Formation of In Situ Composite Layer on Magnesium Alloy Surface by Casting Process

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In order to develop a process to obtain a functional layer on the surface of a magnesium alloy, the composite layer including in situ Mg$_2$Si was formed on the surface by a gravity die-casting. The optimum fabrication condition to form the composite layer and the formation mechanism of the layer were clarified by observing the microstructure, and then the wear properties of the composite layer were also investigated. By casting the magnesium alloy melt into the permanent mold on which the slurry mainly consisting of Si particles was coated, the magnesium alloy composite layer in which the in situ Mg$_2$Si particles were dispersed was formed. The melt temperature and mold temperature required to form the composite layer, which perfectly covers the casting, were above 1073 K and above 673 K, respectively. The composite layer was a magnesium alloy in which the fine Mg$_2$Si particles of approximately 40 vol% were dispersed. The thickness and hardness of the layer was about 600 µm and 180 HV, respectively. Under the dry sliding wear, the weight loss of the composite layer was lower than that of the magnesium alloy. These results lead to the conclusion that the wear resistant magnesium alloy composite layer in which the in situ Mg$_2$Si particles were dispersed can be formed in the present process. [doi:10.2320/matertrans.MER2008198]

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1. Introduction

From the viewpoint of the global environment and energy savings, reduction in the weight and size of the products has been recently promoted in the industrial automobile, aerospace and electrical fields. This trend leads to the requirements of lightweight and high strength materials. Based on these requirements, magnesium alloys have recently been suggested as an alternative to steel and aluminum alloys in many products because magnesium is the lightest in the practical alloys. However, the magnesium alloy easily deforms and wears from impact and frictional forces due to its low hardness. In addition, a surface treatment for preventing oxidation is generally required because the magnesium alloy is easily oxidized. These problems would be resolved by forming a composite layer having a high hardness and corrosion resistance on the alloy surface. To improve the wear and corrosion resistance of the magnesium alloy, coatings of ceramics by laser-cladding\textsuperscript{1)} and spraying\textsuperscript{2,3)} have been mainly performed. However, these techniques involve many processes such as a pretreatment, leading to a high cost. Moreover, a recycling problem remains when the coat includes the elements different from the ones usually added to commercial magnesium alloys. Mg$_2$Si, an intermetallic compound, has a good oxidation resistance, high melting point and high hardness.\textsuperscript{4)} Therefore, the formation of Mg$_2$Si on the magnesium alloy surface would improve its corrosion resistance and wear resistance. The magnesium alloy coated with Mg$_2$Si can be reused as the AS alloy (Mg-Al-Si alloy), which is classified by ASTM specifications; therefore, it would be easy to recycle. In addition, Mg$_2$Si can be in situ formed by a reaction between magnesium and silicon. Kondoh \textit{et al.}\textsuperscript{5,6)} fabricated a magnesium alloy coated with Mg$_2$Si by sputtering. If the in situ composite layer including Mg$_2$Si can be formed by a casting process, it is industrially beneficial because it leads to a considerable reduction in the fabrication processes and cost. However, there are no reports on the microstructure and properties of the composite layer including Mg$_2$Si fabricated by the casting process.

In the present study, the composite layer including Mg$_2$Si fabricated by the casting process was formed to develop an in situ formation process of the functional layer on the magnesium alloy surface. The microstructure, formation mechanism and wear properties of the composite layer were then investigated.

2. Experimental Procedure

The AZ91D alloy with its chemical composition shown in Table 1 was used as the cast alloy. Pure silicon (Si) particles (99.9 mass%Si) were used as the starting material to form Mg$_2$Si by the reaction with magnesium in the alloy melt. Figure 1 is a SEM micrograph of the Si particles. The average size of the Si particles measured by an image analyzer using 10 fields in the SEM micrographs was 4 µm.

Figure 2 shows a schematic illustration of the mold. The mold has 5 cavities in a radial manner and 5 specimens can be obtained per one casting process. To obtain a plate specimen

Table 1 Chemical composition of AZ91D alloy (mass%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>9.20</td>
</tr>
<tr>
<td>Zn</td>
<td>0.71</td>
</tr>
<tr>
<td>Mn</td>
<td>0.30</td>
</tr>
<tr>
<td>Si</td>
<td>0.03</td>
</tr>
<tr>
<td>Cu</td>
<td>0.001</td>
</tr>
<tr>
<td>Fe</td>
<td>0.003</td>
</tr>
<tr>
<td>Mg</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Fig. 1 SEM micrograph of Si particles.
with a composite layer containing Mg₂Si, the slurry including Si particles was coated on the upper plane of the cavities, followed by drying. The AZ91D alloy melt is poured from the sprue, and then the composite layer containing the Mg₂Si is obtained by the reaction between the melt and Si in the coat. A vent hole was situated at the end of each cavity to prevent blow holes from forming in the specimen. The slurry was fabricated by mixing distilled water, Si particles and silica (SiO₂) sol to improve the adhesion of the coat, and then brushed on the cavity in the mold. In order to determine the coating conditions to obtain the optimum coat, a preliminary experiment was performed. As a result, the optimum conditions were as follows: Si content in the slurry: 40 mass%; SiO₂ sol content: 7 mass%; mold temperature: 323 K; and coat thickness: 0.5 mm. Figure 3 shows a SEM micrograph of the cross-section of the coat.

One hundred grams of the AZ91D alloy melt was poured into the coated mold, and then pressure of 4 MPa was quickly applied by a plunger and maintained until the solidification was complete. The melt temperatures ranged from 1003 to 1123 K, and the mold temperature ranged from 473 to 723 K. The macrostructure of the surface and cross-section of the specimens and microstructure of the composite layer were observed. X-ray diffractometry (XRD) and electron probe microanalysis (EPMA) were performed to identify the composite layer. Hardness of the composite layer was measured by a Vickers hardness tester under a load of 1.47 N. Dry sliding wear tests were performed using a pin-on-disc type wear apparatus, as schematically illustrated in Fig. 4. The pin test piece having a 5 mm diameter and 5 mm length was machined from the specimen. JIS-SK4 disc test piece having a 30 mm diameter and 5 mm thickness was used as the counterpart. The disc test pieces were quenched and tempered to obtain the hardness of 700 HV. The wear tests were carried out at a sliding distance of 500 m, at a load of 19.6 N, and at sliding velocities of 0.1, 0.3 and 0.5 m s⁻¹. The weight losses were calculated from the differences in weight of the test piece measured before and after the test every 100 m.

3. Results and Discussion

3.1 Macrostructure and microstructure

Figure 5 shows the macrostructure of the specimen surface (melt temperature: \( T_m = 1073 \) K). When the mold temperature (\( T_p \)) was 643 K, a dark substance, probably formed by the reaction between the coat and the alloy melt, was partially observed on the surface, as shown in Fig. 5(a). However, the product comprised only half of the surface under this condition. When the \( T_m \) was 1073 K and \( T_p \) was 673 K, the product formed over the entire surface, as shown in Fig. 5(b). When the \( T_m \) was below 1073 K and \( T_p \) was below 643 K, no products were formed on the surface. On the other hand, the product covered the entire surface when \( T_m \) was above 1073 K and \( T_p \) was above 673 K. Therefore, the specimens fabricated by setting \( T_m \) at 1073 K and \( T_p \) at 673 K were selected to examine the microstructure and the wear properties.

Figure 6(a) shows the macrostructure of the vertical cross-section of a specimen (melt temperature: \( T_m = 1073 \) K). When the mold temperature (\( T_p \)) was 643 K, a dark substance, probably formed by the reaction between the coat and the alloy melt, was partially observed on the surface, as shown in Fig. 5(a). However, the product comprised only half of the surface under this condition. When the \( T_m \) was 1073 K and \( T_p \) was 673 K, the product formed over the entire surface, as shown in Fig. 5(b). When the \( T_m \) was below 1073 K and \( T_p \) was below 643 K, no products were formed on the surface. On the other hand, the product covered the entire surface when \( T_m \) was above 1073 K and \( T_p \) was above 673 K. Therefore, the specimens fabricated by setting \( T_m \) at 1073 K and \( T_p \) at 673 K were selected to examine the microstructure and the wear properties.

Figure 6(b) is an optical micrograph of the vertical cross-section near the layer of the specimen, showing that the thickness of the layer is about 600 \( \mu m \). The enlarged views of the microstructure enclosed by squares in Fig. 6(b) are shown in Figs. 6(c) and 6(d), indicating that the layer consists of a magnesium alloy matrix and fine dispersed particles. Figure 6(d) shows the typical microstructure of the layer. The area fraction of the particles measured by an image analysis using 10 fields in the micrographs was 40%. Figure 6(c) is the microstructure near the boundary between the layer and
alloy part, showing that the particles gradually decreased towards the alloy part near the boundary.

Figure 7 is SEM and X-ray images of the layer, showing that the particles dispersed in the layer consists of Mg and Si. Figure 8 is the XRD pattern of the layer, showing that Mg, Mg$_{17}$Al$_{12}$, and Mg$_2$Si were detected. Based on the results shown in Figs. 7 and 8, it can be concluded that the particles are Mg$_2$Si, while no residual Si exists in the layer.

Subsequently, the shape and size of the Mg$_2$Si were investigated in detail. Figure 9 is a SEM micrograph of the Mg$_2$Si particles extracted from the layer by 30% nitric acid, showing that the average size of the Mg$_2$Si particles in the layer is less than 5 µm and many of them appear to agglomerate with each other.

These results lead to the conclusion that the layer obtained in the present process is the magnesium alloy composite layer in which fine Mg$_2$Si particles are dispersed.

### 3.2 Formation mechanism of composite layer

Based on these results, the formation mechanism of the Mg$_2$Si in the present study is discussed. Mg$_2$Si is formed by the reaction between Mg in the alloy and Si, as designated by eq. (1):$$2\text{Mg} + \text{Si} \rightarrow \text{Mg}_2\text{Si} \quad (1)$$

A binary equilibrium phase diagram of the Mg-Si system shows that the minimum temperature to form Mg$_2$Si is 912 K. As shown in Fig. 5, in the present study, the composite layer covered the entire surface of the specimen when $T_m$ was above 1073 K and $T_p$ was above 673 K. Although a previous report showed that this reaction occurs at approximately 800 K, at which both the Mg alloy and Si are in the solid state, higher temperatures of the melt and mold would be
required in the present study because the solidification rate of the melt by the gravity die-casting is high. Since the coat thickness is approximately equal to the composite layer thickness, the coat was infiltrated with the magnesium alloy melt followed by the reaction between the melt and Si with subsequent formation of the composite layer. The fine dispersion of the Mg$_2$Si particles is probably due to the suppression of the coarsening of the particles based on the rapid cooling in the permanent mold.

In addition, it is reported that the Mg$_2$Si is formed by the reaction between Mg and SiO$_2$, as designated by eq. (2):$^5$

\[ 4\text{Mg} + \text{SiO}_2 \rightarrow \text{Mg}_2\text{Si} + 2\text{MgO} \quad (2) \]

Since the slurry used in the present study includes a SiO$_2$ sol, MgO might exist in the composite layer. However, as shown in Figs. 7 and 8, MgO was not detected in the composite layer. This indicates that the amount of MgO in the layer is minor even though it exists.

### 3.3 Hardness and wear properties of composite layer

Figure 10 shows the Vickers hardness plot of a specimen versus distance from the surface. The error bars in the figure indicate the scatter in the measured values. The hardness of the composite layer was about 180 HV, while that of the AZ91D alloy part was about 80 HV. This indicates that the composite layer was about 180 HV, while that of the AZ91D alloy was about 180 HV, indicating that the amount of MgO in the layer is minor even though it exists. The hardness at the boundary was about 180 HV, while the wear rate was 16.7 $\mu$g/m for the AZ91D alloy. This result also indicates that the Mg$_2$Si particles offer an effective improvement in the wear resistance of the magnesium alloy.

Figure 11 shows the weight loss of the AZ91D alloy, composite layer and disc counterfaces (SK4) plotted versus sliding distance ($v = 0.3$ m s$^{-1}$).

The composite layer containing in situ Mg$_2$Si particles was formed on the AZ91D alloy surface by a casting process. The microstructure, formation mechanism and wear properties of the composite layer were investigated. The following results were obtained.

1. By casting the AZ91D alloy melt into the permanent mold on which a slurry mainly consisting of Si particles was coated, the composite layer in which the in situ Mg$_2$Si particles were dispersed was formed.
2. The composite layer was a magnesium alloy in which the fine in situ Mg$_2$Si particles were dispersed. The hardness of the layer was about 180 HV, which was higher than that of the magnesium alloy.
3. Microscopically, the Mg$_2$Si particles gradually decreased towards the alloy part near the boundary. No residual Si was observed in the composite layer.
Under the dry sliding wear at a load of 19.6 N and at sliding velocities ranging from 0.1 to 0.5 m s\(^{-1}\), the weight loss of the composite layer was lower than that of the AZ91D alloy. This result indicates that the formation of the composite layer improved the wear resistance of the alloy.

REFERENCES