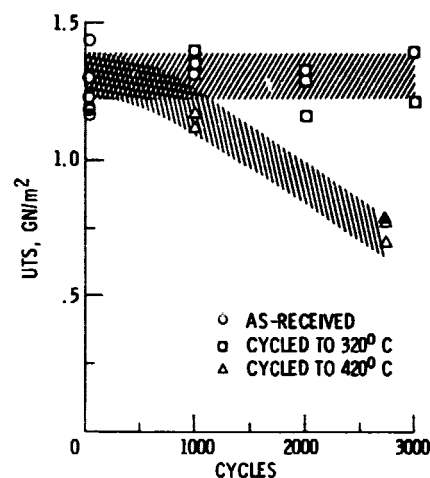
Figure 2. - Room temperature ultimate strengths of 143 µm B-1100 Al matrix composites after cycling to 320° and 420° C for indicated numbers of cycles. As-received strengths are shown at zero cycles.
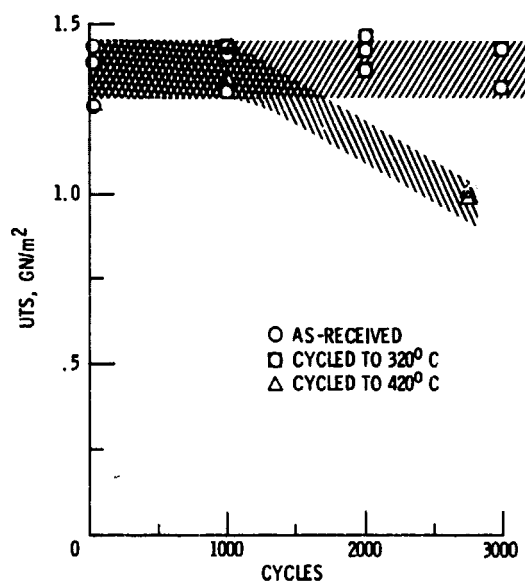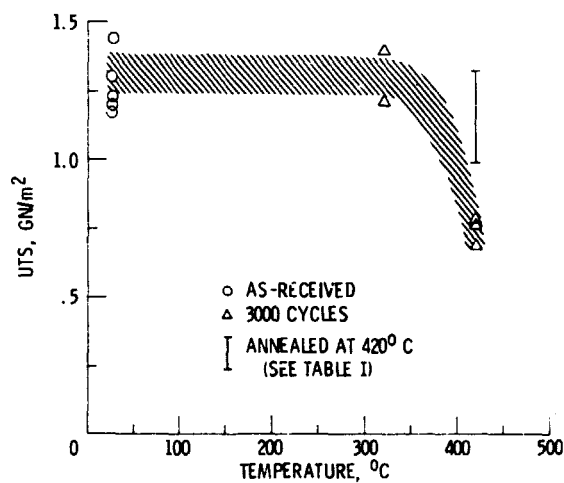

Figure 3. - Room temperature ultimate tensile strengths of 143 µm B-6061 Al matrix composites after cycling to 320° and 420° C for indicated numbers of cycles. As-received strengths are shown at zero cycles.

E-9097
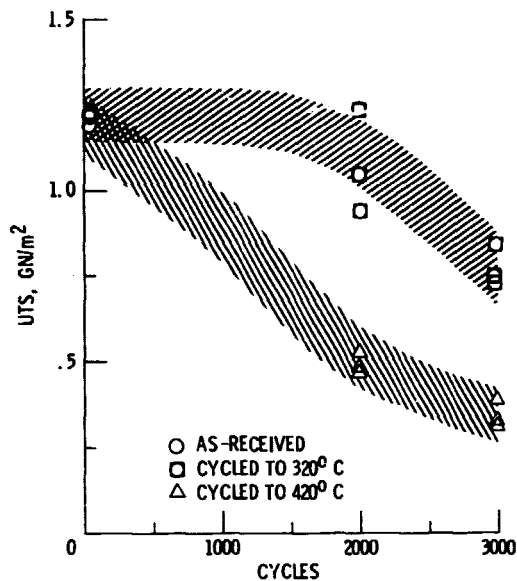
Figure 4. - Room temperature ultimate tensile strengths of 203 μm B-1100 Al matrix composites after cycling to 320° and 420° C for indicated numbers of cycles. As-received strengths are shown at zero cycles.
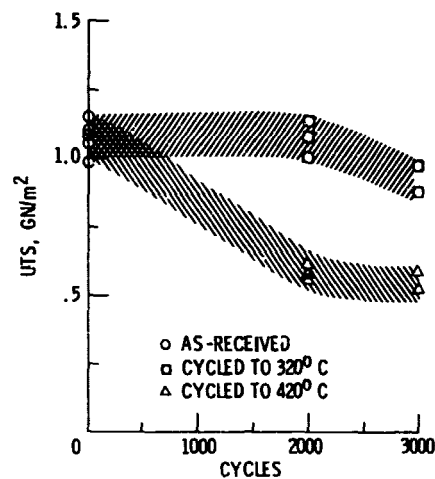
Figure 5. - Room temperature ultimate tensile strengths of 203 μm B-6061 Al matrix composites after cycling to 320° and 420° C for indicated numbers of cycles. As-received strengths are shown at zero cycles.

Figure 6. - Room temperature ultimate tensile strengths of 143 μm B-1100 Al matrix composites cycled 3000 times to indicated temperatures. Range of strengths of similar composites annealed at 420° C are also shown.
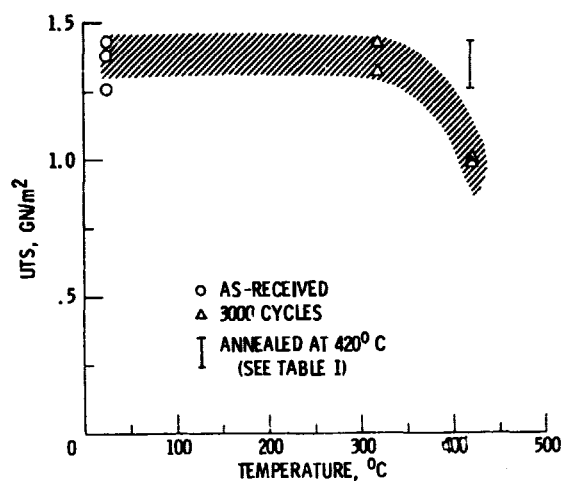
Figure 7. - Room temperature ultimate tensile strengths of 14 µm B-6061 Al matrix composites cycled 3000 times to indicated temperatures. Range of strengths of similar composites annealed at 420° C are also shown.
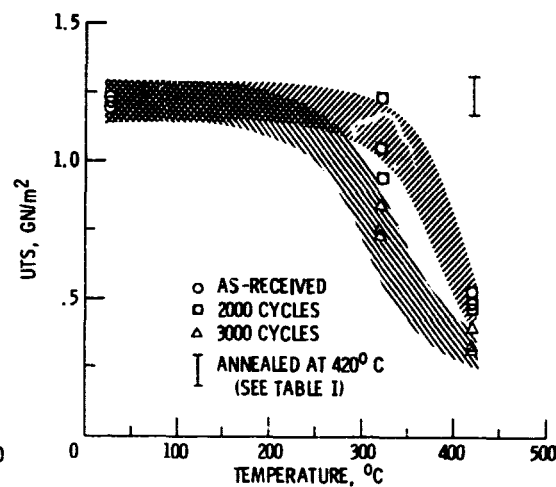

Figure 8. - Room temperature ultimate tensile strengths of 203 µm B-1100 Al composites cycled 2000 or 3000 times to indicated temperatures. Range of strengths of similar composites annealed at 420° C are also shown.
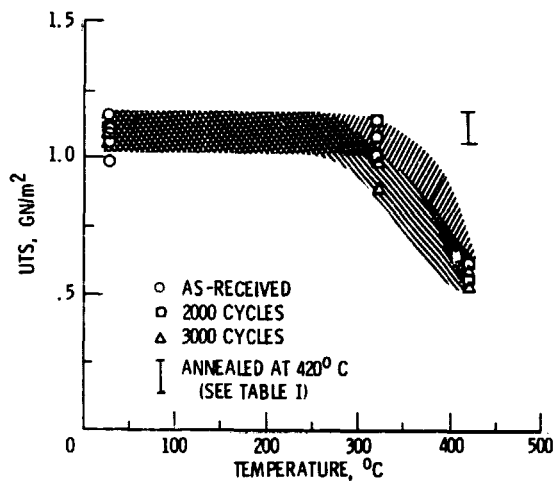

Figure 9. - Room temperature ultimate tensile strengths of 203 µm B-6061 Al composites cycled 2000 or 3000 times to indicated temperatures. Range of strengths of similar composites annealed at 420° C are also shown.
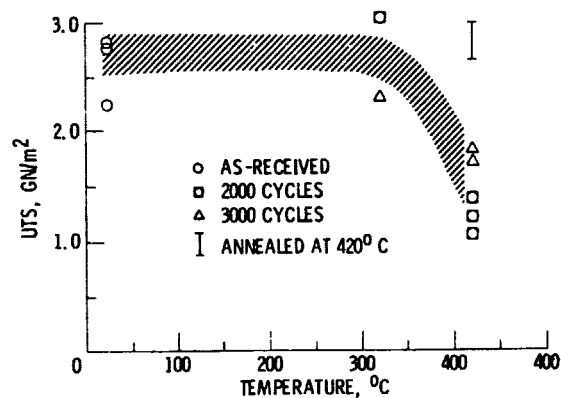
E-1017

Figure 10. - Room temperature ultimate tensile strengths of fibers removed from 203 μm B-1100 Al composites cycled 2000 or 3000 times to indicated temperatures. Range of fiber strengths from similar composites annealed at 420° C are also shown.
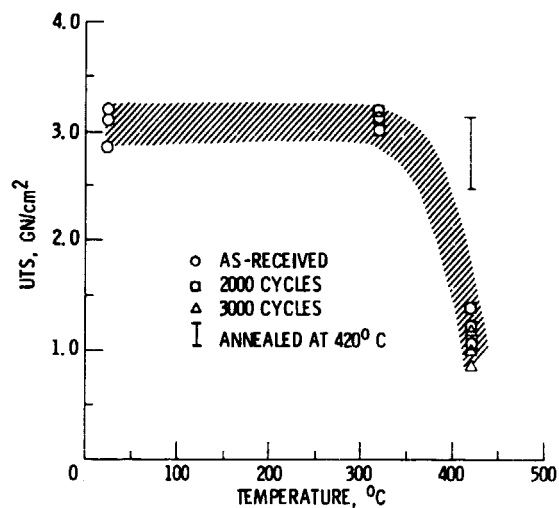

Figure 11. - Room temperature ultimate tensile strengths of fibers removed from 203 μm B-6061 Al composites cycled 2000 or 3000 times to indicated temperatures. Range of fiber strengths from similar composites annealed at 420° C are also shown.
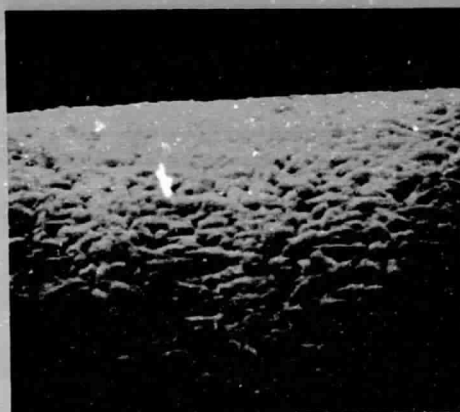
AS RECEIVED

2000 CYCLES TO 320° C

2000 CYCLES TO 420° C

ANNEALED 90 HOURS AT 420° C

Figure 12. - Scanning electron micrographs of the surfaces of fibers removed from 203 μm B-6061 Al composites after the indicated thermal treatment.
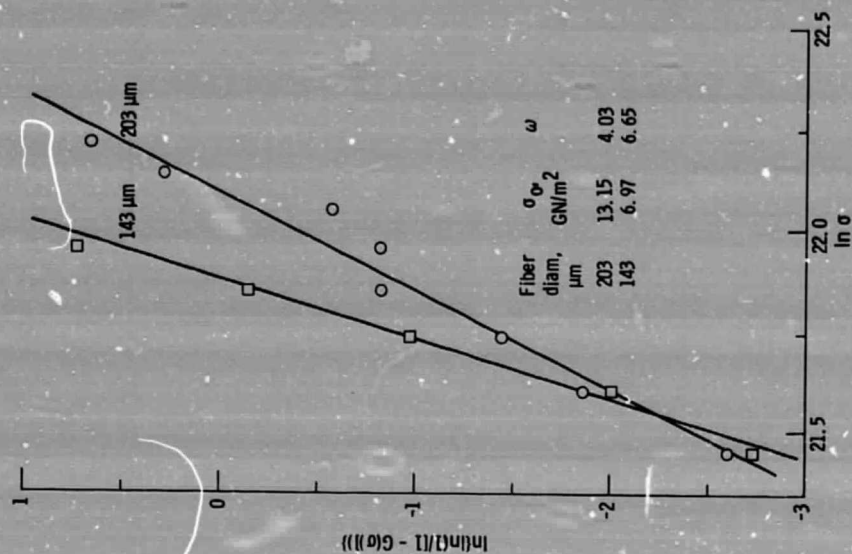
Figure 14. - ln(ln(1/(1 - G(σ))) versus ln σ for the nominal 143 (squares) and 203 μm (circles) boron fiber strengths measured by Smith (ref. 5). The parameters σ_0 and ω are shown.

Fiber diam, μm	σ_0, GN/m^2	ω
203	13.15	4.03
143	6.97	6.65

Figure 13. - Micrograph of typical 203 μm B-6061 Al specimen after thermal cycling 3000 times to 320° C.