Microstructural Evolution and Thixoformability of Semisolid SiCp/AZ91D Mg Composites

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Rotation-Cylinder method (RCM) as a primary manufacturing process and thixoforming as a secondary forming process are discussed. RCM allows the production of U-shaped laminar melt surface with Rankine vortex, thus significantly reducing particle agglomeration and entrapped slags. Thixoforming is of particular interest as a secondary forming process because of the low fluidity of the composites and the significant wear produced on machining tools and extrusion and forging dies. Some indications about mechanical properties of the composites are also presented.

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1. Introduction

In the last three decades, many studies have been devoted to metal matrix composites (MMCs), with the aim of obtaining materials that combine the beneficial properties of the metal matrix with those of the reinforcement phase.1-3 Discontinuously reinforced MMCs, which are essentially light metallic alloys reinforced with ceramic particles, are an important subclass of MMCs that are being developed for weight critical applications in the automobile industry.4-6 If the desired component is to be irregular in shape or subjected to complex, multiaxial mechanical or thermal stresses, or if material processing costs are to be kept to a minimum, these composites have a distinct advantage over continuously reinforced MMCs.3,7,8

In magnesium-based MMCs, the system most studied is SiC particle reinforced AZ91D magnesium (SiCp/AZ91D) composite because SiC particle is one of the most suitable reinforcements for magnesium-based MMCs.3,9-13 It is well known that SiC is thermodynamically unstable in molten aluminum alloys causing undesirable chemical reactions and reaction products, while SiC is stable in molten magnesium.3,14,15

SiC particle reinforced magnesium composites can be manufactured by various techniques including liquid processing, powder metallurgy and spray deposition. However, the most widely used process is a molten metal mixing method, which consists of stirring a melt using a specially designed impeller and incorporating particles into a melt.3,9-13 The potential advantage of preparing these composites by a molten metal mixing method results from the ready availability of a bulk composite slurry in a simple and cost-effective manner. However, in composite materials made by this method, the composition, shapes, sizes and relative amounts of two phases are either fixed or restricted within narrow ranges.1,3,14,16 This method also has some problems in terms of reactivity and wettability between a matrix and particles as well as of the uniform distribution of particles. This restriction can be largely circumvented by Rotation-Cylinder method (RCM), which has been developed to incorporate SiC particles into molten magnesium in ambient atmosphere.17 RCM is based on the thermodynamic consideration of SiC with molten magnesium and on the low surface tension and scavenging effect of molten magnesium and its alloys.

The successful commercial production of composites depends on their cost effectiveness for different applications. This requires optimum methods of manufacturing and subsequent forming processes. Thixoforming is considered as one of the suitable subsequent forming processes for particle reinforced MMCs. These composites are difficult to machine and shape in the solid state owing to the significant wear produced on machining tools and extrusion and forging dies. Forming in the solid state can also lead to degradation of the reinforcement phase. Furthermore, while magnesium based SiC particle reinforced composites have been demonstrated as inexpensive, lightweight wear resistant materials,12 they suffer from a major process restriction in fluidity. Above about 10 volume percent loading of the reinforcement, they become too viscous to handle even in simple casting processes such as direct chill casting to produce cylindrical billets.13 Probably for this reason, thixoforming is a viable net shape forming process for above 10 volume percent SiC particle reinforced magnesium composites. A more important feature of thixoforming these composites is that the thixotropic structure, non-dendritic globular solid grains surrounded by the liquid phase, can be obtained by a simple partial remelting procedure.21-24 This is because coarsening alone leads in the end to globularization of the solid phase because the total interfacial free energy should be an absolute minimum and the presence of reinforcement particles leads to finer globules of the solid phase.21-23

The purpose of the present study was to evaluate the microstructural evolution and thixoformability of SiC particle reinforced AZ91D magnesium composites prepared by Rotation-Cylinder method (RCM). The microstructural evolution during partial remelting of the composites was characterized as a function of isothermal holding temperature and time and particle mass fraction. The associated thixoformability was evaluated through thixoforming trials as a function of slurry temperature and particle mass fraction. Structure-property relationships were also presented and comparison
was made with those of the thixoformed AZ91D magnesium alloy.26)

2. Experimental Procedures

2.1 Material
Commercially available Norsk-Hydro AZ91D magnesium alloy was selected as the matrix. The reinforcement particles were high purity silicon carbides (98.5% β-SiC with an aspect ratio of less than 3:1) from Takai Carbon, Japan, with average diameters of 5, 15, and 50 μm. The chemical composition of the as-cast composite with 5 mass% particles was analyzed by a Polymac 2000 Hilger analytical emission spectrometer, as given in Table 1. The composition of the composite is mainly characterized by quite large silicon and iron contents. The composite preparation, partial remelting experiments, and subsequent thixoforming process were carried out under a dilute oxidation inhibiting sulphur hexafluoride gas.

2.2 Composite preparation
The desired fraction and size of SiC particles were incorporated into AZ91D alloy melt and dispersed simultaneously by RCM.17) About 800 g of the alloy melt were prepared in an electric resistance furnace using a steel crucible under a SF6/CO2 protective atmosphere. The melt was then rotated by a steel rotation cylinder at 923 K and the particles were added with a feed rate of 10 g/min under a rotation speed of 800 rev/min. The particles were preheated to 473 K in order to avoid local temperature change during the addition. Post rotation of 5 min was carried out after the addition of the desired fraction of particles. After that, the resultant composite melt was cast into a steel mold. The as-cast specimen for optical examination was finally polished with 0.05 μm α-Al2O3. Etching was affected by immersion for 15 s in 5% citric acid in order to reveal the particle distribution.

2.3 Partial remelting experiments
Composites billets (ϕ15 mm × 150 mm) were prepared for microstructural evolution. The billets were cut into approximately 10 mm thick specimens and partial remelting experiments were carried out in a gold image furnace at the predefined temperatures for times varying from 0 to 3600 s. The predefined isothermal holding temperatures were 837, 848, 856.5, 862.5, 867.5, and 871 K, which correspond to the liquid fractions of 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 based on the Scheil equation.25,26) The specimen was held in a steel tube in order to avoid deformation of the specimen under its own weight during partial melting. The reheating profile, 0.19 K/s to the predefined temperatures after the preheating at 437 K for 600 s, was applied and the temperature change was monitored by a thermocouple placed in the middle of the specimen. After the predetermined isothermal holding, the specimen was withdrawn with the tube and quenched in water. After that, the specimen was prepared for metallography by polishing with an 0.05 μm α-Al2O3 and etching using 5% nital, and then examined by an optical microscopy. The specimen was carefully prepared for the good contrast between the solid phase and the remaining constituents of the quenched liquid phase and the particles. An image analysis system (Image-Pro Plus) was used to determine the size of solid grains.

2.4 Thixoforming
Composites billets (ϕ32 mm × 180 mm) were manufactured by RCM and cylindrical specimens (ϕ32 mm × 60 mm) were prepared by machining for thixoforming. Specimens were thixoformed into the step die cavity designed for evaluating thixoformability and the testing die cavity for thixoforming mechanical testing specimens. A more detailed description about the machine and die cavities is given in Refs. 26 and 27. Two thermocouples, located in 3 mm holes in the both ends of the specimen, were used to assess and control the temperature variation in the specimen. Using the reheating procedure obtained in the partial remelting experiment, the specimen was reheated inside the sleeve and then thixoforming was carried out at a die temperature of 437 K. The optimum thixoforming condition established from thixoforming AZ91D magnesium alloy was utilized (plunger speed 0.5 m/s, casting pressures 13.8 MPa, dwell time 5 s).26,27)

2.5 Mechanical properties
Thixoformed specimens were tested for mechanical properties. Hardness tests were conducted utilizing a Vickers hardness tester (100 N, 10 s). The tensile testing was carried out with an initial strain rate of 5.7 × 10⁻⁴ s⁻¹ using an Instron machine. The tensile property data of 0.2% yield strength YS, ultimate tensile strength UTS, and elongation to failure EF, are based on the average of 12 tests. Oghoshi wear test was undertaken under the wet sliding condition against a rotating austenite cast iron disc (hardness 200 Hv, 57.0 HRA) with a constant load (50 N) and sliding velocity (10 m/s) for 1000 s. Prior to testing, both the disc and the specimen were ground on 1000 grit SiC paper, and then cleansed in acetone. The wear resistance measured was expressed by specific wear loss W.

3. Results and Discussion

3.1 Microstructural evolution
Figure 1 shows the grain structures of the composites in the as-cast condition with that of the as-cast alloy. These clearly show homogeneous distribution of SiC particles with regions free of the particles and the grain refinement effect of the particles. The regions free of the particles originate from the fact the particles are usually pushed by the solidification front, so that they are preferentially located in the eutectic mixture. Table 2 summarizes the grain size and relative hardness of the as-cast alloy and 5 mass% SiCp/AZ91D composites with the particle sizes of 5, 15, and 50 μm in the case of being cast into a cylindrical mold of 437 K. This table shows that the grain size is reduced by a factor of approximately 5 in all the composites. It is reported that the grain refinement in cast SiCp/AZ91D composites is due to the combined
effects of heterogeneous nucleation of primary magnesium on SiC particles and restricted growth of magnesium grains during solidification, although there is the discrepancy in the mechanisms for heterogeneous nucleation.\textsuperscript{28-30} However, in the present composites manufactured by RCM followed by permanent mold casting, SiC particles are found only intergranularly, which provides no evidence for heterogeneous nucleation. Notwithstanding these remarks, it should be noted that the significant grain refinement achieved in the present composites is important for microstructural evolution in the semisolid state. This is because the initial grain size determines the size of solid grains generated within short times in the semisolid state.\textsuperscript{5,21,22,26}

In the reheated semisolid state, partial remelting starts at the intergranular region, followed by an apparent decrease in the proportion of the eutectic phase. During anisothermal and isothermal holding in the semisolid state, coarsening first proceeds predominantly through coalescence of dendrite arms. This dendrite arm coalescence causes the intergranular liquid with the liquidation of small grain boundaries and the segregated regions. After this, the globularization of the solid phase occurs to reduce surface energy by diffusion of solid matters from areas with high curvature to areas with low curvature. Simultaneously, coarsening takes place through the dissolution of smaller globules. Coalescence of solid grains should be also considered for coarsening in the reheated semisolid state with high volume fraction of solid. The above phenomena are demonstrated in Fig. 2, which shows the as-quenched microstructures as a function of isothermal holding time for 5 and 10 mass% SiC particles, with size 5 μm, reinforced composites. In Fig. 3 is shown the as-quenched microstructures of the composites as a function of isothermal holding temperature after isothermal holding for 1800 s at the given temperatures. The temperatures of 837, 856.5, and 867.5 K correspond to the liquid fractions of 0.4, 0.6, and 0.8 according to the Scheil equation. It is clear from the Figs. 2 and 3 that the general feature for the microstructural evolution of the composites during anisothermal and isothermal holding in semisolid state are similar to those of AZ91D magnesium alloy.\textsuperscript{26,27} However, compared to the alloy, the presence of particles leads to fine globules of the solid phases, and the finer globules are achieved with increasing particle mass fraction. It is well known that the initial size of the globules in the semisolid state is mostly affected by the initial grain size.\textsuperscript{26,27} Besides the grain refinement achieved during solidification by the presence of the particles, the achievement of the finer globules also stems from the altered Ostwald ripening and reduced coalescence during partial remelting. Ostwald ripening is altered because of the reduction of the effective diffusion coefficient in the liquid. Coalescence is also reduced since the globules are more isolated one with respect to the other by the presence of SiC particles in intergranular regions. Therefore, any significant coarsening does not occur even after the isothermal holding for 60 min. It is also clearly seen that the presence of particles also accelerates globularization of the solid phase. This might be because diffusion of solid matters from areas with high curvature to areas with low curvature is accelerated due to the isolation of the diffusion field by the presence of par-

**Table 2.** Dependence of the alloy and composites grain size and relative hardness on SiC particle size at the mold temperature of 437 K.

<table>
<thead>
<tr>
<th>AZ91D</th>
<th>5 mass% SiCp/AZ91D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (μm)</td>
<td>5 μm</td>
</tr>
<tr>
<td>Grain size (μm)</td>
<td>250</td>
</tr>
<tr>
<td>Hardness (HRE)</td>
<td>51.5</td>
</tr>
</tbody>
</table>

Fig. 1 As-cast microstructures showing grain structure and SiC particle distribution of the composites with particle size of (a) 0 μm, (b) 5 μm, (c) 15 μm, and (d) 50 μm.
Fig. 2 As-quenched microstructures of 5 mass% (a, b, c, d) and 10 mass% (e, f, g, h) SiCp/AZ91D magnesium composites after isothermal holding at 856.5 K for (a) and (e) 60 s, (b) and (f) 300 s, (c) and (g) 1800 s, and (d) and (h) 3600 s.

Fig. 3 As-quenched microstructures of the composites after isothermal holding for 1800 s at (a) 837 K, 5 mass%, (b) 856.5 K, 5 mass%, (c) 867.5 K, 5 mass%, (d) 837 K, 10 mass%, (e) 856.5 K, 10 mass%, and (f) 867.5 K, 10 mass%.

ticles in the liquid. The aforementioned results that the presence of particles accelerates the globularization and leads to finer globules of the solid phase are very promising for practical applications. For short holding times would reduce the cost and increase the productivity, and small globules will favor the flow of the slurry, allowing more intricate parts to be thixoformed.

Figure 4 shows the average diameter of solid grains with isothermal holding temperature, which shows the average diameter is independent of temperature and indicates that is a function of isothermal holding time based on the initial size of the globules determined by the initial grain size. In each temperature after isothermal holding for 1800 s, the average globular diameters are about 100, 80, and 60 μm for the alloy and the composites, respectively. However, the case of the alloy shows that the size of the globules does not depend only on isothermal holding time. There is a critical temperature, above which remelting rather than coarsening is dominant.

Another parameter, which is necessary for defining the microstructural evolution of the composites, is the temperature that determines the fraction liquid needed to contain the particles. The thixotropic structure is not obtained in the semisolid state if the fraction liquid is not large enough to contain all the particles and distribute them homogeneously, as shown in Figs. 3(a) and (d). The result thus demonstrates that a critical fraction liquid seems to be necessary for achieving the thixotropic structure for the composites. In this study, the thixotropic structures could not be achieved below 848 and 856.5 K for 5 and 10 mass% SiC particles, with size 5 μm, reinforced composites, respectively.

3.2 Thixoformability

Figure 5 shows the dependency of thixoformability on slurry temperature and SiC particle fraction of 5 μm. With increasing particle fraction, the thixoformability of the composites decreases. At a given temperature, this is due to the lower fraction liquid and latent heat and the higher composite viscosity. However, the observed decrease in the thixoformability is considerably small compared with the expected increase in viscosity and the decrease in fraction liquid and latent heat. It is well known that a large portion of the flow resistance of semisolid slurries derives from the dissipative
interaction of solid grains. SiC particles of size 5 \( \mu \text{m} \) are normally smaller than the solid globules so that they can remain among the globules in the liquid regions. Thus 5 \( \mu \text{m} \) SiC particles appear to prevent the contact of the globules and thereby reduce coalescence, as mentioned before. This may influence thixoformability of the composites with higher SiC particle fraction.

It is observed from Fig. 5 that all specimens fill the die cavity with essentially laminar flow, unique flow behavior of semisolid slurries even in incomplete filling at the lower temperature. It has been found that the sound thixoformings can be obtained if the specimen temperature is chosen above a fraction liquid of 0.5, based on the effective fraction liquid of the composites. The effective fraction liquid of the composites, \( f_E \), is proposed in the following formula

\[
f_E = f_L(1 - f_P) - f_P
\]

where \( f_L \) is the fraction liquid of AZ91D based on the Scheil equation and \( f_P \) is the volume fraction of SiC particles.

However, thixoformability depends inversely on particle size. 50 \( \mu \text{m} \) SiC particles, which are not normally smaller than the globules, cannot act effectively to hinder contact of the solid globules during partial remelting, as shown in Fig. 6.

### 3.3 Mechanical properties

In Table 3 are given the hardness, tensile properties, and specific wear loss data of the thixoformed composites with the data of the thixoformed alloy. The data obtained indicate that the hardness of the composites strongly depends on the particle mass fraction with a weaker dependence on the particle size. In contrast, the tensile properties data show that the strength of the composites increases mainly as the particle size decreases, although, compared with the alloy, the increase of the strength is small, and in some cases, is not even obtained. The strength of the composites can be understood from the generally acknowledged strengthening mechanisms in discontinuously reinforced MMCs. At a typical particle fraction, Orowan strengthening is not a major factor with 5 \( \mu \text{m} \) and larger particles, but the particles of this size can result in quench hardening and work hardening. The dependency of the strength of the composites on particle mass fraction and size can also be explained from quench hardening and work hardening. The degree of quench hardening, which produces an increase in dislocation density due to CTE mismatch strain between the particles and the matrix, is obtained as the product of the total number of the loops per particle and the number of particles per unit volume. Work hardening, which is caused by elastic misfit back stress between the elastic particles and the plastic matrix and by the slip constraining effect of the particles, depends on the particle distribution and the number
of particles per unit volume. However, there remain questions pertaining to the details of the strengthening mechanism based on a change in the microstructure by thixoforming. The microstructure of the thixoformed composites is characterized by the globular α phase surrounded by the intergranular eutectic β phase, Mg17Al12, and SiC particles located in the eutectic region. During deformation, the slip behavior of each α grain is highly constrained by low plastic β phase as well as the elastic SiC particles, which resist slip to increase the work hardening rate and thus the YS. As mentioned previously in 3.2, the globular α grain size and the distribution of the particles are determined mainly by the particle size. Based on the above discussions, the increase of the YS of the composites with 5 μm SiC particles over the alloy may be explained well.

Although the dependency of the UTS of the composites on the particle mass fraction and size shows the same behavior as the YS, however, the UTS of the composites are lower than that of the alloy, except the composites with 5 μm particles. The work of Luo shows that the strong internal stress developed between SiC particles and the matrix causes the localized damages leading to final fracture of the composites. Hence, AZ91D alloy has the higher UTS than the composites because of the absence of these localized damages. Recent work has also demonstrated that the microscopic non-uniformity of the particle distribution is considered as the reason for internal stresses and also stress triaxiality, which are

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle size (μm)</th>
<th>Hv</th>
<th>UTS (MPa)</th>
<th>YS (MPa)</th>
<th>EF (%)</th>
<th>Specific wear (W, 10^{-5} mm²/Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ91D</td>
<td>—</td>
<td>75</td>
<td>163</td>
<td>90</td>
<td>4.64</td>
<td>275.4</td>
</tr>
<tr>
<td>10 mass%</td>
<td>5</td>
<td>80.2</td>
<td>168.7</td>
<td>110</td>
<td>4.79</td>
<td>39</td>
</tr>
<tr>
<td>SiCp/AZ91D</td>
<td>15</td>
<td>76.5</td>
<td>160.1</td>
<td>85.34</td>
<td>4.21</td>
<td>20.5</td>
</tr>
<tr>
<td>20 mass%</td>
<td>5</td>
<td>94</td>
<td>170.8</td>
<td>115.6</td>
<td>5.14</td>
<td>17</td>
</tr>
<tr>
<td>SiCp/AZ91D</td>
<td>15</td>
<td>90.1</td>
<td>160</td>
<td>91.03</td>
<td>3.93</td>
<td>13</td>
</tr>
<tr>
<td>30 mass%</td>
<td>5</td>
<td>102</td>
<td>186.2</td>
<td>112.3</td>
<td>4.07</td>
<td>13.5</td>
</tr>
<tr>
<td>SiCp/AZ91D</td>
<td>15</td>
<td>101.5</td>
<td>163.8</td>
<td>108.3</td>
<td>3.71</td>
<td>5.5</td>
</tr>
<tr>
<td>50</td>
<td>15</td>
<td>101.5</td>
<td>158.2</td>
<td>90</td>
<td>3.39</td>
<td>2</td>
</tr>
</tbody>
</table>
in turn responsible not only for work hardening, but also for the early appearance of particle cracking, particle interface debonding, and void formation in the matrix. In addition, particle cracking is more prevalent in coarse particles, because they are loaded by conventional fiber loading and end loading mechanisms and have a higher probability of containing fracture-initiating defects. The above arguments are well consistent with the results of the present composites. However, although it is not large enough, a slight increase in the UTS of the composite with 5 μm SiC particles is achieved over the alloy. Although a quantitative understanding is lacking, the uniform distribution of fine (< 10 μm) SiC particles and the reduced size of the solid globules, achieved by RCM in conjunction with thixoforming, may maximize the strength and the ductility of the composites. It should be also noted that the 5 μm particles located in the eutectic region alters the brittle nature of the alloy that has the brittle, interdendritic, eutectic network in the thixoformed condition.

It is generally accepted that the wear resistance of ceramic particle reinforced composites is improved, and the wear resistance is mainly dependent on the size of ceramic particles with a somewhat weaker load dependence, especially under abrasive and lubricated sliding conditions. The results of the present work are consistent with the general wear behaviors of ceramic particle reinforced composites. The wear resistance of the composites is greatly improved and sensitive to the size of SiC particles even with the comparatively high-applied load (50 N). The relationship between the particle size and the wear damage can be explained by the particle size relative to surface roughness (e.g., 1 to 2 μm). Coarser particles are more effective either in abrading the iron, the counterpart, or holding the transfer layers on the contact surfaces than fine particles. Interestingly, the wear resistance of the composite with 50 μm SiC particles (HRA 26.6) is comparable to D2 tool steel that has higher hardness value of HRA 60.5. If the particle size and the fractions are carefully designed, SiC particle reinforced magnesium composites may be tailor-made to give rise to inexpensive, lightweight wear resistant materials.

4. Conclusion

(1) The presence of SiC particles leads to fine globules of the solid phase, and the finer solid globules are achieved with increasing SiC particle fraction. Coalescence is also reduced since the globules are more isolated with respect to each other by the presence of the particle in intergranular regions.

(2) Thixotropic structure cannot be achieved below 848 and 856.5 K for 5 and 10 mass% SiC particle reinforced composites respectively. This is because the fraction liquid is not large enough to contain all the SiC particles and distribute them homogeneously.

(3) The results of the microstructural evolution seem to suggest that the thixoforming of the composites should be carried out at relatively high temperature after short isothermal holding times.

(4) All specimens fill the step die cavity with essentially laminar flow, unique flow behavior of semisolid slurries. The sound thixoformings can be obtained if the specimen temperature is chosen above the fraction liquid of 0.5, based on the effective fraction liquid of the composites.

(5) The observed decrease in thixoformability for the composites is considerably small compared with the expected increase in viscosity and decrease in fraction liquid. It is because 5 μm SiC particles can well prevent the dissipative interaction of solid grains.

(6) The composites show some attractive mechanical properties. Improvement of the YS and a slight increase of the UTS in the composite with 5 μm SiC particles have been achieved. The wet-sliding wear resistance of the composites is strongly influenced by the SiC particle size, and the wear resistance of the composite with 50 μm SiC particles is comparable to D2 tool steel.

REFERENCES