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Degradation of Al_2O_3–SiC–Al composites prepared by the oxidative growth of Al-alloys into SiC particulate

SANDEEP KUMAR, VIKRAM JAYARAM
Department of Metallurgy, Indian Institute of Science, Bangalore 560 012, India
T. V. MANI, K. G. K. WARRIER
Structural Ceramic Unit, Regional Research Laboratory (SIR), Trivandrum 695 019, India

Composites of Al_2O_3–SiC–Al have been prepared by the oxidative infiltration of Si-free aluminium alloys into SiC particulate that were coated with spray-pyrolysed alumina. Moisture degradation studies were carried out to evaluate the extent of formation of aluminium carbide, the formation of which was also inferred by the determination of the residual silicon content in the composite. The efficiency of the coating technique in protecting the SiC from attack by the melt was evaluated at 1000 and 1200 °C.

1. Introduction

One of the attractive wear-resistant composite microstructures that may be created by melt oxidation of aluminium alloys is Al_2O_3–Al with SiC reinforcements [1, 2]. Alloys used for infiltration into SiC particulate invariably contain Si, partly to promote infiltration but primarily to avoid reaction between Al and SiC which leads to the formation of Al_4C_3. For equilibrium between SiC and the melt, the latter needs to contain 10–18% Si at 900 °C [3, 4]. Aluminium carbide is particularly undesirable since it is hygroscopic and Al_2O_3–SiC–Al composites containing Al_4C_3 are known to disintegrate in ambient conditions. If it were possible to coat and protect the particulate from the melt there would be additional flexibility in the alloy composition. For example, greater toughening may be expected by plastic stretching from the alloy channels in the absence of silicon. Coatings to reduce interfacial strength have been employed on Nicalon fibres prior to infiltration by Al_2O_3–Al and the resulting composite has been shown to exhibit substantial fibre pull-out, thereby leading to high fracture toughness [5]. In the present work we report the infiltration of Al_2O_3–Al into SiC particulates that were coated by a spray-pyrolysed boehmite sol. The alloy used for oxidative infiltration did not contain silicon and the extent of formation of Al_4C_3 was monitored on the composite by an analysis of the residual silicon content and the extent of deterioration in moisture. Uncoated particles were similarly infiltrated and analysed in order to evaluate the efficiency of the coating.

2. Experimental procedure

Aluminium alloy billets (Al–5Zn–0.3 Mg) were placed in alumina crucibles with protective coatings, as shown in Fig. 1. Particulate SiC (mean particle size of 50 μm) was cold-pressed with binder into pellets which were placed on top of the alloy. The crucible assembly was heated at $40° \min^{-1}$ to 1000 or 1200 °C and held for several hours before cooling.

SiC particles were coated with alumina in the following manner. The particles were washed with acetone to remove any organic material and then treated with 1:10 HF–H_2O solution to remove SiO_2. The suspension was filtered, washed with distilled water and acetone and dried at 80 °C for 3h in an air oven. The activated powder was ultrasonically dispersed in boehmite sol containing 2 wt% boehmite. The system was continuously stirred for 5 h and then filtered. The sol-coated SiC particles were again dispersed in *n*-butanol and then spray dried in a Buchi Mini spray drier, keeping the inlet and outlet temperature at 180 and 100 °C, respectively. The spray-dried powder was calcined at 900 °C to remove all volatiles and used for composite preparation, as described above.

After infiltration, samples were sectioned for optical metallography to determine the volume fraction of SiC, Al_2O_3 and metallic constituents. Aluminium content was determined by leaching the crushed composite with hydrochloric acid followed by atomic absorption analysis. Moisture degradation studies were carried out by placing pieces of the composite in a beaker which was in turn placed in a covered container of water at room temperature. Weight measurements were made on the composite over a period of approximately 1 month.

3. Results

Fig. 2 shows uncoated and coated powders after pyrolysis at 900 °C. The latter are agglomerated, a

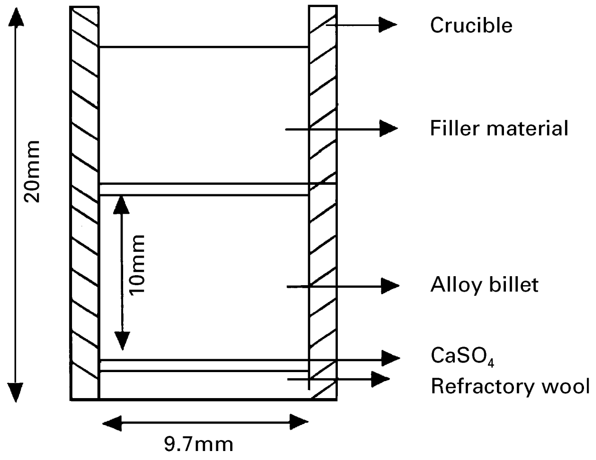

Figure 1 Schematic of experimental set-up used for infiltration.

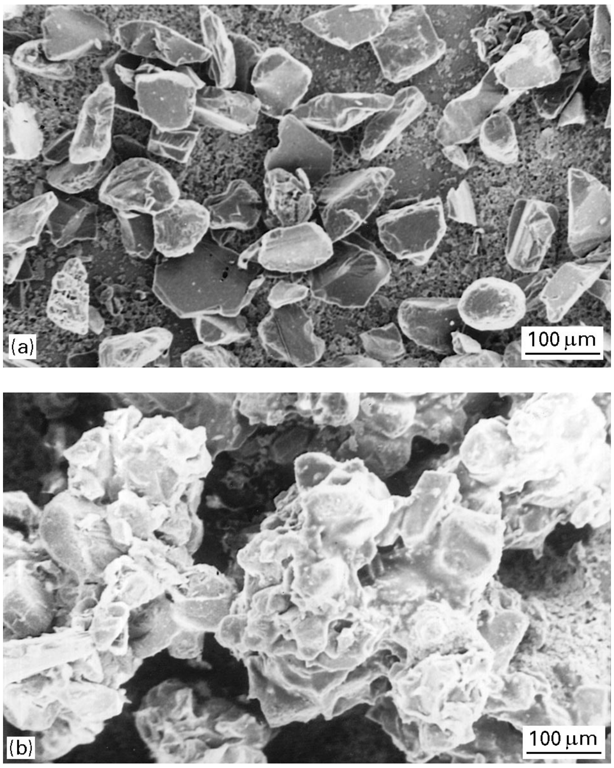

Figure 2 SiC powders (a) uncoated and (b) boehmite spray coated and pyrolysed.

feature which is manifest in the lower packing fraction of preforms made from coated particulate (Table I). The oxidation of the two sets of particulate in air at 1400 °C is shown in Fig. 3. The coated particles were previously heated to 1000 °C to completely eliminate moisture before the oxidation experiment was begun. The oxidation curve levels off after an initial rise for both samples. The coated particles display an asymptotic weight gain after 8 h that is approximately one-third the corresponding value for the uncoated particles, but the oxidation appears to recommence subsequently, suggesting that the coating becomes non-protective, possibly through spalling.

Fig. 4 shows the overall microstructures of composites prepared with coated (a,b) and uncoated (c,d) particulate while Fig. 4e is a typical high-magnification view from which the volume fraction of metallic constituent was evaluated in each sample. A small amount of free alumina is also present in the coated composites and is visible as alloy free regions in Fig. 4a and b. Table I summarizes the proportions of the various phases of which the volume fractions of SiC, total alloy, alumina and of porosity were determined by direct image analysis while the weight percentage of Al was obtained from atomic absorption spectrometry. Volume fractions of silicon and aluminium were deduced from

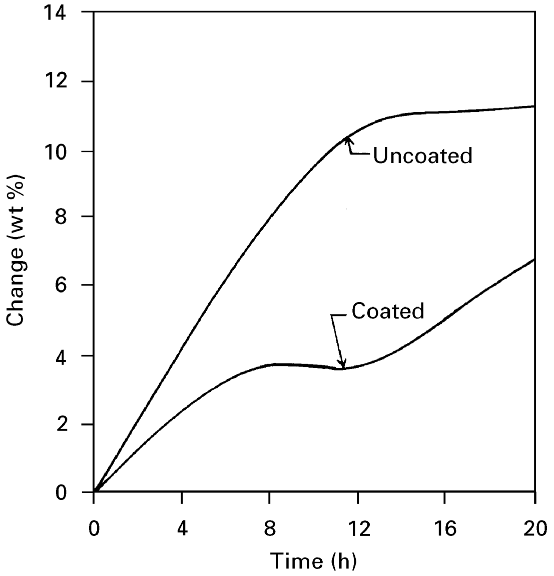

Figure 3 Weight change after oxidation of SiC in air at 1400 °C.

TABLE I Volume fractions of phases

	1000 °C		1200 °C	
	Coated	Uncoated	Coated	Uncoated
SiC[a]	24.1	44.6	28.3	45.5
Al_2O_3[a]	62.4	41.6	50.7	37.3
VOIDS[a]	4.0	4.1	9.0	7.6
TOTAL ALLOY[a]	9.5	9.7	12.0	9.6
Al[b]	8.6	7.9	10.5	7.8
Si[c]	0.9	1.8	1.5	1.8

[a] Optical image analysis.
[b] Atomic absorption.
[c] Difference between total alloy and Al. Precision in Si ≃ ± 5% total alloy, i.e. ± 0.5%.

$$W_{Al} = V_{Al}\rho_{Al}/(\rho_{Si}V_{Si} + \rho_{Al_2O_3}V_{Al_2O_3} + \rho_{SiC}V_{SiC})$$

and

$$V_{Si} + V_{Al} = V_{Alloy}.$$

where W and V are weight and volume fractions respectively and ρ is one density.

The weight gain after exposure to moisture is shown graphically for the composites formed from coated and uncoated powders in Fig. 5. In addition, for comparison, a similar curve is shown for composites made with Al–10Si–5Zn–0.3 Mg oxidized into uncoated SiC. Degradation is clearly the highest for uncoated particles that were infiltrated at 1000 °C. However, coated particles at 1000 and 1200 °C do not behave significantly differently from the uncoated particles at

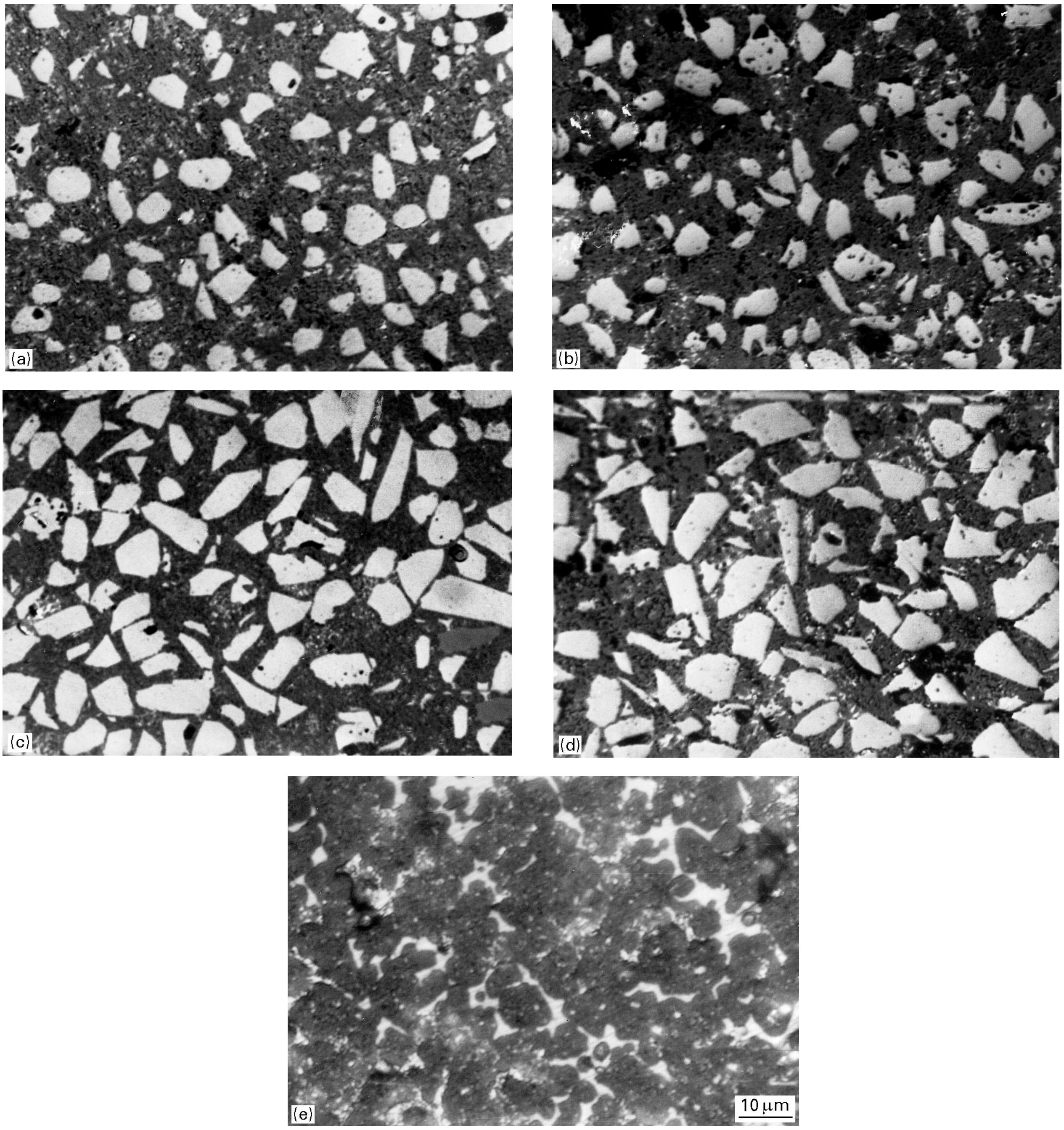

Figure 4 Microstructures of composites prepared with (a) coated powders at 1000 °C; (b) coated powders at 1200 °C; (c) uncoated powders at 1000 °C; (d) uncoated powders at 1200 °C; (e) A typical high magnification view from which alloy (bright) volume fractions were determined. Arrow in (a)–(d) is 100 μm.

1200 °C. Even lower rates of degradation are displayed by the composite made from a Si containing alloy, as expected.

The residual silicon level is comparable in both the uncoated composites as well as in the coated 1200 °C sample, whereas it is significantly lower in the composite made with coated SiC at 1000 °C.

4. Discussion

The degradation of the composite is assumed to occur by means of the formation and hydrolysis of Al_4C_3 according to the reactions

$$4Al + 3SiC \rightarrow Al_4C_3 + 3Si$$

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

comparison of the weight gain in Fig. 4 shows that all the composites made with Si-free alloys undergo degradation that probably arises from such a reaction. In that sense the coatings do not provide complete protection in the absence of Si in the alloy. However, at the lower temperature of 1000 °C the consequence of absence of coating is marked both in the weight gain as well as in the residual silicon content of the composite, whereas at 1200 °C when one might expect greater reaction there is little difference. A plausible explanation for these results is that at higher infiltration temperatures, oxidation of SiC yields a silica layer that not only delays direct contact between SiC and the melt but also acts as a source of silicon that brings its activity in the melt closer to that in SiC, thereby reducing the rate of formation of Al_4C_3. Such

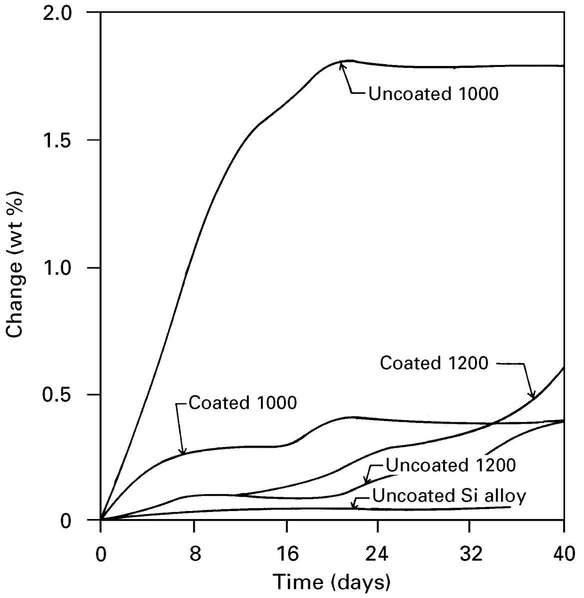

Figure 5 Weight change with time of exposure to 100% humidity at room temperature. The lowest curve shows the weight change for a composite made under normal conditions by using uncoated SiC and an alloy with approximately 10% Si, in addition to Mg and Zn.

oxidation is minimal at 1000 °C thus leading to greater interfacial Al_4C_3 in the absence of a coating. Thus, coated particulates are not a significant improvement at 1200 °C, because the coating itself appears to spall and re-expose the SiC, as suggested by the oxidation curve in Fig. 2.

5. Conclusion

Spray-pyrolysed alumina coatings on SiC particulate offer some protection with respect to attack by aluminium alloys that do not contain Si during oxidative infiltration at 1000 °C. At higher temperatures, the native silica layer on uncoated SiC is equally effective as a barrier, partly due to the non-protective nature of the Al_2O_3 coating and partly due to the dissolution of SiO_2 into the melt, which brings the activity of Si closer to that in equilibrium with SiC.

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