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Role of Mg and Ti on a SiC_P,ZrC_P/Al composite at elevated temperatures

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Metal-matrix composites have been considered as new materials with many attractive properties. One of the characteristics of particulate composites is high strength at elevated temperatures. In this work, a SiC- or ZrC-particle-reinforced composite was fabricated through a casting route and the effect of Ti and Mg alloying on the wettability between ceramic particles and a liquid aluminium alloy was measured with the time required for particulate incorporation. The formation of a reaction product was observed and it was identified by scanning electron microscopy (SEM) and X-ray microanalysis. Observations by SEM revealed that the incorporation time was closely related to the interfacial reactions. The degradation of the composite at an elevated temperature was measured, and the roles of the interfacial reaction and the formation of the reaction product were investigated. Decomposition of the ceramic phase due to the elevated-temperature holding depended on the thermodynamical properties of the ceramic phase. The formation site of the reaction product also affected the degradation of the composite material.

1. Introduction

Metal-matrix composites (MMCs) have attracted many researchers because of their high strength, high elastic modulus and excellent mechanical properties at elevated temperatures. Since particulate composites can be fabricated by a casting technique, the manufacturing process for particulate MMCs is simpler than that of fibre MMCs. But the casting technique still has some difficulties which strongly affect the following properties of the composite materials: wettability between the ceramic particles and the liquid metal, and decomposition of the ceramic phase. Of course complete wetting is necessary for satisfactory bonding between ceramic particles and the metal matrix. Many researchers have indicated that reaction or diffusion at the interface is required for good wettability [1–4], although decomposition of the ceramic phase produces a brittle reaction product. Furthermore, high strength at elevated temperatures is one of the characteristics of MMCs, diffusion or reaction at the interface, however, decreases the strength of composite materials. In this work, the wettability between ceramic particles and liquid aluminium and the strength of the particulate composite were measured and they are discussed from the viewpoint of the interfacial reaction; degradation of strength due to decomposition of the ceramic phase at elevated temperatures was also investigated.

2. Experimental procedure

A total amount of 100 g of aluminium or aluminium alloy was heated in a magnesia (MgO) crucible in an argon atmosphere. The melt was held at a temperature of 1073 K. Then silicon carbide (SiC) or zirconium carbide (ZrC) particles wrapped in aluminium foil were preheated above the melt surface for 600 s. Then particles were added to the melt and melt stirring was conducted with an alumina (Al_2O_3) rod. The time necessary for particulate incorporation was measured from a time/melt temperature chart. Melt stirring was continued for a certain period after the particulate incorporation had finished to improve the uniformity of particulate distribution. The liquid aluminium containing ceramic particles was poured into a metallic mould after melt stirring. The as-cast ingot was hot extruded at a temperature of 773 K. Some of the test pieces for a tensile test were held at 803 K for 50 and 100 h to investigate the degradation of mechanical properties at elevated temperatures. The volume fraction, V_f, of SiC and ZrC particles was 12% in both cases. The average diameter of SiC was 20.0 and 3.0 μm and that of ZrC particles was 2.4 μm. Cross-sections of the composite materials were observed by scanning electron microscopy (SEM) and X-ray micro analysis.

3. Results and discussion

3.1. Definition of the incorporation time

A typical relation between the ratio of the incorporated particles, temperature of the liquid aluminium and the stirring time is shown in Fig. 1 [4]. As mentioned in the experimental procedure, the wettability between the ceramic particles and liquid aluminium was estimated from the time required for the particulate incorporation. As shown in Fig. 1, particles, which were added to the surface of liquid aluminium,

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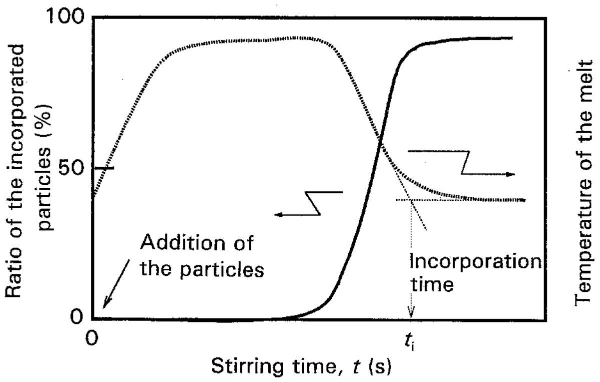

Figure 1 Typical relation between the ratio of incorporated particles, temperature of the liquid phase and the stirring time.

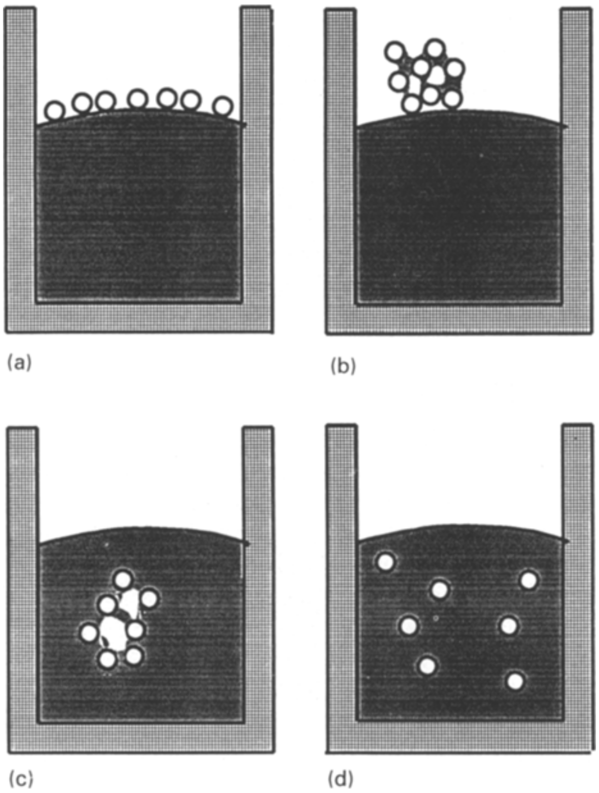

Figure 2 Schematic drawings of the incorporation process of ceramic particles into liquid aluminium: (a) addition of particles, (b) lumping, (c) incorporation, and (d) dispersion.

were incorporated into the liquid phase abruptly after a constant period. So it is apparent that there is an incubation period before particles begin to incorporate. Fig. 2 shows schematic drawings of the incorporation process. First, particles, which were just added to the surface of the liquid aluminium, Fig. 2a, were gradually wetted. Partly wetted particles made a lump of particles, and particles in the lump were bridged by liquid aluminium, Fig. 2b. Then sufficiently wetted particles were incorporated into the liquid phase as a lump of particles, Fig. 2c. Finally, completely wetted particles were dispersed uniformly in the liquid phase, Fig. 2d. In this measurement of the incorporation process, particles were observed by separating into: as-powder particles, lump of particles and incorporated particles. The amount of particles in each phase was measured by dissolving the aluminium matrix with sodium hydroxide (NaOH) [4]. From these observations, it becomes clear that the particles were gradually wetted by liquid aluminium during the incubation period. The length of the incubation period could be identified by measuring the heat generation due to the interfacial reaction and the change in the surface energy ($\sigma_{sv} - \sigma_{sl}$) during the wetting process. This heat generation is shown by a dotted line in Fig. 1, and the increase in the liquid temperature was seen during the incubation period. So the incorporation time could be easily identified from the graph of stirring time versus temperature of the liquid phase as shown in Fig. 1. The wettability of ceramic particles was estimated by this incorporation time and the shorter incorporation time indicates the improved wettability in this work.

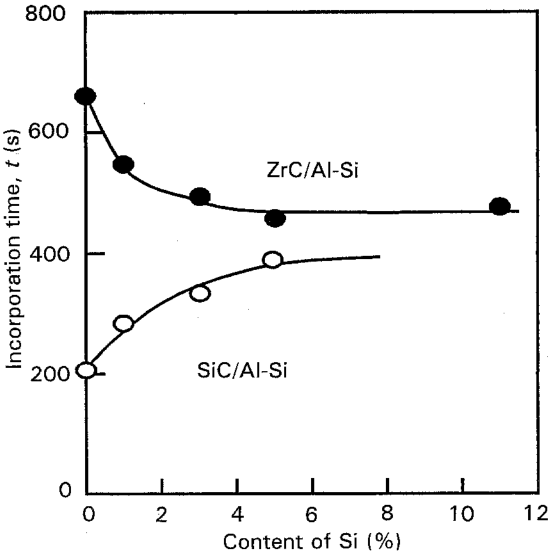

Figure 3 The effect of Si alloying on the incorporation time of SiC (20 μm) and ZrC (2.4 μm) particles into liquid aluminium, at 1023 K.

3.2. The effect of Zr and Si alloying on the incorporation time of ZrC and SiC particles

Fig. 3 shows the effect of Si alloying on the incorporation time of SiC and ZrC. According to Fig. 3, the incorporation time of SiC was prolonged by Si alloying, whereas that of ZrC was shortened. This indicates that the wettability of ZrC was improved, and that of SiC was not. An observation by SEM revealed the formation of Zr silicide in the matrix of the ZrC/Al–Si system as shown in Fig. 4. Note that, as shown in Fig. 5, the incorporation time of SiC was shortened, and that of ZrC was prolonged, by Zr alloying. Zr silicide was also observed in the matrix of the SiC/Al–Zr alloy system. As is widely known, interfacial reactions improve wettability due to a decrease in the interfacial energy of the solid–liquid interface. In these systems, good wettability can be achieved by the following reactions [5],

$$\mathrm{SiC} \rightarrow (\mathrm{Si}) + (\mathrm{C}) \qquad (1)$$

$$\mathrm{ZrC} \rightarrow (\mathrm{Zr}) + (\mathrm{C}) \qquad (2)$$

where (Si), (Zr) and (C) are the dissociated elements. A reduction in the interfacial energy and the appearance

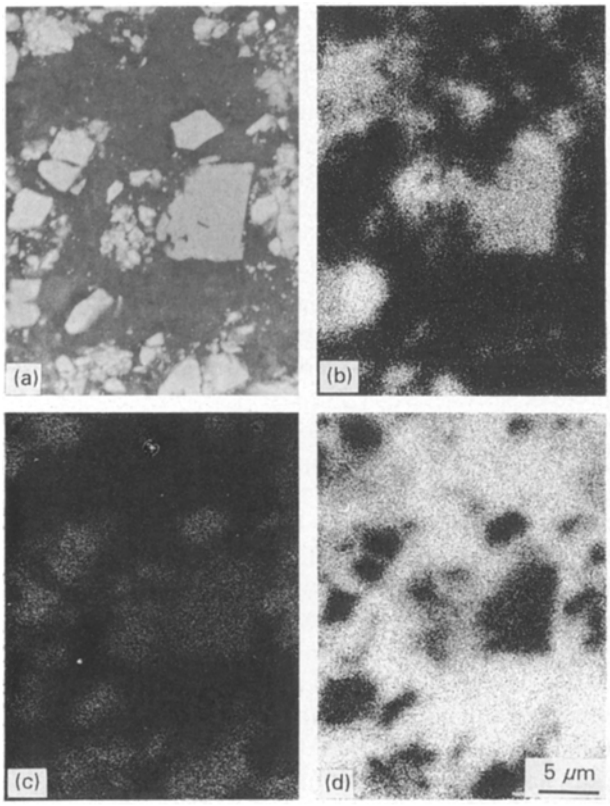

Figure 4 (a) Scanning electron micrograph; and X-ray images of (b) Si, (c) Zr and (d) Al for a cross-section of a ZrC (2.4 μm)/ Al–11.6% Si composite.

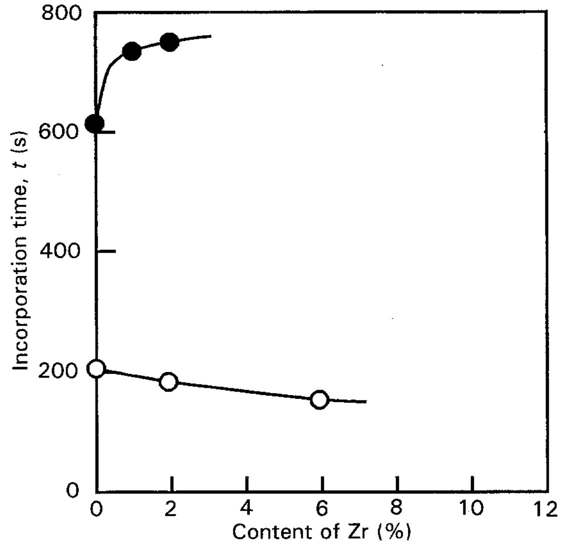

Figure 5 The effect of Zr alloying on the incorporation time of SiC (20 μm) and ZrC (2.4 μm) particles into liquid aluminium at 1023 K: (●) ZrC/Al–Zr, and (○) SiC/Al–Zr.

of an activated surface of the ceramic phase are considered to be the reasons for the wetting progress by this reaction. Since the following reaction:

$$m\text{Zr} + n\text{Si} \rightarrow \text{Zr}_m\text{Si}_n \quad (3)$$

enhances the progress of Reactions 1 and 2, the incorporation time of SiC and ZrC were shortened by alloying Zr and Si, respectively, in this work. On the other hand, by alloying a constituent of the ceramic phase, the progress of Reactions 1 and 2 might be controlled. So the incorporation time of SiC and ZrC were prolonged by alloying Si and Zr, respectively.

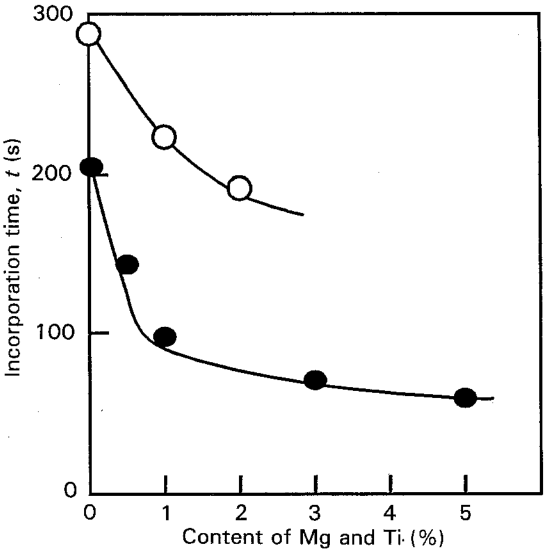

Figure 6 The effects of Mg and Ti alloying on the incorporation time of SiC (20 μm) particles into liquid aluminium at 1023 K: (●) SiC/Al–Mg and (○) SiC/Al–10Sn–Ti.

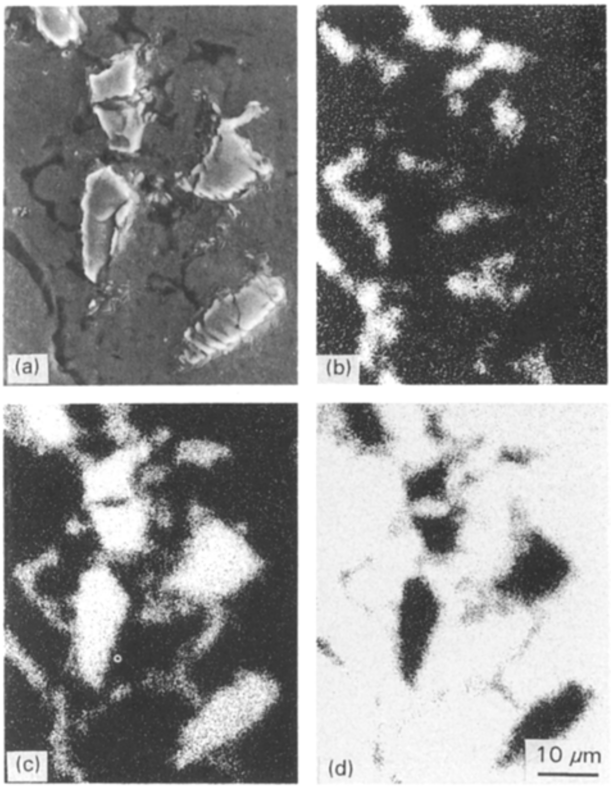

Figure 7 (a)Scanning electron micrograph, and X-ray images of (b) Mg, (c) Si and (d) Al for a cross-section of a SiC (20 μm)/Al–5.0% Mg composite.

3.3. Effect of Mg and Ti alloying on the incorporation time of SiC particles

The effect of Mg and Ti on the incorporation time of SiC is shown in Fig. 6. A decrease in the incorporation time of SiC by Ti and Mg alloying was seen, and the reaction product was also observed by SEM in both systems. Fig. 7 shows a cross-section of a SiC/Al–5% Mg composite and X-ray images of Al, Si and Mg. Since this specimen was prepared for observation of the reaction product, a relatively longer stirring time (1200 s) than incorporation time (60 s) was used, and larger particles (20 μm) were used. The formation of Mg_2Si was confirmed, as shown in Fig. 7, because the X-ray images of Si and Mg overlapped. For the SiC/Al–Mg alloy system, the formation site of Mg_2Si was not at the interface but in the Al–Mg alloy matrix. The reaction product was formed at the interface for a SiC/Al–Ti composite (Fig. 8). This reaction product was identified as titanium carbide (TiC) from the analysis of an X-ray microanalyser, although the formation of Ti_5Si_3 had also been reported for a SiC/Ti composite [6]. It is notable that the formation sites of the reaction product are different in the two composites. From these results, it is assumed that the improved particulate wettability is closely related to the interfacial reaction as well as the wettability measured by the sessile-drop method.

3.4. Decomposition of the particle phase at the elevated temperature

One of the advantages required for composite materials is high strength at elevated temperatures. However, if MMCs are in an elevated-temperature environment, interfacial reactions such as decomposition of particles, diffusion and formation of a reaction product might cause a degradation in the composite's strength. So we measured the strength and observed the microstructure of a SiC/Al alloy and a ZrC/Al alloy composite which were held at an elevated temperature, and then evaluated the influence of the elevated-temperature (ET) holding time on the degradation of the composite's strength.

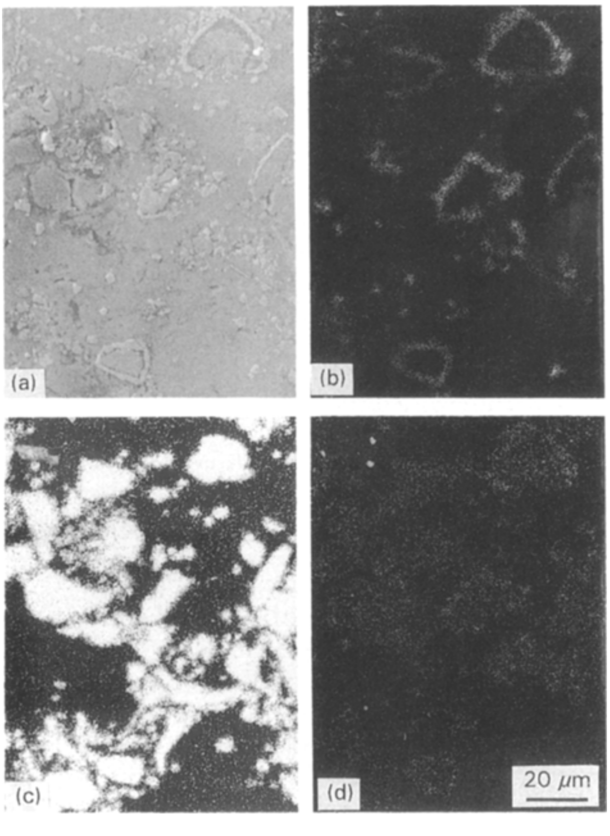

Figure 8 (a) Scanning electron micrograph, and X-ray images of (b) Ti, (c) Si and (d) C for a cross-section of a SiC (20 μm)/Al–1.0%Ti composite.

The tensile strengths of SiC/Al and ZrC/Al composites and those of composites held at the elevated temperature are shown in Fig. 9. The testing temperature (803 K) was settled under the eutectic temperature of Al and Si to prevent formation of a liquid phase. The strength of the SiC/Al composite decreased with holding time at 803 K, whereas that of the ZrC/Al composite did not. The difference in the initial strength of the SiC/Al and ZrC/Al composites might be due to the interfacial strength, particulate strength and the matrix composition which depends on the dissociation of SiC or ZrC during the fabrication process.

Fig. 10 shows the microstructures of SiC/Al and ZrC/Al composites with and without holding at the elevated temperature. The formation of reaction products can clearly be seen in the SiC/Al composites with holding at elevated temperature. According to the X-ray microanalysis, these reaction products were confirmed as being Si and Al_4C_3. Furthermore, for the Al–3%Mg matrix, the strength of the SiC/Al–3%Mg composite decreased rapidly with elevated-temperature holding time, as shown in Fig. 11. SEM observation at the cross-section of the SiC/Al–3.0%Mg composite revealed that most of the particles decomposed during the elevated-temperature holding. A vigorous reaction caused by the presence of Mg is considered to be the main reason for the rapid decrease in the composite's strength. On the other hand, for the ZrC/Al–3%Mg composite, the strength did not decrease rapidly in comparison with the SiC/Al–3%Mg composite because of the stability of ZrC. The strength of a SiC/Al–1%Ti composite is shown in Fig. 12, along with the results for SiC/pure Al and SiC/Al–3%Mg composites. As mentioned above, the presence of Mg remarkably decreased the composite's strength at the elevated temperature because of its strong reactivity with SiC [7]. However, a decrease in the strength of the SiC/Al–1%Ti composite caused by the elevated-temperature holding was much less than that for the SiC/Al–Mg composite shown in Fig. 11,

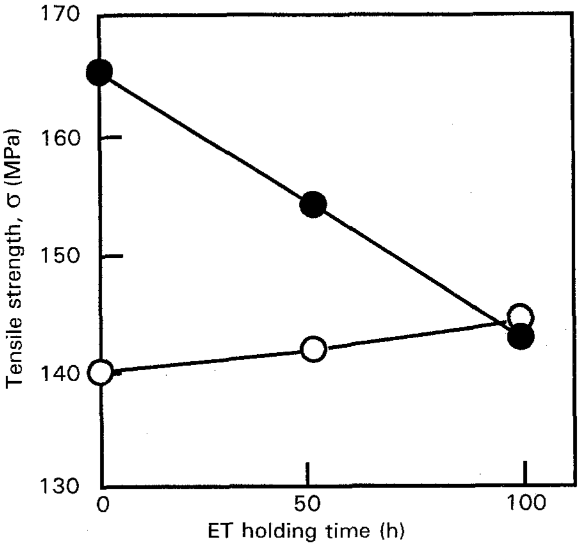

Figure 9 Changes in the SiC (20 μm), and the ZrC (2.4 μm)/Al composites' strengths caused by the elevated-temperature (ET) holding at 803 K: (●) SiC/Al, and (○) ZrC/Al.

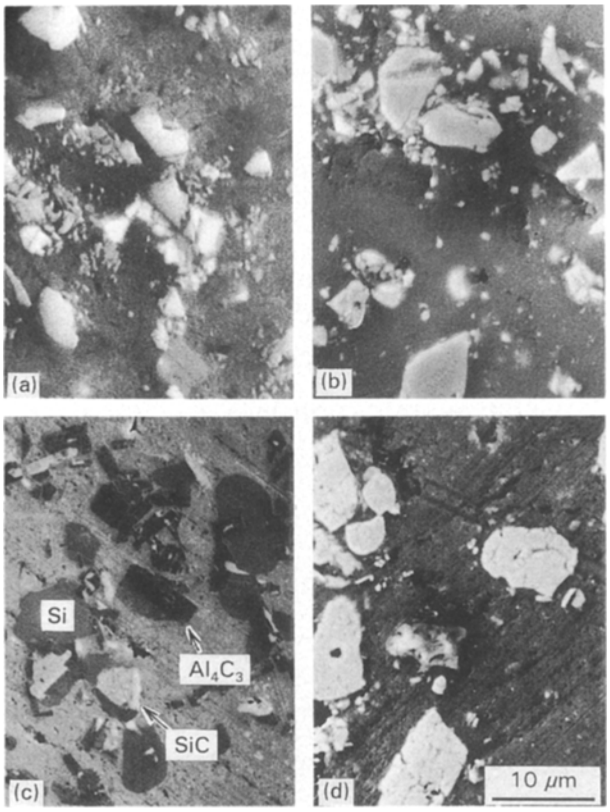

Figure 10 Scanning electron micrographs of (a), (c) SiC (3.0 μm)/Al and (b), (d) ZrC (2.4 μm)/Al composites. (a), (b) Without, and (c), (d) with holding at elevated temperature.

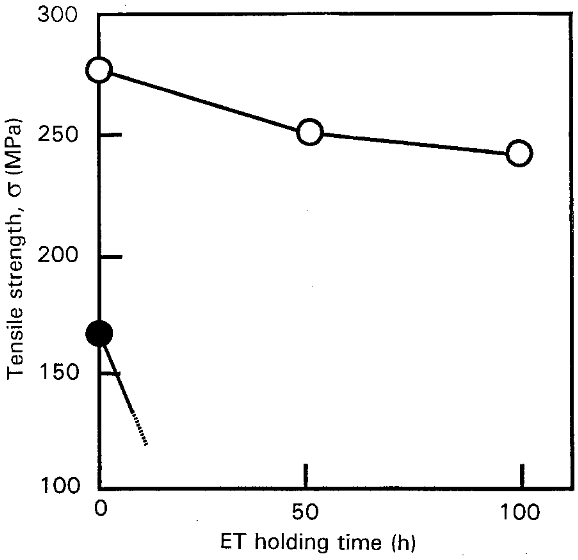

Figure 11 Changes in the (●) SiC/Al–3.0%Mg and (○) ZrC/Al–3.0%Mg (SiC (3.0 μm), ZrC (2.4 μm) composite strengths with the elevated-temperature holding time, at 803 K.

and it was almost equal to that of the SiC/Al composite, in spite of the strong reactivity of Ti with SiC. In this case, TiC formed during the fabrication process and became a diffusion barrier to Ti, Si and C. So the decomposition of SiC was retarded by this diffusion barrier. Titanium alloying, therefore, not only made this system wettable, but played another role by preventing the excessive reactions as well.

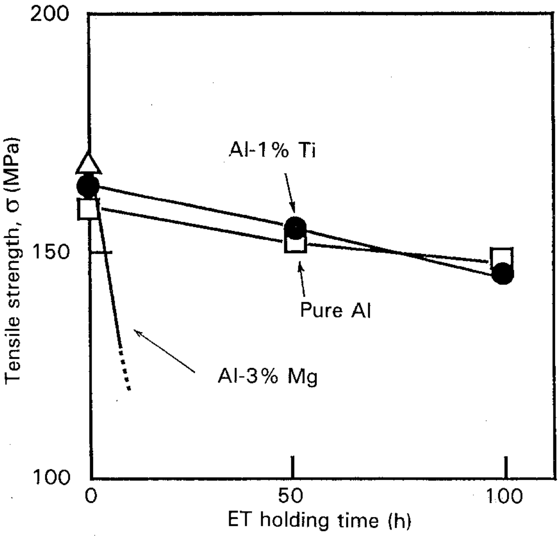

Figure 12 Changes in the SiC (3.0 μm)/Al alloy composite's strength caused by the elevated temperature holding at 803 K.

TABLE I The value of the Gibbs free energy of carbide formation, the logarithmic diffusion coefficient and the solubility in aluminium at 803 K, for Si and Zr

	Si	Zr
Gibbs free energy of carbide formation, ΔG^0 (kJ g^{-1} mol^{-1} C^{-1})	− 42	− 167
Diffusion coefficient, Ln $D_{\text{in Al}}$	− 30	− 40
Solubility in aluminium (%)	2 ∼ 3	≒0

3.5. The factors having an effect on the decomposition of the ceramic phase

From the results obtained in these experiments, three factors are considered to affect the decomposition of the ceramic phase under elevated temperature as shown in Table I. Considering the standard free energy of formation as an index of the thermodynamical stability, the value of ΔG^0 of ZrC being lower than that of SiC means that ZrC is more stable than SiC, which prevents the decomposition of ZrC. Although the stability should be estimated by the total-free-energy change of the interfacial reaction for a more accurate estimation, the difficulty in grasping the strict interfacial reaction and the lack of thermodynamic data prevented the use of the total free-energy change of the interfacial reaction. Furthermore, the constituent of the ceramic phase has to diffuse in the matrix alloy when it decomposes and solubility to some extent might be necessary for particulate decomposition. Hence, a lower diffusion coefficient and a lower solubility of Zr in Al than for Si might also control the decomposition of ZrC.

4. Conclusions

From the investigation of the role of Mg and Ti on the wettability of SiC and ZrC particulate composites and the degradation of the composite's strength, the following results were obtained.

1. Magnesium and titanium alloying shortened the incorporation time of the SiC particles into liquid aluminium. Reaction products between SiC and the alloying elements were observed in both cases.

2. The reaction products in SiC/Al–Mg and SiC/Al–Ti composites were identified as Mg_2Si and TiC respectively. In SiC/Al–Mg composites, Mg_2Si was formed apart from the SiC/Al interface. Titanium carbide was formed at the interface in the SiC/Al–Ti composite.

3. The strength of the SiC/Al composite was decreased by the elevated-temperature holding at 803 K for 50 and 100 h, although the strength of the ZrC/Al composite was not decreased.

4. The strength of the SiC/Al–Mg composite decreased rapidly with the elevated-temperature holding time due to the decomposition of SiC particles.

5. TiC formed at the interface and became a diffusion barrier preventing the decomposition of SiC during the elevated-temperature holding.

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