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Kinetics of the reaction between SiC (SCS-6) filaments and Ti (6 Al–4 V) matrix

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Silicon carbide reinforced titanium alloy matrix composites have been of interest to the aerospace industry because of their high specific strength and thermal stability. The main problem with these materials to date has been the degradation of mechanical properties due to reaction between the fibre reinforcement and the matrix at high temperatures. In an effort to alleviate this problem, there have been several attempts to manufacture fibres which will maintain their strength after prolonged exposure [1–3]. The most successful method has been to apply a barrier layer to the fibres which limits the rate of reaction between the components. It is the purpose of this paper to evaluate the success of one such fibre, the SCS-6 fibre, in achieving this goal.

The SCS-6 fibre is a continuous SiC fibre produced by Avco, by means of chemical vapour deposition. The process involves pulling a 33 μm diameter carbon filament through a reaction chamber where it is resistance heated to a temperature of about 1300° C. Deposition of SiC occurs when the silane gas contacts the hot filament and decomposes to form SiC, HCl and H_2 [4]. The final step in the production of the filament is to add low molecular weight hydrocarbons to increase the carbon content of the gas, yielding a surface layer which is composed of small SiC crystallites in an amorphous carbon matrix [5]. As produced fibres are approximately 149 μm in diameter and have a tensile strength of 4500 MPa (650 ksi).

The matrix used is Ti(6Al–4V), which is the work horse alloy of the aerospace industry. It is an alpha/beta alloy with the alpha–beta transus at 950 to 1010° C. In the annealed condition the alloy has a yield strength of 903 MPa (131 ksi), and an ultimate strength of 938 MPa (136 ksi) [6].

Composites are manufactured using standard hot pressing techniques. Fibres are drum wound around foils of the alloy. A fugitive binder is used to maintain the positioning of the fibres during the lay-up procedure. The lay-ups are placed in a stainless steel envelope and the binder is driven off by heating to 400° C under dynamic vacuum. After sealing the envelope the lay-up is brought to temperature and pressure for the specified time to obtain complete bonding of the foils to themselves and the fibres.

There have been several attempts to model the tensile behaviour of unidirectionally reinforced composites [7–10]. Although these studies vary somewhat in their approach to the problem, and the complexity of the model, they all rely on the distribution of strength of the reinforcing fibres in predicting composite strength.

The prevailing theory for the degradation of strength of brittle fibres is to model the system as a brittle cylinder encased by a brittle layer [11]. This brittle layer acts as a circumferential notch if its strain to failure is less than that of the fibre. By calculating the stress concentration in the fibre due to the imposed notch, the extent of degradation can be calculated.

The most important result of these studies is that there exists a critical thickness below which there is no loss of strength. Once the brittle layer has grown to a thickness greater than the critical value, the strength drops off as the square root of the thickness of the reaction zone [12, 13].

From these results it seems clear that in order to predict the degradation of mechanical properties as a function of time in service, it is imperative to know the kinetics of the reaction which forms the brittle layer.

In order to obtain an accurate description of the kinetics of the reaction between the fibres and the matrix, a set of annealing experiments was performed. To prevent extreme oxidation of the matrix, samples were encapsulated in vycor tubes

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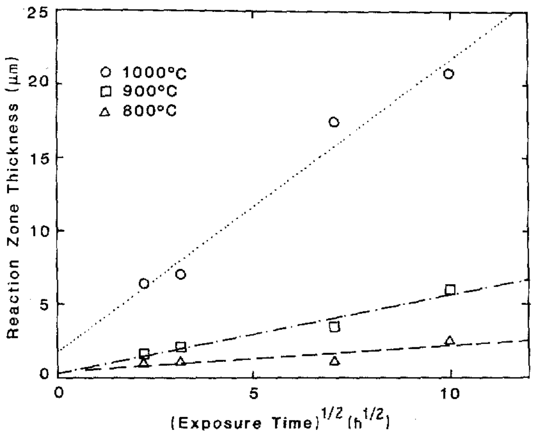

Figure 1 Reaction zone thickness against the square root of exposure time for SiC/TI(6Al–4V) composites annealed at 800, 900 and 1000° C.

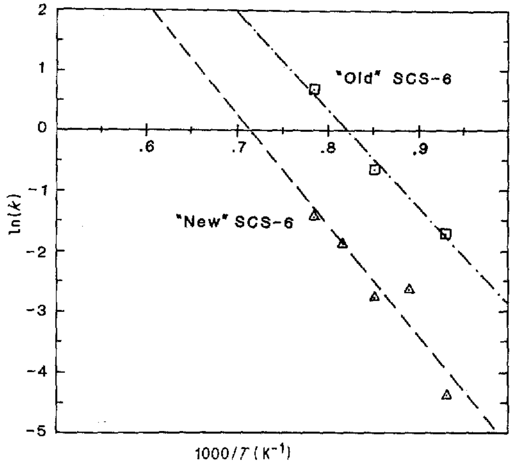

Figure 2 Arrhenius plot of ln (reaction constant) against reciprocal of temperature. The slope of this plot gives the activation energy for the fibre matrix reaction.

under vacuum of approximately 30 millitorr. The encapsulated specimens were annealed at various temperatures for times of five to one hundred hours, and water quenched.

After mechanical testing, sections of the samples were mounted such that the axis of the fibres was perpendicular to the polishing plane. The specimens were then polished using a series of 320 grit SiC paper, 30 μm, 6 μm metal bonded diamond polishing wheels. The procedure gave well polished samples with no relief between the fibres and the matrix. After polishing, the samples were etched using 10% HF, 5% HNO_3, 85% H_2O, swabbed on for 20 sec. The etchant strongly attacked the matrix, mildly etched the reaction zone, and had almost no effect on the fibre.

Samples were observed using a Jeol JSM-35 scanning electron microscope. Measurements of the reaction zone thickness were taken from micrographs of the fibres at high enough magnification to ensure accuracy. Because of the uneven nature of the reaction zone, the average of 20 to 50 measurements of the thickness of the reaction zone was used in all calculations.

The investigations of such systems as boron/aluminium, boron/titanium, silicon carbide/aluminium, and borsic/titanium all have shown that the growth of the reaction zone can be described by the parabolic growth law [14]

$$X = k(t)^{1/2}$$

where X is the average thickness of the reaction zone, t is the exposure time at a given temperature, and k is what is known as the reaction constant. The reaction constant can be related to the diffusion constant by the equation:

$$k = (2D)^{1/2}$$

From these relations it is clear that the reaction constants for different temperatures should follow an Arrhenius relation.

As one would expect, the current investigation showed that the SCS-6/Ti(6Al–4V) reaction exhibited similar kinetics. Plots of reaction zone thickness against the square root of time (Fig. 1) show that for several temperatures the growth of the reaction zone is indeed linear with the square root of time. The slopes of these lines, which correspond to the reaction constants, increase dramatically with increasing temperature. By plotting the natural logarithm of these values against inverse temperature, a linear plot is obtained (Fig. 2). The slope of this line is directly related to the effective activation energy of the reaction process.

Table I shows the results of kinetic experiments using two versions of the SCS-6 filament in the Ti(6Al–4V) matrix. The "old" SCS-6 has a thinner protective coating, which seems to provide a less effective diffusion barrier than the newer version which has a much thicker protective layer. This is seen by the difference in the calculated effective activation energies of the two materials. The effective activation energy for the old SCS-6 was calculated to be 64.7 kcal mol^{-1}, whereas the new SCS-6 demonstrated an effective activation energy of 73.1 kcal mol^{-1}. These values can be compared to values ranging from 36.2 kcal mol^{-1}

TABLE I Reaction constants for "old" and "new" SCS-6 for various temperatures

Temperature (K)	"Old" SCS-6 (cm $sec^{-1/2}$)	"New" SCS-6 (cm $sec^{-1/2}$)
1073	3.05×10^{-7}	1.64×10^{-7}
1123		9.47×10^{-7}
1173	8.88×10^{-7}	8.38×10^{-7}
1223		1.99×10^{-6}
1273	3.33×10^{-6}	3.13×10^{-6}

for early SiC fibres [14], to 62.7 kcal mol^{-1} for uncoated vapour deposited SiC [1].

Although the difference in the activation energies for the two fibres is small, it should be remembered that the effect of the activation energy is seen in the exponential. The seemingly small difference in the activation energies of the two fibres corresponds to a factor of fifty in the rate of reaction at use temperatures. From the above argument, it is clear that the new SCS-6 fibre is much improved over previously available fibres for use in titanium matrices, but there is still too much reaction zone formed on fabrication of the composite.

The rate of reaction zone formation can be adequately predicted by the use of an Arrhenius type rate equation. The current kinetic studies have determined effective activation energies for the reaction between SCS-6 fibres and a matrix of Ti(6Al–4V). The useful life of products formed from these materials can be predicted using the calculated activation energies to estimate the time which it takes to form a reaction zone of critical thickness. This useful life seems to be almost indefinite for use temperatures less than or equal to 700° C.

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