Effects of Alloying Elements on SiC Dispersion in Liquid Aluminum*

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The effects of alloying elements on dispersion of SiC particles into molten aluminum were investigated. The time required for incorporation of SiC particle into molten aluminum was defined as an incorporation time. The incorporation time of SiC was shortened by alloying magnesium, or by alloying titanium together with tin. These alloying elements have strong affinity for SiC and are able to form silicide as a result of reaction with SiC. Magnesium silicide was detected by EPMA, although the existence of titanium silicide could not be conformed. The incorporation time of SiC was prolonged by adding zinc, copper and tin which have no affinity for SiC. Moreover, particulate dispersion is considerably influenced by surface-active elements. The incorporation time of SiC particle was shortened by adding lithium which is a surface-active element with strong affinity for SiC, whereas it was prolonged by adding surface-active elements with weak affinity for SiC such as lead and bismuth. This is probably because lead and bismuth adsorb at the interface and hinder the wetting between SiC particle and molten aluminum. The addition of silicon into aluminum prolonged the incorporation time of SiC because the dissociation of SiC, that might be necessary for good wetting, was retarded by the existence of silicon.

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I. Introduction

Particle-reinforced metal matrix composites (MMC) are expected as a new material with high specific strength and Young's modulus. These composites are fabricated mainly by powder metallurgy, compocasting and melt-stirring method. Although powder metallurgy method gives uniform distribution and high volume fraction of particulate reinforcements, its manufacturing process is complicated and expensive⁽¹⁾. As concerns composites, fabricated by compocasting method, the higher porosity is also a problem⁽²⁾. On the other hand, melt-stirring is the most convenient way of manufacturing and takes minimum cost. However, melt-stirring method also has some problems to be solved. They are the uniformity of particulate distribution and the amount of incorporated particles in the melt. Accordingly, addition of other elements into molten aluminum was tried to obtain the sound composites. In present work, the alloying elements were classified into following four groups of (a) the elements with strong affinity for SiC, (b) the elements with weak affinity for SiC, (c) surface-active elements and (d) Si (a constituent of SiC). And the effects of alloying elements on the incorporation of SiC particles into molten aluminum were investigated.

II. Experiments

Total amount 60 g of aluminum or aluminum alloy

were melted in the MgO crucible (inner diameter 38 mm) by an induction furnace shown in Fig. 1⁽³⁾. After melt was held at a temperature of 1023 K, SiC particles wrapped in an aluminum foil were preheated above the melt for 420 s. Then they were added to the melt and melt stirring was conducted with an alumina rod. It was continued until no particles were found at the surface of melt or crucible corner. Such a time required for the incorporation of SiC particles was defined as an incorporation time, which could be determined within 10% in the relative error. The effects of alloying elements were evaluated by this incorporation time, i.e. whether the incorporation time was shortened or prolonged by alloying element was measured. The melt containing reinforcement was air-cooled in the crucible, because the viscosity of specimen

Fig. 1 Schematic view of induction furnace.

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is too high to cast. Distribution of SiC particles and a behavior of alloying elements were observed by SEM and EPMA.

In this experiments, SiC (20 μm in diameter) was used as particulate reinforcement and volume fraction of SiC particle was 17.7%. Component of experimental materials are given as follows. Al: pure metal (99.75%Al), Mg: pure metal (99.9%Mg), Zn: pure metal (99.9%Zn), Si: Al-24.3%Si alloy, Sn: pure metal (99.95%Sn), Ti: Al-5.01%Ti alloy, Cu: pure metal (99.99%Cu), Pb: pure metal (99.9%Pb), Bi: pure metal (99.9%Bi), Li: Al-18.5%Li alloy.

III. Results

1. Effects of alloying elements with strong affinity for SiC

First of all, the effect of magnesium on the incorporation time of SiC was measured. It is clear that the incorporation time was shortened by alloying magnesium as shown in Fig. 2. For example, the incorporation time of SiC particles into the Al-3.0%Mg alloy was 59 s and it was about one-fourth comparing with that of SiC particles into pure aluminum. EPMA analysis of SiC dispersed Al-5.0%Mg alloy shows that magnesium enriched region overlaps with silicon image as shown in Fig. 3. Furthermore, the formation of magnesium silicide was confirmed thermodynamically from the Ellingham diagram shown in Fig. 4, and it is apparent that the standard free energy of formation of Mg_2Si is negative at the experimented temperature (1023 K). Thus Mg_2Si seems to be formed in this case. In addition, it is clear, in the case of the Al-Mg-Zn and Al-Mg-Si systems, that the effect of magnesium was not influenced by the coexistence of zinc or silicon as shown in Fig. 2. In both cases, Mg_2Si was also detected in the matrix. For example, Fig. 5 shows silicide formed in the Al-1%Zn-5%Mg matrix.

The effect of titanium on the incorporation time of SiC particle is shown in Fig. 6. According to Fig. 4, the standard free energy of formation of titanium silicide is low enough to form TiSi, Ti_2Si and Ti_3Si_3 , so titanium, in this

Fig. 2 Effect of magnesium on the incorporation time of α -SiC particles in liquid aluminum or aluminum alloy at 1023 K.

case, seems to react with SiC and makes its silicide. However, by EPMA analysis of Al-Sn-Ti system, titanium enriched zone was not found as shown in Fig. 7 and titanium silicide could not be detected in the matrix. From the point of view of standard free energy for the carbide formation, TiC can be also formed⁽⁶⁾. By Martineau *et al.*⁽⁶⁾, the formation of Ti_5Si_3 , TiC and Ti_3SiC_x were confirmed at the interface between Ti and CVD-SiC filament after annealing at the temperature range from 973 to 1273 K. Thereby, a fraction of SiC may dissolve and react with matrix, especially with titanium, even though, intermetallic compound was not detected by EPMA.

As mentioned in previous work⁽⁷⁾, the dissociation of SiC seems to be a dominant factor of wetting. (eq. (1))

where, (Si) or (C) indicates a dissociated state element, $\underline{\text{Si}}$ or $\underline{\text{C}}$ is a soluted one. Equation (1) is promoted by the increase in solubility of Si or C and by consumption of these elements due to the reaction with alloying elements (eq. (2), eq. (3)).

Fig. 3 α -SiC particles dispersed in Al-5%Mg alloy at 1023 K. (a) SEM, (b) magnesium image and (c) silicon image.

Fig. 4 Standard free energies of silicide formation.

Fig. 6 Effect of titanium on the incorporation time of α -SiC particles in liquid aluminum alloy at 1023 K. Fig. 5 α -SiC particles dispersed in Al-1%Zn-5%Mg alloy at 1023 K. (a) SEM, (b) magnesium image and (c) silicon image. Fig. 7 α -SiC particles dispersed in Al-10%Sn-2%Ti alloy at 1023 K. (a) SEM, (b) titanium image and (c) silicon image.

Owing to the reactions related above, new active surface of SiC particle may appear and provide a good wettability resulting in shortening the incorporation time. From this point of view, it is reasonable to consider that magnesium and titanium contribute to shortening of the incorporation time through the reaction of silicide or carbide formation.

Titanium had almost no effect on the incorporation time of SiC into pure aluminum as given in the previous work⁽³⁾. On the other hand, the incorporation time of SiC into the Al-10%Sn alloy was shortened by adding titanium as shown in Fig. 6. Although it is well-known that the wettability between SiC and liquid tin at the temperature below 1390 K⁽⁸⁾ is poor, Allen, *et al.*⁽⁹⁾ reported that SiC showed a good wettability to liquid tin by adding 0.1%Ti at the temperature range from 1373 to 1473 K. Standing, *et al.*⁽¹⁰⁾ also described that owing to an increase in titanium activity by alloying tin, the contact angle between copper sessile drop and amorphous carbon substrate was decreased remarkably by adding titanium together with tin. Consequently, the incorporation time of SiC was shortened due to alloying titanium into Al-10%Sn matrix, although it was not shortened in the case of the Al-Ti binary system.

2. Effects of alloying elements with weak affinity for SiC

The effects of zinc and copper on the incorporation time were measured. It is clear from Fig. 8 that the incorporation time is prolonged with increase in copper or zinc addition. Zinc and copper do not form their silicides and have no affinity for SiC. From the results of EPMA analysis of the SiC/Al-5%Zn specimen shown in Fig. 9, inter-metallic compound was not detected in the matrix. Furthermore, they do not show surface activity which reduces the surface energy of liquid aluminum.

Thus, these elements do not contribute to the process of reaction given by eq. (2) or eq. (3). Consequently, an

Fig. 8 Effect of zinc and copper on the incorporation time of α -SiC particles in liquid aluminum at 1023 K.

increase in the incorporation time seems due to a decrease in the activity of aluminum by containing zinc and copper.

3. Effects of surface active elements

Wettability is, generally, improved by reduction of liquid surface energy γ_{lv} . So the surface-active elements such as lead, bismuth, lithium and tin, which reduce the surface energy of liquid aluminum, were also added as alloying elements in this study. It is apparent from Fig. 10 that the incorporation time is shortened by alloying lithium. However, contrary to the expectation, it was extremely prolonged by alloying lead or bismuth even at a small amount of addition (Fig. 10). Especially, at 1% addition of these elements, SiC particles did not incorporate into melt. Figures 11 and 12 show the results of EPMA analysis for SiC/Al-0.5%Pb and SiC/Al-0.5%Bi specimens. In these cases, the inter-metallic com-

Fig. 9 α -SiC particles dispersed in Al-5%Zn alloy at 1023 K. (a) SEM, (b) zinc image and (c) silicon image.

Fig. 10 Effect of lead, bismuth, lithium and tin on the incorporation time of α -SiC particles in liquid aluminum at 1023 K.

pound formed by the reaction between SiC and Pb or SiC and Bi was not detected by EPMA.

On the other hand, with respect to SiC/Al-3%Li specimen, large inter-metallic compounds were found in the matrix as shown in Fig. 13. Since lithium could not be

detected by EPMA, Auger Electron Spectroscopy (AES) was used to analyze the inter-metallic compounds qualitatively. From the result of AES analysis, it is evident that the compound was consisted of aluminum, silicon and lithium. According to the experimental results given in Fig. 2 and 10, it is clear that lead, bismuth, magnesium and lithium show two opposite effects on the incorporation time, although these four elements show surface activity. This is due to whether each alloying element has affinity for SiC or not, as related in III-1 and III-2.

To clarify the difference in the effects of lead, bismuth, magnesium and tin, those elements' excess concentration at the melt surface (surface excess concentration: Γ) was calculated with the help of the surface tension measured by Lang⁽¹¹⁾ and Gibbs' adsorption equation (eq. (4)),

$$\Gamma = -\frac{1}{RT} \cdot \frac{d\gamma_{lv}}{d \ln a_j}, \quad (4)$$

where a_j is the activity of j component, R is the gas constant, T is the temperature (K). Surface excess concentration of lithium could not be calculated because of the lack of the value of lithium activity in aluminum. Figure 14 shows surface excess concentration of bismuth,

Fig. 11 α -SiC particles dispersed in Al-0.5%Pb alloy at 1023 K. (a) SEM, (b) lead image and (c) silicon image.

Fig. 12 α -SiC particles dispersed in Al-0.5%Bi alloy at 1023 K. (a) SEM, (b) bismuth image and (c) silicon image.

Fig. 13 α -SiC particles dispersed in Al-3%Li alloy at 1023 K. (a) SEM, (b) aluminum image and (c) silicon image.

Fig. 14 Surface excess concentration of magnesium, tin, lead and bismuth in liquid aluminum, calculated using the data by G. Lang⁽⁸⁾ at 973 K.

lead, tin and magnesium calculated from eq. (4). It is apparent that the surface excess concentration of bismuth and lead are extremely high even at a small amount of addition less than 0.3%. For example, only by 0.3% addition of lead, surface excess concentration is near to a value of the atomic density of lead's (100) plane shown by the dotted line in Fig. 14. Thus, the surface of the aluminum melt is widely covered by lead atoms. And it is expected that other surface-active elements show a similar behavior. Furthermore, these alloying elements are considered to adsorb at the interface between SiC particle and melt as well as on the melt surface. So the affinity of these surface-active elements for SiC is more important factor than a degree of surface activity. That is to say, lead or bismuth atoms gather at the interface between SiC and melt and behave as an obstacle to the progress of SiC dissociation or reaction of eqs. (2) and (3), because of their weak affinities for SiC. Namely the extreme increase in the incorporation time is reasonably attributed to the adsorption of lead or bismuth at the interface between particle and melt, resulting in retardation of the wetting reaction due to their weak affinities for SiC.

Fig. 15 Effect of silicon on the incorporation time of α -SiC particles in liquid aluminum at 1023 K.

On the other hand, lithium and magnesium seem to gather at the interface and form inter-metallic compounds such as Mg_2Si and Al-Si-Li alloy as shown in Fig. 3 and Fig. 13. Thus the incorporation time was shortened by alloying magnesium or lithium. As concerns SiC/Al-Sn system, the incorporation time was prolonged until tin addition was about 3%, and after once reached at a maximum, it was shortened with increasing in tin concentration (Fig. 10). The reason for this change in the effect of tin still remains uncertain.

4. Effect of silicon on the incorporation time of SiC

According to the results given in III-1 and III-2, the incorporation time was shortened by alloying elements which form silicides and consume silicon. Then the effect of silicon, which is a constituent of SiC, on the incorporation time was measured. It was clarified that silicon made the incorporation time longer as shown in Fig. 15. That is because the existence of silicon in the melt prevents the dissociation, which is necessary for good wetting, of SiC particle.

IV. Conclusions

The effects of alloying elements on the incorporation time of α -SiC into molten aluminum were investigated.

(1) The incorporation time was shortened by alloying magnesium or by alloying titanium together with tin. And Mg_2Si was detected in the matrix by EPMA in the case of SiC/Al-Mg system.

(2) The incorporation time was prolonged by alloying zinc or copper which does not form silicides. In these systems no inter-metallic compound was detected in the matrix.

(3) The incorporation time was extremely prolonged by alloying lead or bismuth, which reduces the surface energy of aluminum but has weak affinity for SiC. At 1% addition of these elements, SiC particles did not disperse in melt. Lithium, which has affinity for SiC and forms Al-Si-Li ternary compounds, makes the incorporation time shorter.

(4) Dissociation of SiC was retarded by adding silicon, so the incorporation time was prolonged by alloying silicon.

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