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Thermal degradation of silica fibre-reinforced aluminium

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At elevated temperatures, the aluminium matrix reduces the reinforcing silica fibres to silicon, severely lowering the mechanical properties. The kinetics of the degradation process have been studied and results of previous work, in which silica rods were attacked by molten aluminium, have been confirmed. Fibres corrode at a constant rate (of penetration) at a fixed temperature and the activation energy for the silica reduction/alumina formation process was found to be 280 kJ mol^{-1}, in close agreement with previous work. The alumina is formed within the boundaries of the original silica fibres. An activation energy of 170 kJ mol^{-1} has been determined for the commencement of the reaction and it appears that a higher activation energy is required for initiation if solid, rather than liquid aluminium is participating in the reaction. A technique is proposed for the production of alumina fibres *in situ* in composite materials, based on the deliberate reduction of silica and other oxides in aluminium matrices. It is suggested that the effectiveness of the method may depend upon the relative volumes of the products and the reactants. Shrinkage may cause fibre–matrix separation and porosity formation, as in the Al/SiO_2 composite.

1. Introduction

1.1. The aluminium–silica fibre system

Silica fibre-reinforced aluminium is a useful model material – like tungsten-reinforced copper, it can give reasonably predictable properties [1], although it has certain disadvantages. For instance, there is little load transfer when the composite is elastically deformed at room temperature, because the elastic moduli of aluminium and silica are so similar. At elevated temperatures, however, the lower temperature coefficient of elasticity of the silica would give rise to appreciable load transfer to the strong silica fibres. Another practical advantage of the system is that the aluminium is strengthened and the density is reduced by the silica additions.

The system has been examined by various investigators, particularly from the laboratories of Rolls Royce, where the technique originated of pre-coating newly drawn fibres by passing them continuously through a bead of molten aluminium [2] sometimes containing small additions of bismuth or antimony to control the chemical reaction between the silica and the aluminium [3]. These pre-coated fibres were the starting material for the present investigation; the fibres were hot-pressed into aligned composites, using a technique similar to that developed by Cratchley [4].

1.2. Thermal degradation

In all fibre-reinforced systems, the achievement of adequate bonding at the fibre/matrix interface is a compromise. There must be sufficient affinity between fibre and matrix to ensure at least some mechanical keying, if not actual adhesion, between their surfaces. Some affinity is achieved if "wetting" of the fibre surface occurs (and this appears to be the case in the aluminium/silica system). In general, however, too great an affinity between the components causes thermal degradation.

Some reaction products are known to lower mechanical properties because cracks in the reaction zone initiate premature composite fracture [5].

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Many other forms of thermal degradation have been identified, including corrosion [6], diffusion controlled shape instability [7], thermal cycling [8] and volume changes during allotropic transformation [9].

Bonding between the silica fibres and the aluminium matrix in hot-pressed composites is adequate to transfer load. This has been indicated by the results of fatigue and other mechanical tests, and also by fracture studies [10]. Mechanical property deterioration caused by chemical interaction has been observed, however, after exposure at elevated temperatures [11]. The system is unstable thermodynamically, since alumina is formed when silica fibres are reduced with aluminium at high temperatures:

$$4\mathrm{Al} + 3\mathrm{SiO_2} \rightarrow 2\mathrm{Al_2O_3} + 3\mathrm{Si}.$$

Three forms of alumina, (η, θ and α alumina) were observed by Standage and Gani [12] after interaction between silica rods and molten aluminium. The other reaction product, silicon, was observed in X-ray photographs by Standage [3] and by Cratchley and Baker [10] in a heat-treated composite microstructure; the latter also observed an appreciable reacted layer which they identified as alumina in samples heated above 400° C. Above 565° C (which is close to the aluminium–silicon eutectic temperature of 577° C), they observed an abrupt increase in the rate of degradation, probably due to the presence of a liquid phase. At 643° C, a violent exothermic reaction occurred.

Brondyke [13] studied the kinetics of the reaction between molten aluminium and silica crucible material and concluded that the rate of formation of alumina was controlled by the diffusion of aluminium and silicon through the alumina layer. Standage and Gani [12] showed that there was a linear thickening of this reaction product with time in molten aluminium.

The present investigation was undertaken because the kinetics of degradation previously observed for aluminium in contact with silica might be appreciably modified in composite material, due to its finer microstructure (in previous work ~ 5 mm rods of silica were used [12, 14]), the nature of the solid-state bonding and the restricted availability of aluminium between the fibres.

2. Experimental details

2.1. Composite preparation and micro-examination

The pre-coated silica fibres were supplied with a pure aluminium coating. The coating comprised 50% of the total volume of the coated fibres which were approximately 75 μm in diameter. Since antimony and bismuth can have significant effects on the degradation of the composite, spectrographic analysis was performed for these elements,

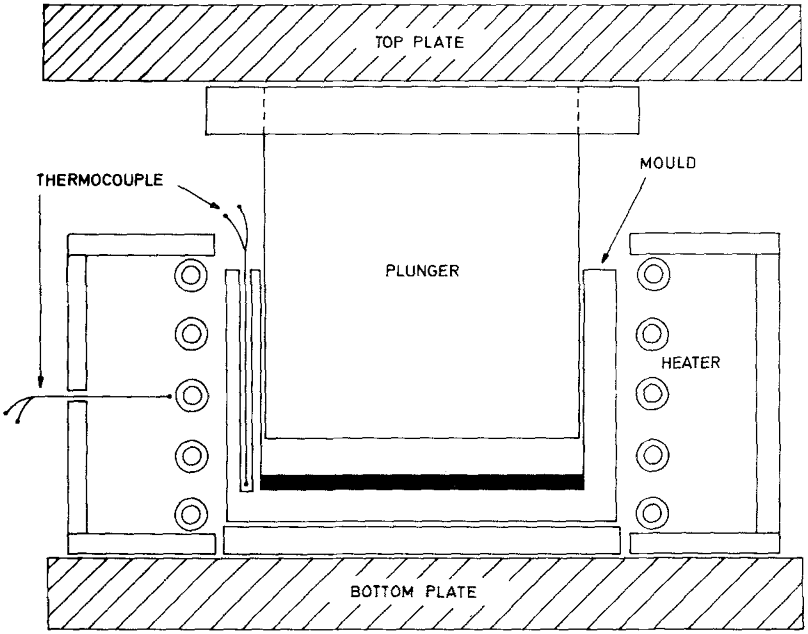

Figure 1 Apparatus for hot-pressing of composites.

which were not present in detectable quantities in the aluminium. The coated fibres were fabricated into an aligned composite, without further addition of aluminium, using a hot pressing technique. The assembled tool steel mould used for hot pressing is shown diagrammatically in Fig. 1. Difficulties encountered due to interaction of the composite with the tool steel mould were overcome by placing a stainless steel insert in the base of the mould cavity. Combed, aligned fibres cut to the length of the mould were placed in the cavity and the die assembly was heated to 500° C for 1 h, with an applied pressure of $77\,\mathrm{MN\,m^{-2}}$. These conditions had previously been found suitable for composite fabrication. The mould was very slowly heated and allowed to reach thermal equilibrium for 30 min before pressure was applied. During pressing, the temperature was controlled to within ± 3° C. The size of the resulting composites, which were used for creep and other mechanical property tests described elsewhere [15] in addition to the present thermal degradation studies, was approximately 102 mm x 12.7 mm x 2.5 mm.

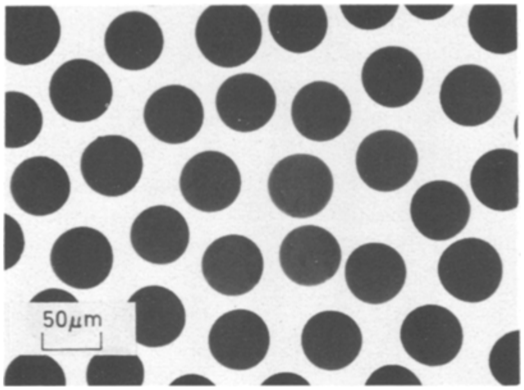

Figure 2 Typical cross-section of as-pressed aluminium–silica composite.

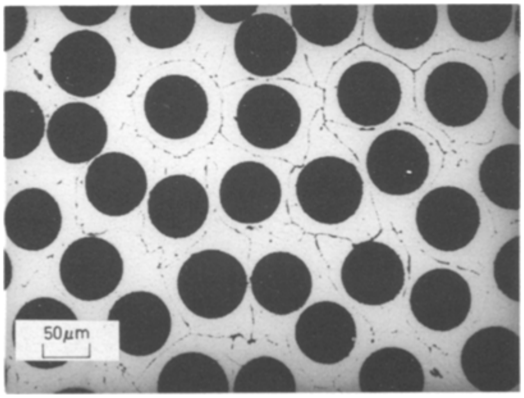

Figure 3 Aluminium–silica composite showing interfaces between the pre-coated fibres.

Prior to metallographic examination, the composites were mechanically polished, terminating with $\frac{1}{4}$ μm diamond.

A typical composite cross-section is shown in Fig. 2. This indicates the uniformity of fibre distribution and the absence of fibre–fibre contacts. Aluminium/aluminium interfaces were revealed by etching in a 2% HF solution (Fig. 3). Specific gravity determinations confirmed metallographic observations that the pressing operation had resulted in composites free from porosity.

2.2. Composite degradation by heat-treatment

This aspect was investigated in detail after the structure of an inadvertently overheated tensile creep specimen was examined by scanning electron microscopy. Fig. 4 shows that gross interaction had occurred between fibres and matrix, the reaction product forming rims around the individual fibres.

Composite samples approximately 7 mm x 2.5 mm in cross-section were progressively heat-treated in salt baths at 500, 575 and 600° C. Bath temperatures were controlled to within ± 0.5° C. Specimens were periodically removed from the bath to determine the time of onset of microscopically resolvable interaction. Incubation periods were noted, which were dependent on reaction temperature. Structural degradation was progressively developed by subjecting the specimens to

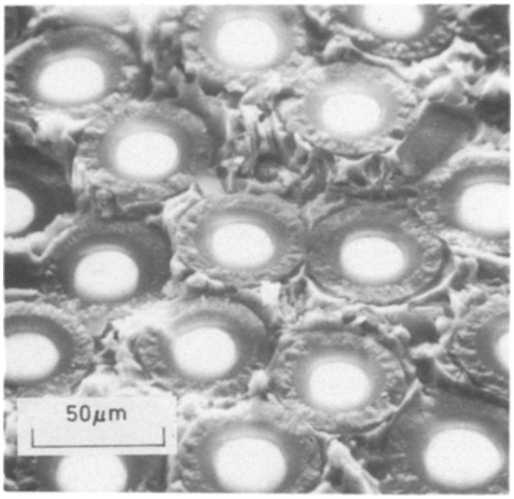

Figure 4 SEM of the fracture surface of an overheated composite tensile creep specimen, showing interaction between the fibres and the matrix.

successive increases in thermal exposure.

Fibre diameters of the reacted samples were measured, both inclusive and exclusive of the reaction zone, and the extent of reaction was expressed as a percentage of the original fibre area. The measurements were made at a magnification of × 1000 on a projection microscope incorporating a movable transparent scale graduated in 0.5 mm intervals.

In addition to micro-examination, microprobe analysis was carried out to provide information on the chemical composition and composition gradients in the reaction zone.

2.3. Experimental results

Fibre/matrix interaction can be severe, as illustrated in Fig. 4, which shows an SEM of the fracture surface of the overheated tensile creep specimen. The fracture mode is extremely brittle, compared with that of the creep failure observed in the unreacted material (Fig. 5), which was tested to destruction at 400° C, giving fibrous fracture and extensive matrix/matrix debonding.

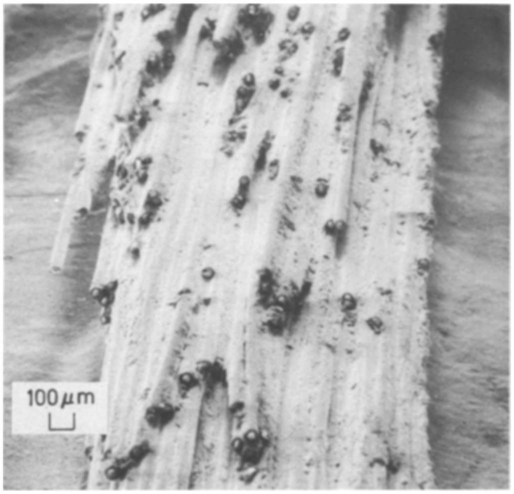

Figure 5 SEM showing the fracture surface of a composite creep specimen tested at 400° C.

Figs. 6 and 7 further illustrate the deterioration in composite microstructure caused by the interaction of aluminium with silica.

The typical reaction zone product was a single layer, and the formation of duplex layers such as those illustrated in Figs. 6 and 7 was an infrequent occurrence.

It was deduced from electron probe microanalysis that the grey areas formed in the aluminium matrix, which sometimes completely enclosed the original fibre area (see Fig. 7), were rich in silicon. The reaction product layers situated within the areas originally occupied by the unreacted silica fibres, were aluminium-rich. The present and previous observations [11] indicate that these two products were, in fact, silicon and alumina.

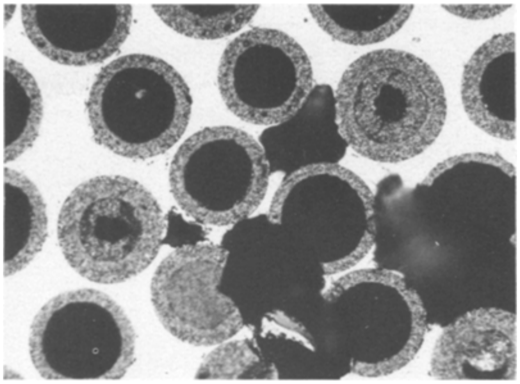

Figure 6 Microstructural degradation occurring during the heat-treatment of the composite at 575° C, × 290.

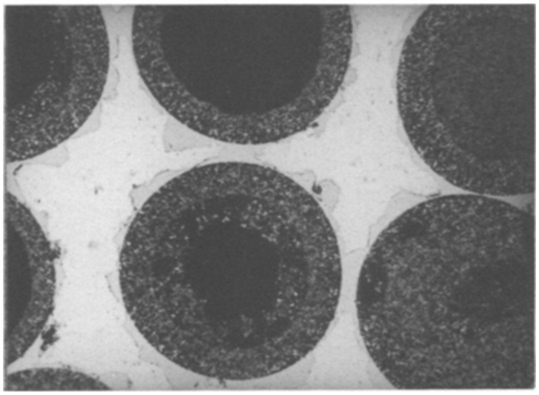

Figure 7 Alumina and silicon reaction products formed in the composite during heat-treatment at 575° C, × 580.

In some areas the aluminium matrix adhered to the alumina degradation product, as indicated in Fig. 8. There is no evidence of major interfacial debonding after exposure to elevated temperatures (cf. Figs. 4 and 5). Thus it is unlikely that poor adhesion at either of the interfaces created during degradation (the Al/Al_2O_3 and Al_2O_3/SiO_2 interfaces) is the cause of deterioration in mechanical properties of the composite, such as the decrease in longitudinal tensile strength observed by Cratchley and Baker [16] after heating above 300° C.

The results of the kinetic studies are presented in Table I. The induction periods prior to the onset of microscopically resolvable interaction are included. About 25 measurements of reacted layer

TABLE I Degradation data for aluminium–silica composites

Temp. (°C)	Incubation period (h)	Time (h)	Cross-sectional area of fibre reacted (%)			Standard deviation (σ)	Rationalized time for a given % cross-sectional area of fibre to become reacted (h)		
			Minimum	Maximum	Mean		$t_{30\%}$	$t_{40\%}$	$t_{70\%}$
500	320	413.00	16.3	32.4	24.8	5.50	123	186	417
		625.00	49.0	64.0	57.6	4.16			
		800.00	70.5	86.5	76.5	4.34			
575	1.50	3.00	17.3	29.6	24.7	3.77	2.60	4.90	13.4
		5.00	25.5	47.9	38.0	6.93			
		12.50	55.1	70.7	62.2	4.00			
		26.25	75.0	100.0	94.0	3.06			
600	0.66	1.05	11.0	19.0	15.4	2.45	0.90	1.29	2.74
		1.50	20.8	36.3	28.8	4.17			
		2.00	36.6	48.3	43.4	4.48			
		2.50	44.9	57.5	52.6	3.68			
		3.75	68.9	80.5	75.9	3.67			
		5.00	81.1	100.0	87.1	7.16			

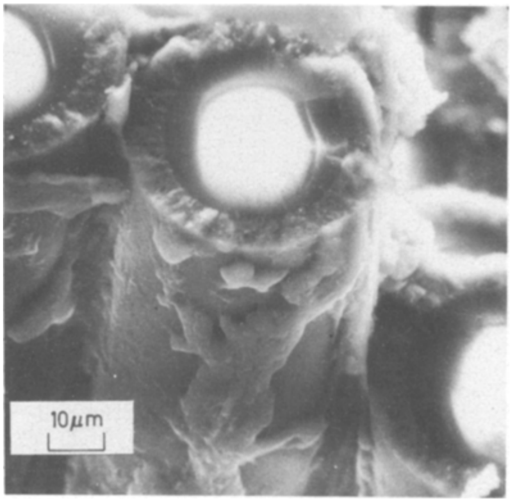

Figure 8 Adherence of aluminium to the surface of an alumina layer surrounding a silica fibre in a structurally degraded composite.

thickness were made for every indicated time of exposure, and the results are expressed in the table as mean values; the maxima, minima and standard deviations are also given. Fractional diametral penetration is plotted against expsoure time in Fig. 9. The function $1-(1-R)^{\frac{1}{2}}$ on the vertical axis compensates for the changing geometry of the interface [17]. It is seen that the reaction front advances at a constant rate from about 10% to 75% linear penetration (and presumably also beyond this range, unless factors such as porosity formation eventually interfere). The induction periods have been subtracted from the total times of exposure shown in Fig. 9, and thus the effective times for 30%, 40% and 70% of the fibre cross-sectional areas to become reacted have been determined. (Table I). The activation energy for the degradation process, 280.1 kJ mol^{-1}, has been deduced from Fig. 10.

3. Discussion

3.1. Reaction kinetics

In the present work, two alumina reaction zones were very occasionally observed in reacted fibres, but there was generally only a single alumina zone, of undetermined structure. The linear rate of thickening of the alumina layer previously observed in molten aluminium [12] was confirmed also for the solid state reaction. The activation energy of 280.1 kJ mol^{-1} derived here for the formation of the alumina layer may be compared with 183.6 kJ mol^{-1} and 255.9 kJ mol^{-1} reported for the formation of η and θ alumina respectively [12]; it would appear that formation of θ controls the rate of degradation in the present investigation. If the reaction rate were controlled by diffusion of aluminium or silicon through the alumina layer it is unlikely that the linear rate of reaction would be observed, since the concentration gradients would be reduced as the reaction later thickness increased. Waudby *et al.* [18] have studied the reaction between aluminium and silicate inclusions in steel, concluding that Si^{4+} and Al^{3+} diffuse very readily through alumina since these ions are much smaller than the O^{2-} in the alumina. They also considered that rapid diffusion was facilitated by defects at alumina crystal boundaries. The existence of

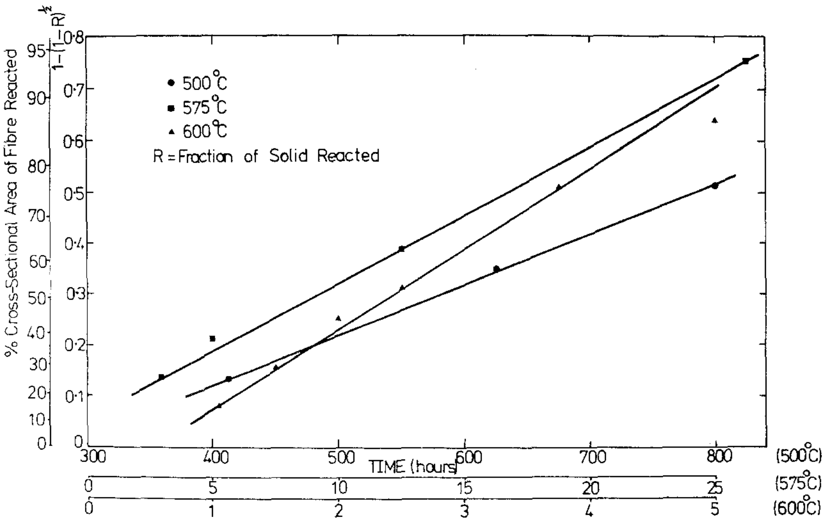

Figure 9 Rates of reaction of the fibres at various temperatures.

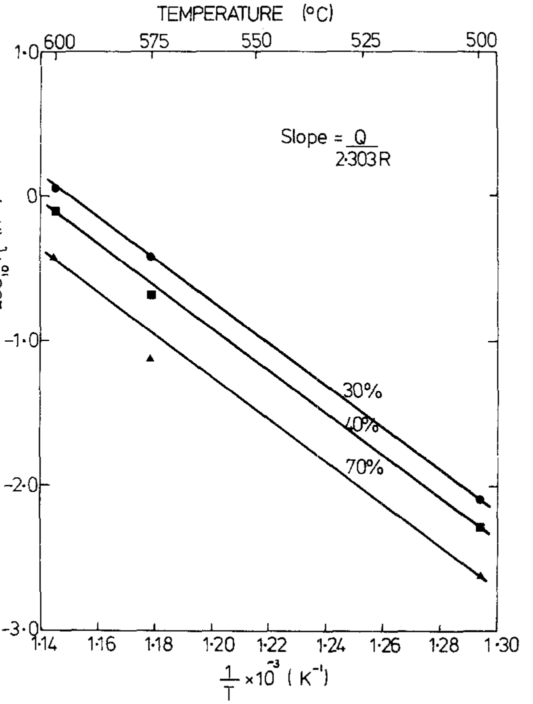

Figure 10 Illustrating activation energies for thermal degradation of the aluminium–silica composite.

cationic vacancies in alumina structures should also encourage cationic diffusion.

3.2. The induction period

In the presence of liquid aluminium or dilute liquid aluminium alloys containing bismuth and antimony, appreciable times may elapse before commencement of the reduction of the silica [12]. This conclusion was verified for composite material in the presence of solid aluminium. Such large incubation periods might not be anticipated if the reaction were diffusion controlled, and therefore some form of nucleation, or interface, control may be indicated. It was shown [12] that small alloying additions, particularly of bismuth, appreciably modify both the incubation period and the activation energy for the reduction process (which again would be unlikely under diffusion control). To compare the reactions with solid and liquid aluminium, the incubation periods, deduced approximately from graphical data [12] on pure aluminium and aluminium 0.38% Bi are compared in Fig. 11 with those observed in this investigation, in which two methods were used to determine the induction periods. Values obtained by direct observation of degradation at 500, 575 and 600° C have been plotted in Fig. 11; in addition, points obtained by

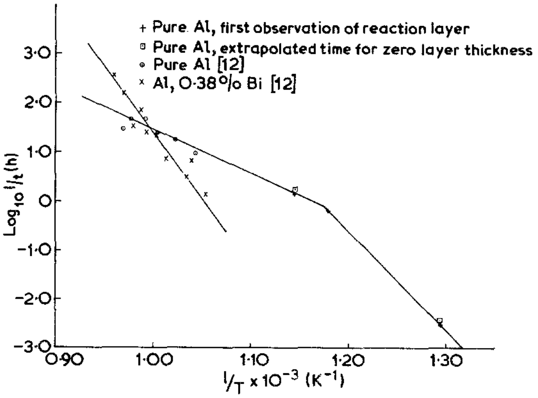

Figure 11 Temperature dependence of the time required to initiate reaction between aluminium and silica.

linear extrapolation of the penetration/time curves of Fig. 9 were also plotted for temperatures of 500 and 600° C (extrapolation at 575° C gave a negative time intercept). As might be anticipated, the times obtained by extrapolation were slightly less than the times for microscopically resolvable layers to appear. In both the 575 and 600° C samples, partial liquefaction was inferred from the incidence of widespread porosity in the microstructures (Fig. 6). It is concluded that results at these temperatures are in good agreement with the previous work, which involved liquid aluminium. The combined data may be used to derive an activation energy for the initiation of the alumina-forming reaction ($170.3\,\mathrm{kJ\,mol^{-1}}$) in the presence of liquid aluminium. The deviation of the solid reaction point (500° C) in the sense of requiring a longer induction period, may be connected with decreased energy of the aluminium atoms in the solid. Otherwise, the agreement with previous work is good, considering that the available aluminium supply is potentially limited in the matrix volume surrounding each fibre. Fig. 11 also shows the times for initiation of the reaction in the presence of 0.38% Bi. As might be anticipated, present data do not correlate so well with this curve, which indicates a higher activation energy and increased incubation periods in the low temperature region. Additions which inhibit initiation of interface reactions are obviously of value for increasing composite stability at high temperatures. Exposure to high temperatures is unavoidable (in aluminium/silica composites) at the pre-coating stage, when contact with the liquid aluminium occurs, if only for a few msec.

3.3. Microstructural and physical aspects of the interaction mechanism

Initially, direct reduction of silica by aluminium can be envisaged and this may be connected with the induction period. Once a layer of alumina is formed, two interfaces are present, namely Al/Al_2O_3 and Al_2O_3/SiO_2, and, in some cases, there may be further interfaces due to allotropic transformation of alumina, as observed in relatively few reacted fibres (see Figs. 6 and 7). The alumina layer thickens inwardly.

The main stages of the degradation process can be outlined as follows: at the Al_2O_3/SiO_2 interface, surplus aluminium, effectively in solution in alumina because of the aluminium adjacent to it at the other interface, reacts with silica, forming (i) more alumina, of lower Al content, and (ii) silicon, which, since it is not observed metallographically inside the alumina layer, must dissolve in that layer and diffuse outwards, subsequently precipitating in the aluminium matrix (possibly after transferring from solid solution in Al_2O_3 to solid solution in metallic aluminium). Thus if any of the following are kinetically slow processes, they may control the reaction rate:

(a) solution of Al in alumina, exceeding stoichiometric requirements;

(b) Al (in Al_2O_3) + SiO_2 → more Al_2O_3 + Si (dissolved in Al_2O_3);

(c) Si (in Al_2O_3) → Si (in Al solid solution);

(d) Si (in Al solid solution) → precipitated Si;

(e) Once a layer of silicon has completely encased the alumina (as shown in Fig. 7), aluminium must diffuse through the silicon in order to maintain the reaction.

If one of these reactions (preferably the rate controlling one) could be further retarded, degradation would be minimized. An explanation of the retardation of the degradation in the presence of bismuth in liquid aluminium has been given [12], in which it is proposed that the reaction of aluminium with silica is inhibited by the formation of a lamellar surface compound, BiO(OH), resulting from reaction between adsorbed bismuth, water and oxygen on the silica surface. It seems unlikely that bismuth would have this effect on composite material since the silica fibre is freshly drawn immediately before coating and would probably be free from adsorbed water.

It is possible that the aluminium/silica interaction, if carried out in a controlled manner, might lead to the development of a more stable composite material. The end product would consist of alumina fibres in an aluminium-silicon alloy, which is generally an effective matrix, giving greater strengths than predicted by the rule of mixtures, for example, when reinforced with graphite fibres [19]. Alumina whiskers have been considered as a reinforcement for high temperature composites [7, 20] and there is evidence in Fig. 9 of some bonding between the aluminium and the Al_2O_3.

The overall reaction can be examined in terms of product and reactant volume, e.g. considering gram-atomic quantities and taking the density of Al, Si, alumina and transparent silica (quartz) fibre as 2700, 2300, 3800 and 2210 $\mathrm{kg\,m^{-3}}$ respectively,

$$4\,Al + 3\,SiO_4 \rightarrow 2\,Al_2O_3 + 3\,Si$$

Reactant and product volumes:

$$4 \times 10^{-5}\,\mathrm{m}^3 + 7.15 \times 10^{-5}\,\mathrm{m}^3 = 11.15 \times 10^{-5}\,\mathrm{m}^3$$

$$5.370 \times 10^{-5}\,\mathrm{m}^3 + 3.653 \times 10^{-5}\,\mathrm{m}^3 = 9.023 \times 10^{-5}\,\mathrm{m}^3.$$

The above reaction gives an overall contraction of about 19%. This contraction would be reduced to 14.9% in a 50 vol % composite, such as that used in the present investigation, since some of the aluminium would not react, being surplus to the requirements of the reaction. In the region originally occupied by the fibre and finally taken up by alumina, porosity of nearly 25% must be accommodated. A lower level of shrinkage (about 11%) is required in the matrix for the composition represented by the equation. For a 50% composite, 4.9% porosity would occur in the matrix region, unless the composite dimensions changed during the reaction. If the newly formed aluminium–silicon matrix and the replacement fibre were free to change their size to absorb these shrinkage effects, a gap would be left between the fibre and the matrix. By causing separation at the fibre–matrix interface, these volume changes would destroy the mechanical properties of the composite and stifle the degradation reaction.

Considering now the actual behaviour, the alumina occupies completely the original fibre volume. No gap is produced between the new "fibre" and the matrix, but since the properties of alumina are very dependent on a low porosity level, considerable loss of strength is anticipated. Scanning electron microscopy shows that the degraded composite fracture formed under creep conditions is of a very brittle type (Fig. 4). Fibrous fractures are observed (see Fig. 5 for example) when the composite is not degraded [15], whereas the fracture shown is planar. The brittle reaction product (alumina) promotes the change in fracture mode, by facilitating the initiation and propagation of cracks, i.e. no energy is absorbed in debonding matrix/matrix interfaces in this degraded state.

4. Conclusions

Alumina, a product of thermally induced composite degradation, is located within the original silica fibre boundaries. A silicon reaction product is also observed, outlining the original fibre boundaries and possibly precipitated via solid solution in the aluminium matrix after passing through the reacted alumina layer. Growth of the alumina layer is associated with the diffusion of aluminium and silicon through it. An activation energy of about 280 kJ mol^{-1} is associated with the degradation process. There is a linear advance of the reaction front with time, which, together with the induction periods involved, suggests that the diffusion of aluminium and silicon are not the rate controlling mechanisms, but that some form of interface control is involved. By combining present observations with previous work, an activation energy of 170 kJ mol^{-1} has been deduced for the initiation of alumina layer formation. This value appears to increase when no liquid phase is present during the reaction between aluminium and silica.

The possibility of developing a strong, fibre-reinforced material by completely reacting the silica and replacing it with the more stable alumina has been considered. Success is unlikely because of porosity formation and crack initiation in the brittle alumina reaction product, although this technique may be applicable to other systems if their volume changes are more compatible.

Acknowledgements

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References

1. P. W. JACKSON and D. CRATCHLEY, *J. Mech. Phys. Solids* **14** (1966) 49.
2. R. G. C. ARRIDGE, Proceedings, Union Scientifique Continental du Verre (1964) p. 639.
3. E. STANDAGE, Amer. Ceram. Soc., Symposium No. 2, Paper, 6 Philadelphia (1965).
4. D. CRATCHLEY, *Powder Met* **11** (1963) 59.
5. A. G. METCALFE, *J. Comp. Mater.* **1** (1967) 356.
6. N. D. GREENE and N. AHMED, *Materials Protection* **9** (3) (1970) 16.
7. A. J. STAPLEY and G. J. BEEVERS, *J. Mater. Sci.* **4**, (1969) 65.
8. K. C. ANTONY and W. H . CHANG, *Trans. ASM* **61** (1968) 550.
9. A. R. T. de SILVA and G. A. CHADWICK, *J. Mech. Phys. Solids* **17** (1969) 387.
10. A. A. BAKER and D. CRATCHLEY, *Appl. Mat. Res.* **3** (1964) 215.
11. D. CRATCHLEY and A. A. BAKER, Proceedings, Union Scientifique Continental du Verre (1964) p. 669.
12. A. E. STANDAGE and M. S. GANI, *J. Amer. Ceram. Soc.* **50** (1967) 101.
13. K. J. BRONDYKE, *ibid* **36** (1953) 171.
14. K. PRABRIPUTALOONG and M. R. PIGGOTT, *ibid* **56** (1973) 184.
15. H. V. SQUIRES and H. W. RAYSON, to be

published.
16. D. CRATCHLEY and A. A. BAKER, *Metallurgia* **69** (1964) 153.
17. F. HABASHI, "Principles of Extraction Metallurgy", Vol. 1 (Gordon and Breach, New York, 1969) p. 131.
18. P. E. WAUDBY, W. J. M. SALTER and F. B PICKERING, *JISI* **211** (1973) 486.
19. R. T. PEPPER, J. W. UPP, R. C. ROSSI and E. G. KENDALL, *Met. Trans.* **2** (1971) 117.
20. R. E. TRESSLER and T. L. MOORE, *Met. Eng. Q.* **11** (1) (1971) 16.

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