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MODIFICATION OF SILICON CARBIDE FIBERS FOR USE IN SiC/Ti COMPOSITES

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Error in the title on the cover of the report. "Si/Ti" should read "SiC/Ti."

Replace the cover of the report with the attached corrected cover.

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SUMMARY

SiC/Ti composites have been marked by tensile strengths well below those predicted by rule-of-mixtures (ref. 1). A commercially available high-strength SiC fiber was found to degrade significantly after exposure to chemical and thermal conditions typical of composite consolidation. Several modifications to the fiber surface have been utilized to investigate fiber strenghthening mechanisms, and to develop techniques to minimize the loss of fiber strength during composite fabrication. SiC fibers were coated with various thin metal films and subjected to elevated temperatures typical of composite fabrication. Changes in fiber tensile properties were related to fiber-matrix interaction. The effects of fiber strength and strength distribution on expected composite properties were investigated analytically.

INTRODUCTION

In recent years, filament reinforced composites have gained increased acceptance in materials applications calling for high strength-to-weight and stiffness-to-weight ratios. Since polymer matrix composites degrade at moderately elevated temperatures, much work has been done on fiber reinforced metal-matrix composites.

Titanium matrix systems, although theoretically very promising, have been hindered by developmental problems. Specifically, titanium is very reactive with most ceramic fibers at the high temperatures necessary for composite consolidation. Although silicon carbide is thermally and chemically one of the most stable fiber types known, significant amounts of brittle titanium carbides and titanium silicides have been shown to form at the fiber-matrix interface during consolidation (ref. 1). These compounds degrade the composite mechanical properties as stress-intensifying microcracks form in the reaction layers at low strains (refs. 2, 3 and 4).

This paper presents some preliminary results of research in which various surface modifications to the silicon carbide fiber were investigated in an attempt to reduce the amount of fiber-matrix interaction. Because of the high cost and long turn around time associated with composite fabrication, the titanium/silicon carbide system was studied in its component parts. Preliminary work in this study showed that no significant composite degradation can be ascribed to the titanium matrix (commercially pure TiA55) itself. Moreover, with the silicon carbide fiber used in this study, no degradation was associated with the heating of the fiber itself. It was therefore concluded that the investigation should focus on the interaction of the fiber and the titanium matrix, specifically on the fiber-matrix interface.

The general approach has been to study the effects of thin-film diffusion barriers on this interaction, and the associated changes in tensile strength. Because the fibers used in this study have intrinsically large variations in tensile strength, an analytical model was developed to predict composite strengths based on experimental fiber strength distributions.

SYMBOLS

E_c = composite modulus

E_f = fiber modulus, from ref. 5

E_m = matrix modulus, experimentally determined

Q = unbroken fibers/total fibers

V = volume fraction of fibers

σ_{appl} = stress applied to the composite

σ_f = fiber stress

σ_{fr} = fiber residual stress, from differences in the coefficients of thermal expansion for the fiber and the matrix

σ_m = matrix stress

σ_{mr} = matrix residual stress

σ_{my} = matrix yield stress, experimentally determined

EXPERIMENTAL METHODS

In this investigation, a composite was simulated by sputtering thin metal films (1-2 μm) directly onto individual silicon carbide fibers. All specimens had an outer layer of titanium so that the diffusion boundary conditions resembled those of a composite.

The coated fibers were subjected to a heat treatment typical of that necessary for composite consolidation, 870°C for one hour under vacuum. Some aluminum coated fibers were given an initial heat treatment at 635°C for 10 minutes, followed by the standard one hour anneal at 870°C. The reasons for this two-stage treatment will be discussed later in the paper. Although actual composite consolidation requires pressures in the 70-100 MPa range, no account was made for these mechanical pressures in the present study.

Fibers were mounted for individual tensile testing as follows (see figure 1): each fiber was bonded to two aluminum tabs with cyanoacrylate adhesive. The fixture was mounted by pins (to allow for self-alignment) in a displacement controlled Instron tensile testing machine, and the fiber loaded to failure.

Figure 2 provides a comparison between an actual composite and a schematic diagram of an experimental specimen used to model the composite. Whether the specimen had an aluminum or tungsten diffusion barrier, or no barrier at all, an outer layer of titanium was deposited so that the diffusion and reaction kinetics at the fiber-matrix interface resembled those in the actual composite. Although a thicker titanium coating would be desirable, sputtered coatings greater than 2 μm were found to debond during handling, presumably because of large internal stresses generated during the sputtering process.

Since the ultimate objective of this research is to develop a composite material, some method of predicting composite properties from the experimental fiber strength distributions was needed. Because of the wide scatter in the SiC fiber systems of this investigation, simple rule-of-mixtures predictions based on an average fiber strength were considered inadequate (refs. 6 and 7). The computer program developed in this project takes explicit account of the variations within a fiber strength distribution.

The computer model is based on the following assumptions: strain is assumed to be uniform. That is, composite strain equals fiber strain equals matrix strain. The matrix is assumed to be elastic-ideally plastic, and the fibers are assumed to be elastic to failure. A fractured fiber is assumed to have no load carrying capacity, and no stress intensification is assumed in the neighborhood of such a fractured fiber.

The resulting governing equations are given below.

$\sigma_m < \sigma_{my}$:

1) $E_c = (1-V)E_m + QVE_f$

2) $\sigma_f = \sigma_{fr} + \sigma_{appl} \dfrac{E_f}{E_c}$

3) $\sigma_m = \sigma_{mr} + \sigma_{appl} \dfrac{E_f}{E_c}$

$\sigma_m \geq \sigma_{my}$:

1) $\sigma_f = \sigma_{fr} + \dfrac{\sigma_{appl} - (1-V)\sigma_{my}}{QV}$

2) $\sigma_m = \sigma_{my}$

RESULTS AND DISCUSSION

In order to establish a baseline and account for any variability in the as-received and as-sputtered fibers, the fracture strength of each type of fiber before annealing was investigated. The as-fabricated fiber strength distributions are shown in figure 3. The wide scatter in the as-received SiC fiber strengths is typical of present fiber technology. A significant improvement in the filament strength distribution due to the deposition of 1 μm of titanium was observed. One μm of tungsten (followed by 1 μm of titanium) was found to degrade the silicon carbide fibers, particularly the high strength fibers (ref. 6). One μm of aluminum (followed by 1 μm of titanium) was the most effective in increasing the as-sputtered fiber strengths, eliminating most of the low-strength fiber failures.

The degradation associated with annealing can be seen in figure 4. The most dramatic decrease in strength occurred for the fibers with no diffusion barrier (SiC/Ti). Since the same degradation is to be expected during actual composite consolidation, these fiber-matrix interactions may be a major reason why experimental composite strengths have been somewhat disappointing. Although tungsten degrades the fibers in the as-sputtered state, it does provide some protection after annealing, relative to SiC/Ti. The most encouraging results occur in the SiC/Al/Ti system. Although some loss of strength does occur during annealing, after heat treatment the SiC/Al/Ti fibers have a better strength distribution than even the as-received SiC fibers. (This assessment is made on the basis of the predictions of composite ultimate tensile strength by the computer model, using the actual fiber strength distributions.)

The data presented in figure 4 as annealed SiC/Al/Ti fibers resulted from the two-stage heat treatment: a 10 minute pre-anneal at 635°C and the one hour at 870°C common to all of the annealed fibers. The benefits of the pre-treatment can be seen in the comparison of the histograms in figure 5.

The proposed mechanisms are as follows: if no pre-anneal is given, the diffusion of titanium toward the fiber is greatly facilitated as soon as the temperature exceeds the melting point of aluminum (660°C). The molten aluminum can also diffuse rapidly into the titanium matrix to form a solid solution. In this case, the protection afforded the fiber is minimal.

On the other hand, at 635°C the formation of titanium aluminides is thermodynamically favored. These compounds have high melting temperatures and are relatively stable. After 10 minutes at 635°C, it is assumed that most of the aluminum layer has been converted to aluminides of various compositions ($TiAl_3$ to Ti_3Al). These compounds provide an activation barrier to reaction compound formation. Locally high concentrations of aluminum at the fiber-matrix interface (due to the decomposition of aluminides and the formation of titanium carbides and silicides, refs. 8, 9 and 10), also tend to inhibit further reaction. Moreover, bulk diffusion of titanium through the aluminide layers is much more difficult than through molten aluminum and, apparently, through tungsten. In reality, the diffusion barrier is not aluminum, but the titanium aluminides.

Some typical results from the computer program are shown in figure 6. The fiber strength distribution is for the SiC/Al/Ti fiber system after annealing and a 0.40 volume fraction of fibers is assumed.

In the computer generated curve, the discontinuity at 0.002 strain represents the fracture of the low strength (500 MPa) fiber. The failure of this fiber causes an instantaneous decrease in the composite modulus, and a consequent increase in strain at the same load. At 0.003 strain the matrix stress becomes equal to the matrix yield stress and the composite modulus is again lowered. At 0.0044 strain, the next fiber fails, beginning a chain reaction of increased fiber stress and more fiber failures, which results in all of the remaining fibers breaking at this load. It is the applied stress at this point which is presented as the projected composite ultimate tensile strength (UTS).

The simple rule-of-mixtures plot shows a different type of behavior. Here the average fiber strength is the only fracture parameter. No account is taken of the low strength fiber, except as it affects the average. In this model, matrix yielding is postponed and composite failure is not predicted until the applied stress reaches nearly 1100 MPa, as opposed to 875 MPa for the computer model.

By utilizing this computer program, each experimental fiber strength distribution was related to a single number of some significance: the projected composite UTS.

The projected composite ultimate tensile strengths for each fiber system, assuming an 0.40 volume fraction of fibers, are presented in figure 7. A SiC/Ti composite with no diffusion barriers can be expected to have a UTS of only 350 MPa. A tungsten barrier offers a mild improvement, as 435 MPa is the projected composite UTS for the SiC/W/Ti system. However, the SiC/Al/Ti system promises an increase over baseline of 150% in composite UTS, to 876 MPa.

On the basis of these preliminary results, further optimization of the aluminum duffusion barrier approach seems warranted. It is also expected that the knowledge gained from the study of this particular type of silicon carbide fiber will be applicable to newer higher-strength silicon carbide fibers currently being developed.

CONCLUSIONS

The important results of this research program can be summarized in three main points. First, an aluminum coating was found to increase the average as-fabricated SiC fiber strength 35% over the baseline SiC fibers. Second, the aluminum coating was found to increase the average annealed fiber strength 250% over baseline SiC/Ti fibers, provided optimized heat treatments are used. Finally, the aluminum diffusion barrier approach was found to increase the projected composite UTS 150% over baseline, based on the computer model developed for this research.

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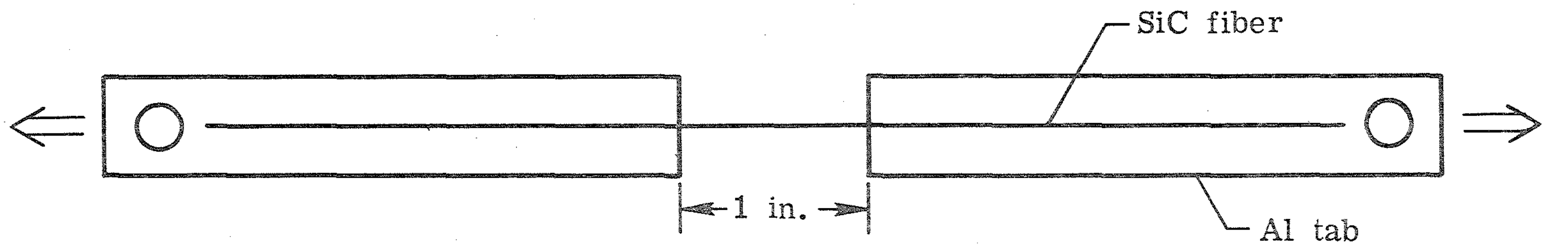

Figure 1.- Fiber tensile test fixture.

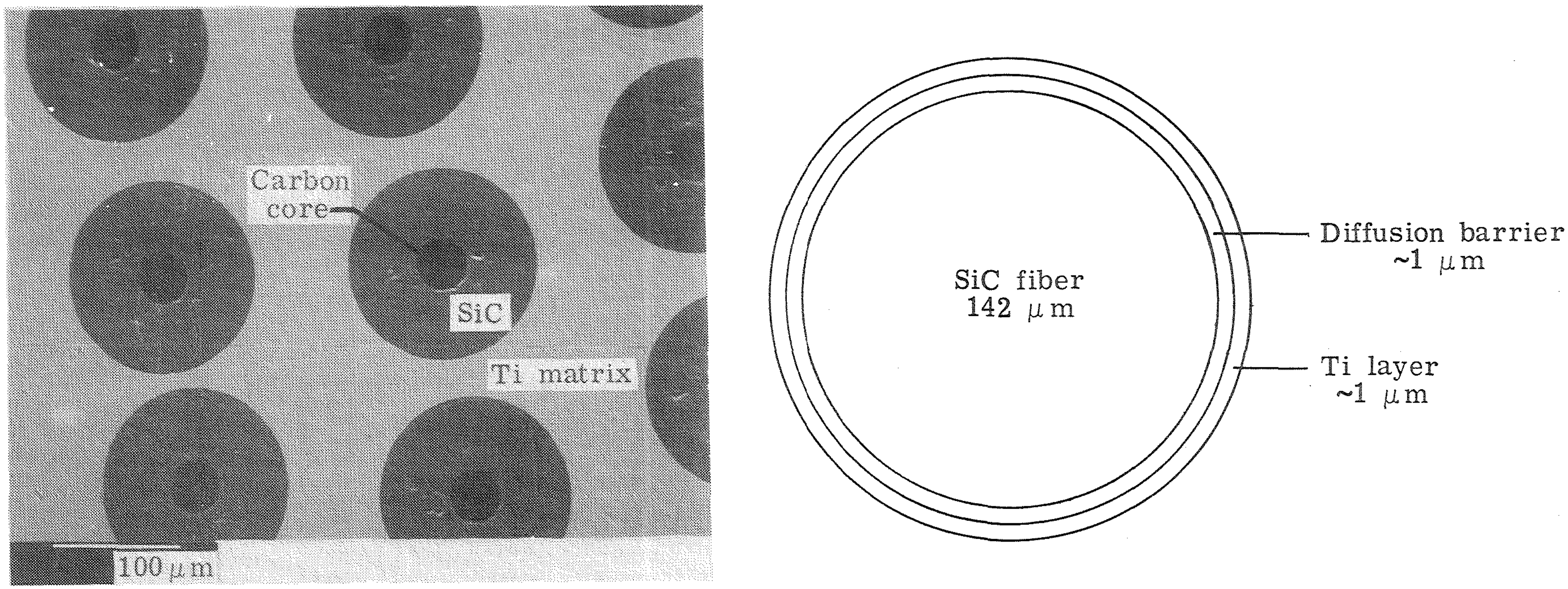

Figure 2.- Composite cross-section and schematic diagram of an experimental fiber specimen.

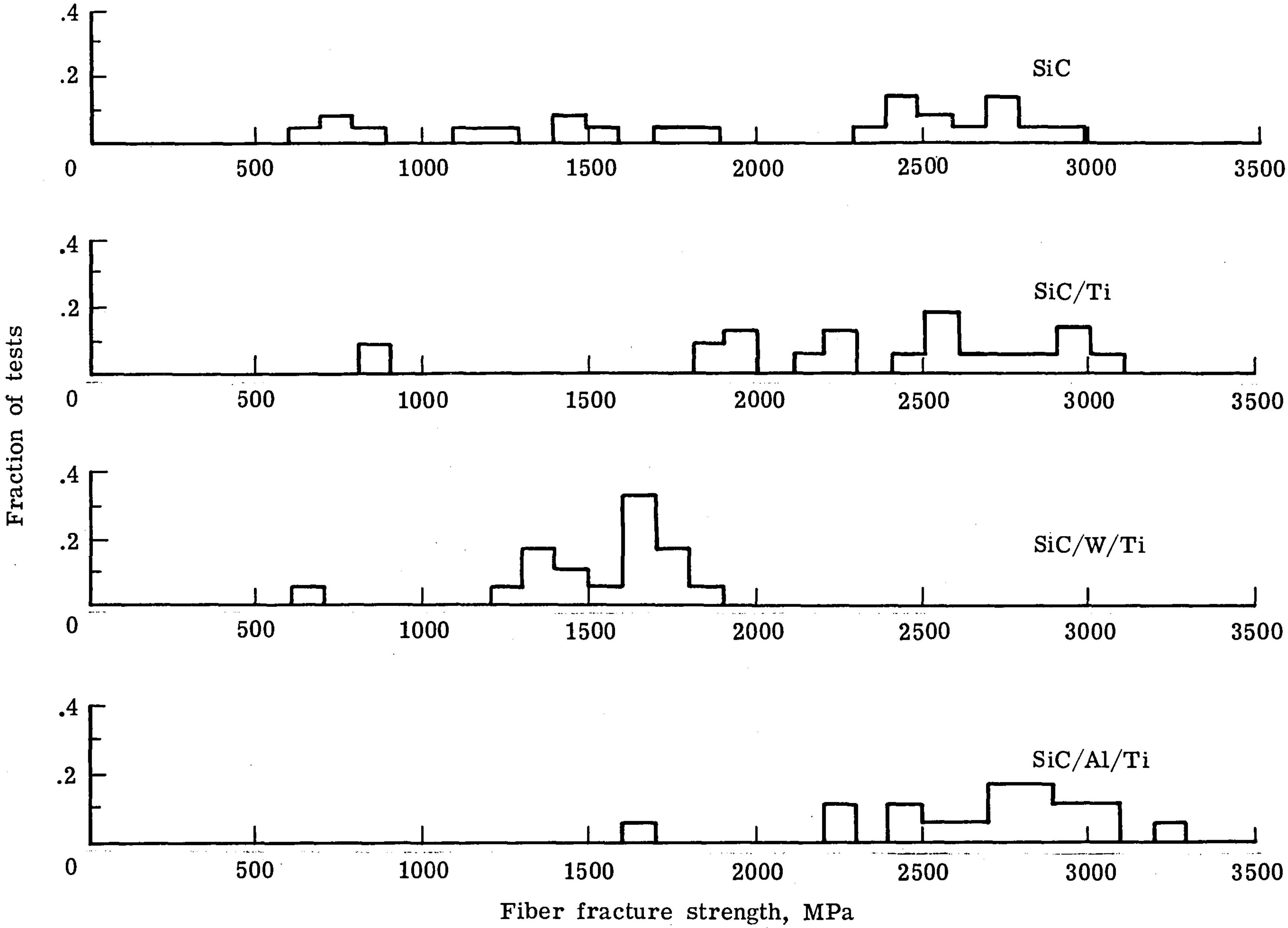

Figure 3.- As-fabricated fibers strength distributions.

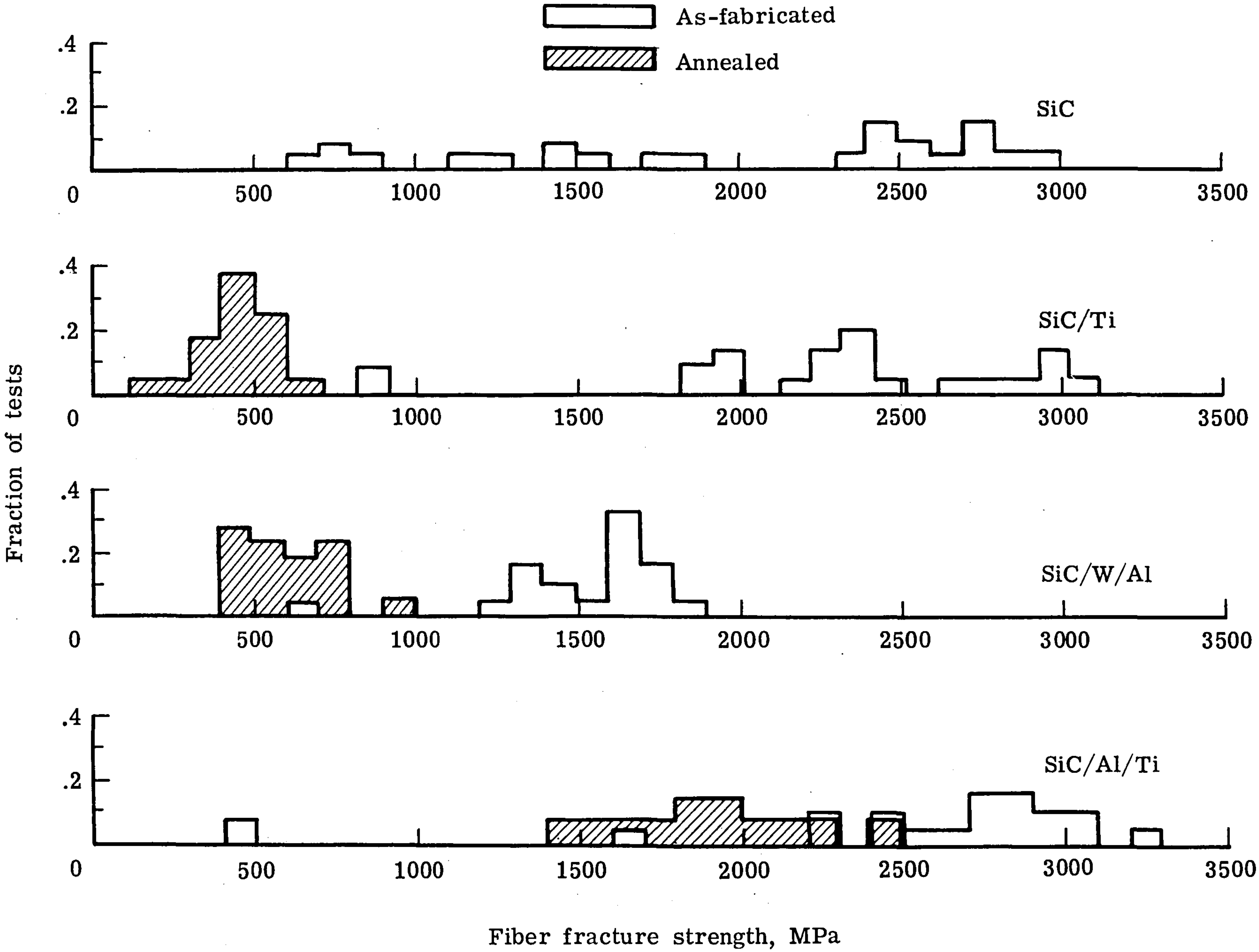

Figure 4.- As-fabricated and annealed fiber strength distributions.

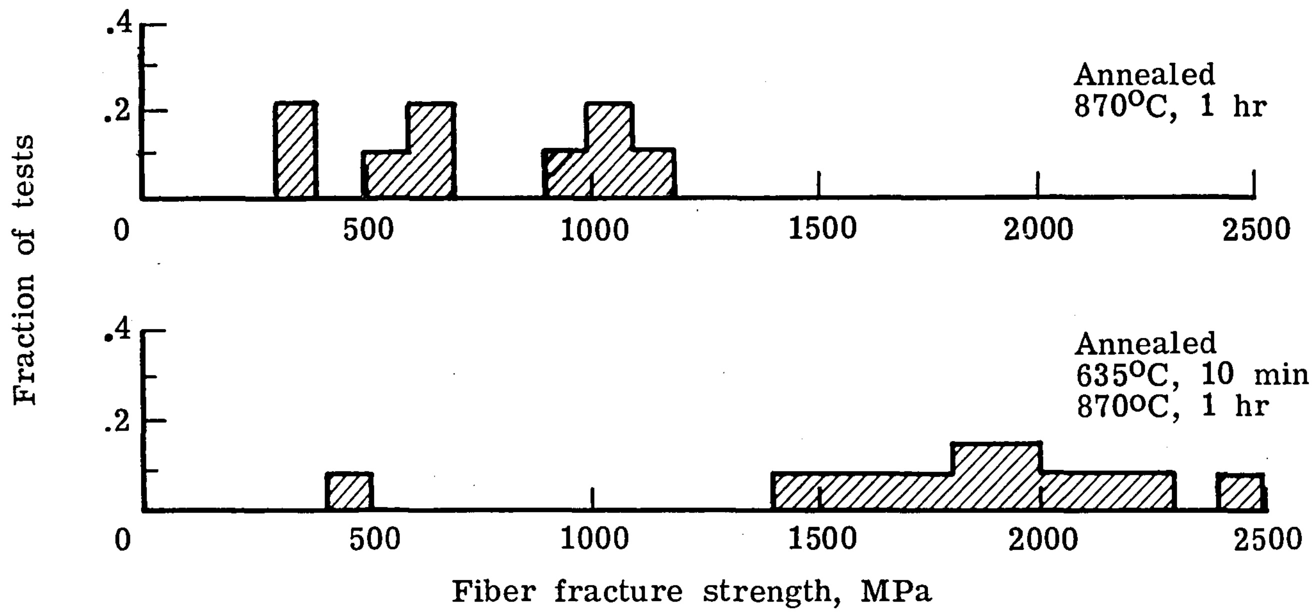

Figure 5.- Effects of heat treatments on SiC/Al/Ti fibers.

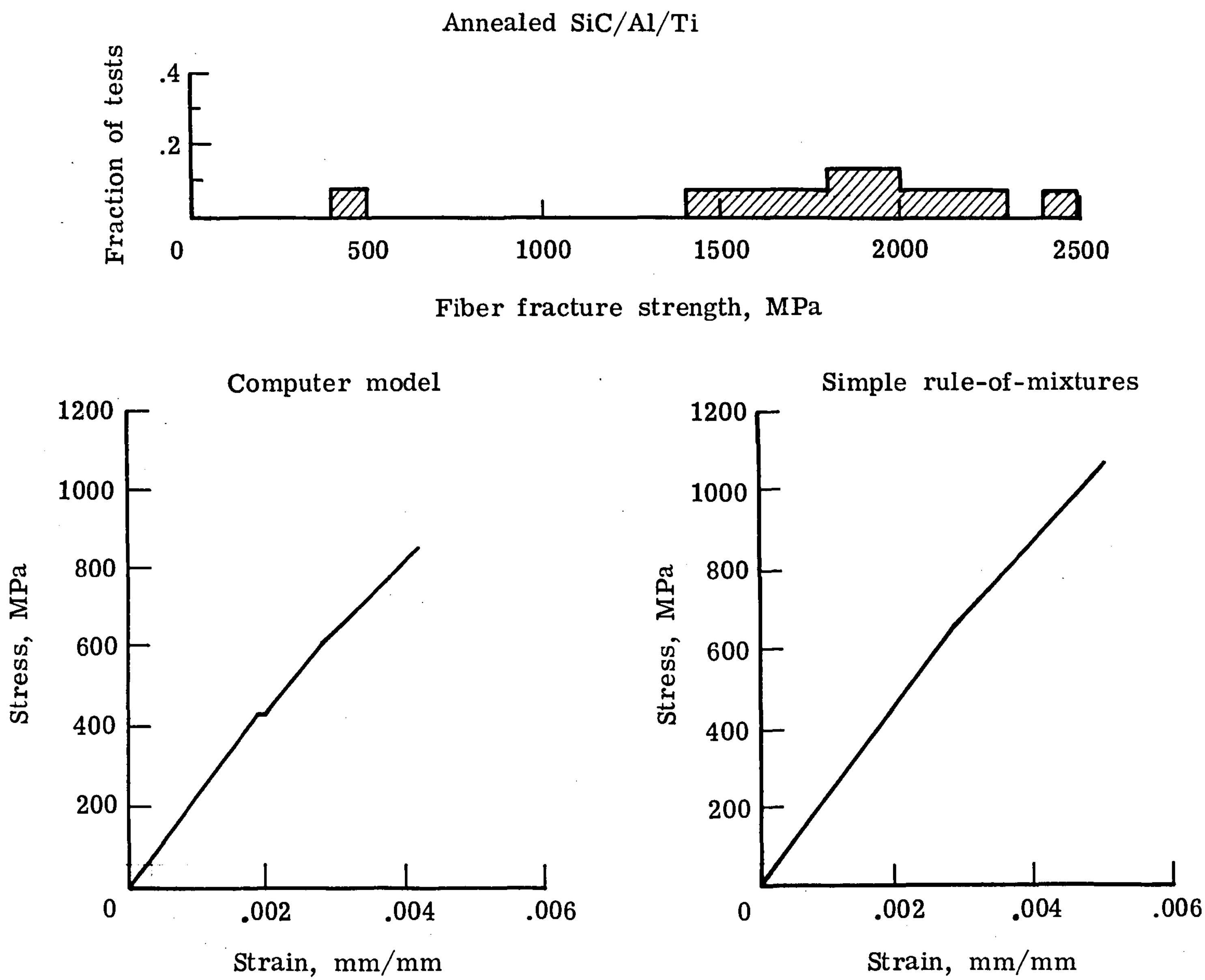

Figure 6.- A comparison of the computer program and simple rule-of-mixtures predictions of composite behavior.

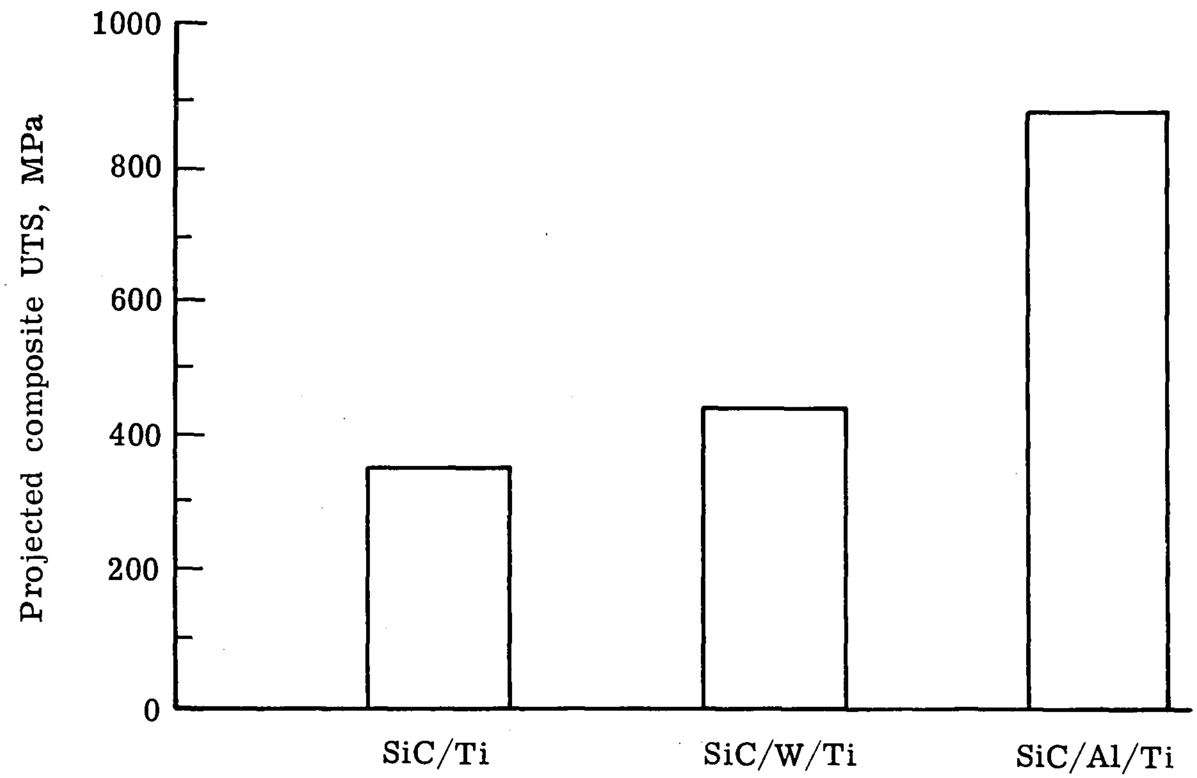

Figure 7.- Projected composite strengths.

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15. Supplementary Notes

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16. Abstract

The degradation of silicon carbide fibers during exposure to conditions typical of composite fabrication was investigated. The tensile strength of pristine fibers and fibers sputtered with thin metal coatings (Ti, Al, W) were determined before and after treatment at 870°C for one hour in vacuum. Each fiber strength distribution was related by an analytical procedure to a projected composite ultimate tensile strength (PC UTS). The results indicate that a thin aluminum diffusion barrier can yield a 150% increase in PC UTS over the baseline SiC/Ti system.

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