Effects of Sr+Ce on Microstructure and Abrasive Resistance of In-Situ Mg$_2$Si/Al-Si-Cu Composites

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In the present study, the modification effect of Sr+Ce in Mg$_2$Si/Al-Si-Cu composites was investigated for controlling both the microstructure and mechanical properties. Furthermore, the hardness and the abrasive resistance after modification were also studied. The results show that when the composites were modified by 0.40 mass% Ce, the morphology of the primary Mg$_2$Si phase changes to a polygonal morphology with a size of 15 μm. However, in those with a 0.40 mass% Ce and 0.05 mass% Sr addition, the morphology changes to an irregular and equiaxed shape, and the size increases to 50 μm. Furthermore, in the 0.40 mass% Ce and 0.10 mass% Sr addition, the primary Mg$_2$Si morphology transforms to a rectangular trapezoid, or "T" shape, with sizes measuring 70 μm. Additionally, in the 1.00 mass% Ce and 0.05 mass% Sr, and the 1.00 mass% Ce and 0.10 mass% Sr addition, the primary Mg$_2$Si morphologies become either polygonal or irregular shaped, respectively. The eutectic phases change shows that, with the addition of Ce or Sr, the eutectic phases exist in the form of the binary eutectic of Al+Mg$_2$Si or the ternary eutectic of Al+Mg$_2$Si+Si. The hardness test illustrates that the hardness of the 1.00 mass% Ce and 0.05 mass% Sr and the 0.40 mass% Ce and 0.05 mass% Sr, modified composites are higher than the unmodified composites. The abrasive resistance data shows that modified composites with the 1.00 mass% Ce and 0.05 mass% Sr are higher than that of the modified and unmodified composites with a 0.40 mass% Ce and 0.05 mass% Sr. The abrasive resistance agrees with the hardness test results, and this demonstrates that the Sr+Ce addition can change the microstructure and enhance the mechanical properties of the material.

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Keywords: Metal matrix composite, casting, modification, abrasive resistance

1. Introduction

Particulate-reinforced aluminium metal matrix composites (MMCs) have received a considerable amount of attention in the recent years owing to their low production costs and improved properties, such as good castability, low density, excellent physical properties and wear resistance. These excellent characteristics make aluminium MMCs an ideal candidate to replace steel and iron in meeting the demand of fuel economization and weight reduction in automotive fields. Two approaches, the in situ and ex situ methods, are commonly used for the production of aluminium MMCs. The various conventional ex situ processes of fabricating aluminum MMCs possess some inherent defects, such as residual microporosity, uneven distribution of reinforcement, non-wetting of the reinforcement, control of matrix-reinforcement interface, scaling up of the process for industrial utilization and processing cost$^{1,2}$. The in situ prepared MMCs have been widely explored in an effort to engineer an interfacial structure by achieving “compatible” interfaces between matrix and reinforcement$^{3-5}$.

In-situ Mg$_2$Si/Al-Si-Cu composite has high potential as a wear resistant material because an intermetallic compound of Mg$_2$Si exhibits the high melting temperature, low density, high hardness, low thermal expansion coefficient$^{6}$ and the potential for cost reduction as well. However, the primary Mg$_2$Si phases in normal in situ Mg$_2$Si/Al-Si-Cu composites are usually very coarse; and thus, lead to poor properties to these composites. Therefore, composites with a predominantly coarse primary Mg$_2$Si crystal must be modified to ensure adequate mechanical strength and ductility$^{5}$. Recently, it was reported that modification of microstructure has been developed through common gravity casting by additions of mischmetal$^{7}$, strontium$^{8,9}$ or phosphorus$^{5,10}$.

Commercial available Al-13 mass% Si alloy (ingot), pure Cu (ingot, >99.7% purity) and magnesium (ingot, >98.0% purity) were used to prepare the experimental alloys. 75 g of magnesium and 20 g of Cu preheated at 573 K were added into the 400 g of Al-Si alloy at 953 K~973 K. After 10 min, the modifiers of Al-10 mass% Sr and Al-10 mass% Ce master alloy bars covering with aluminium foil and preheated at 573 K was added into the melts at 1073 K. The addition amount of modifiers are listed in Table 1 (samples 0–5). After holding for 15 min, the melts were stirred lightly with an iron spoon, and then the in-situ composite melts were poured into a steel die with a temperature of 573 K. The size of steel die had a length of 200 mm, height of 150 mm and width of 12 mm. In order to maintain temperature homogeneity of the steel die at each casting, the bottom of the die was welded with a nickel-chromium-nickel silicon thermocouple. When the steel die temperature decreased to 573 K, the melts were poured. At the same time, a thermocouple was connected to

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both a computer and temperature collection software that was programmed in-house, where the solidification curves were drawn by using the software. The chemical compositions of the studied as-cast alloys are listed in Table 2.

The HB hardness (Brinell Hardness) values of the material were tested using a HB Hardness Tester (3000B, China) under a load of 7350 N with an indenter of Φ30. The hardness value resulted from the average value of three points.

Sliding wear experiments were conducted using a conventional pin-on-disc testing machine in air at room temperature. A commercial 600-grip SiC abrasion paper is used as the disc for the wear test. The pin specimen was 6 mm in diameter and 12 mm in length. The load levels varied from 1 to 12 N. The rotating velocity of disc was selected as 20 rpm. The trail of sliding is identified as Archimedean screw pattern with the test distance of 9420 mm. Before testing, the Mg2Si/Al composites pins were pre-abraded for two times to keeping the surface between the pins and the abrasion paper presenting surface contact. Weight loss were test using 1/100000 electronic balance (Sartorius Genius ME215P). Before weighing, the every pin needed washing with alcohol in a ultrasonic device to eliminating impurity and ablation. The every pin was repeat test for three times to obtaining the exact data.

The samples for metallographic observation were cut from the center of each casting to avoid effects of the cooling rate on the microstructure. Metallographic specimens were polished through standard routines and examined using optical microscopy to see the features of the Mg2Si phase in the composites with or without modification. The 0.5% hydrofluoric acid (HF) water solution was used as etchant and deep etchant of polishing samples. The microstructure characteristics of the etched specimens were examined with scanning electron microscopy (SEM) (JSM-5310, Japan).

3. Results and Discussions

3.1 The modification of primary Mg2Si

According to previous study\(^1\), with the Ce content increased to 0.40% in Mg2Si/Al-Si-Cu composites, the sizes of primary Mg2Si decreased to \(~15\) μm, however, with the Ce content further increased, the sizes of primary Mg2Si increased conversely. And with the Ce content increased to 1.00%, the sizes of primary Mg2Si did not change obviously\(^1\). So in the present study, the amount of Ce addition was selected as 0.40% and 1.00%. Figure 1a-b shows the change of the microstructure of samples 0 and 1 (the composition of the samples 1–5 are indicated in Table 1), while Fig. 1c-d shows the high magnification image of the selected area (rectangle) in Fig. 1a and b, respectively. (It is showed the morphology of the primary Mg2Si phase changes to a polygonal morphology with a size of 15 μm after Ce addition\(^1\).)

Table 1 The addition amount of modifiers (mass%). (The tested samples of samples 0–5 represented the following compositions: 0%, 0.40% Ce, 0.40% Ce+0.05% Sr, 0.40% Ce+0.10% Sr, 1.00% Ce+0.05% Sr, and finally 1.00% Ce+0.10 Sr).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Modifier, mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.4%Ce</td>
</tr>
<tr>
<td>1</td>
<td>0.4%Ce+0.05%Sr</td>
</tr>
<tr>
<td>2</td>
<td>0.4%Ce+0.1%Sr</td>
</tr>
<tr>
<td>3</td>
<td>1%Ce+0.05%Sr</td>
</tr>
<tr>
<td>4</td>
<td>1%Ce+0.1%Sr</td>
</tr>
</tbody>
</table>

Table 2 Chemical compositions of the Mg2Si/Al composites (mass%). (The primary elements are Al, Mg and Si.)

<table>
<thead>
<tr>
<th>Materials Mg2Si/Al-Si-Cu</th>
<th>Al</th>
<th>Si</th>
<th>Cu</th>
<th>Mg</th>
<th>Mn</th>
<th>Cr</th>
<th>Fe</th>
<th>Zn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal.</td>
<td>11.5</td>
<td>3.2</td>
<td>14.3</td>
<td>0.011</td>
<td>0.016</td>
<td>0.2</td>
<td>0.012</td>
<td>0.001</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1 (a) and (b) are the microstructure of samples 0 and 1, (c) and (d) are the high magnification image of the selected area (rectangle) in Fig. 1a and b, respectively. (It is showed the morphology of the primary Mg2Si phase changes to a polygonal morphology with a size of 15 μm after Ce addition\(^1\).)

Fig. 2 (a) and (b) are the microstructure of samples 2 and 3, (c) and (d) are the high magnification image of the selected area (rectangle) in Fig. 2a and b, respectively. (The morphology of the primary Mg2Si changed to an irregular and equiaxed shape, and its size increased to ~50—~100 μm in comparison to the sample 1.)
c, where Fig. 2c shows the high magnification image of the selected area (rectangle) in Fig. 2a, the morphology of the primary Mg$_2$Si changed to an irregular and equiaxed shape, and its size increased to ~50 μm in comparison to the sample 1. The sizes of α-Al increases and the dendritic structure appeared again. This suggested that the effect of Ce on the microstructure was weakened due to the addition of the Sr elements, specifically, the modification of Ce was poisoned by Sr. The microstructure of sample 3 is shown in Fig. 2b and d, where Fig. 2d shows the high magnification image of the selected area in Fig. 2b, the sizes of primary Mg$_2$Si increased to ~70 μm, and its morphology changed from an irregular and equiaxed shape to a rectangular trapezoid, or “T” shape. Also, the inside of the primary Mg$_2$Si particles also presented some white α-Al phase. The morphology and sizes of α-Al phase had no apparent changes.

On the one hand, the increase of the Ce content, visualized in the composite modification with the 1.00 mass% Ce and 0.05 mass% Sr of sample 4, remarkable changes occurred. As shown in Fig. 3a and c, similar to above, where a higher magnification image of the selected area in Fig. 3a is shown, the morphology of the primary Mg$_2$Si became polygonal again, and the size of the primary Mg$_2$Si decreased to ~30 μm. At the same time, the α-Al phase was finer in sample 5; however, the morphology of the primary Mg$_2$Si changed to an irregular shape, and the α-Al phase became larger (see Fig. 3b and d, where Fig. 3d shows the higher magnification of the image of the selected area in Fig. 3b).

In the present study, the modification of a single Ce transformed the morphologies of the primary structure from dendrites to irregular and equiaxed crystals (see Fig. 1b). However, with the addition of Sr, the morphologies of the primary Mg$_2$Si became poor, and the sizes were also increased (see Fig. 2a and c). With the increase of the Sr content, the size of the primary Mg$_2$Si was further increased, while at the same time, the morphologies became T-shaped (see Fig. 2b and d). On the other hand, with a further increase of the Ce content in the Ce+Sr modification alloys, the morphology of the primary Mg$_2$Si transformed to a polygonal morphology again, with a decreased size (see Fig. 3a and c). As further increases in the Sr content occurred, the primary morphologies became poor again, and the size did not change (see Fig. 3b and d). The above image shows the change in the primary Mg$_2$Si phases with the addition of Ce+Sr.

Generally, there were two possible explanations for the modification of alloys. The first describes a heterogeneous nucleation, where the modification elements, or compounds formed by them, including a heterogeneous nucleus or inoculation. The second was described by a poisoning effect, where the modification elements absorbed the forefront of the growth and restricted the crystal growth. The mechanism of Sr modification was previously studied$^{11}$. The modification mechanism of Ce was different when compared with Sr because the Ce addition suppressed the growth of the primary Mg$_2$Si by modifying both the solid-liquid interfacial energy and the surface energy of the solid Mg$_2$Si phase$^{7}$. In one such study, the modification of Ce+Sr was still unclear. However, the crystallization and phase selection may have been one of the reasons explaining this phenomenon. According to another study$^{12}$, when the content of Ce and Sr exceeded a specified value in an alloy, specifically Al-Ce-Sr, the Ce and Sr will exist in the form of Al$_4$(Sr, Ce). The formation of a Ce-Sr intermetallic phase may eliminate the modification effect. Furthermore, the Sr and Ce elements were detected simultaneously at the primary Mg$_2$Si structure in the present study, as shown in Fig. 4 (point 1) and Table 3, which proved the existence of the Ce-Sr compound.

3.2 Modification of the eutectic phases

The detailed microstructures of the eutectic matrix of sam-

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**Table 3** Analysis result of EDS tracing of the point in the Fig. 4 (point 1). (It shows the existence of Sr and Ce.)

<table>
<thead>
<tr>
<th>Element line</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>65.87</td>
<td>68.94</td>
</tr>
<tr>
<td>Si</td>
<td>28.69</td>
<td>28.87</td>
</tr>
<tr>
<td>Cu</td>
<td>4.14</td>
<td>1.84</td>
</tr>
<tr>
<td>Sr</td>
<td>0.48</td>
<td>0.15</td>
</tr>
<tr>
<td>Ce</td>
<td>0.82</td>
<td>0.17</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>99.97</td>
</tr>
</tbody>
</table>
The morphology transformation of eutectic phase with the different Sr and Ce addition. (The samples No. of 0–5 represented the following compositions: 0%, 0.40% Ce, 0.40% Ce+0.05% Sr, 0.40% Ce+0.10% Sr, 1.00% Ce+0.05% Sr, and finally 1.00% Ce+0.10 mass% Sr.)

<table>
<thead>
<tr>
<th>Samples No.</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eutectic Si</td>
<td>Fibrous-like, Ternary eutectic</td>
<td>Coral-like, Binary eutectic</td>
<td>Coral-like, Binary eutectic</td>
<td>Coral-like, Binary eutectic</td>
<td>Coral-like, Binary eutectic</td>
</tr>
<tr>
<td>Mg2Si</td>
<td>Fibrous-like, Ternary eutectic</td>
<td>chrysanthemum-like, Binary eutectic</td>
<td>Fibrous-like, Ternary eutectic</td>
<td>chrysanthemum-like, Binary eutectic</td>
<td>Fibrous-like, Ternary eutectic</td>
</tr>
</tbody>
</table>

Fig. 5 The detailed microstructures of the eutectic matrix of (a) samples 0 and (b) 1. (It is shown that without the Ce addition, the eutectic Mg2Si and the eutectic Si have a fibrous-like morphology. With the 0.40% Ce addition, the eutectic Si changed from a fibrous-like to a coral-like morphology, and the eutectic Mg2Si changed to a chrysanthemum-like structure.)

Fig. 6 The microstructures of the eutectic matrix of (a) samples 2 and (b) 4. (It shows that both the eutectic Mg2Si and the eutectic Si were identified with a fibrous-like morphology in sample 2, and the morphology of the eutectic Si changed to a coral-like structure again, where the eutectic Mg2Si changed to Chinese script in sample 4).
in/flection points. As indicated in Fig. 8c, the first in/flection point descended by ~10 K in comparison to the samples 0 and 2. The second in/flection point ascended by ~10 K. This illustrated that the solidification process of the Al-Mg 2Si alloys was affected by Ce in the sample 4. The reduction of the primary Mg2Si crystallization point indicated that the surplus Ce restrained the nucleation of the primary Mg 2Si, and accordingly led to the decrease in size of the primary Mg2Si. Specifically, the solidification process led to a shift to the left in Fig. 7. Because of this shift of the solidification process, which led to an increase in the eutectic temperature, as shown in Fig. 7 and 8c, the eutectic temperature increased by ~10 K. Accordingly, the eutectic MgSi phase resulted in the formation of the binary eutectic Al+Mg2Si.

3.3 The hardness and wear resistance

Table 5 shows the typical hardness values of the samples 0, 2 and 4. The resulting hardness of the sample 0 measured 110 HB, and by adding a modifier, the hardness increased to 118 HB and 125 HB, respectively. Consequently, the hardness change was caused by an interior structure transformation after the modification occurred. According to these microstructure changes, as shown in Fig. 1–3, the matrix became more compact after the addition of the modifier, and both Mg and Si were distributed throughout the matrix, rather than the primary Mg2Si, which led and increased hardness. Furthermore, according to the presented results, Ce reduced the primary Mg2Si crystallization point and restrained the nucleation of the primary Mg2Si, therefore causing a decrease in the amount of the primary Mg2Si in the sample 4 in comparison to the sample 2. As a result, the hardness of the sample 4 was greater than that of the sample 2.

The data presented in Fig. 9 shows the relationship between the weight loss and applied load for the in-situ Mg2Si/Al-Si-Cu composite with different modifiers additions. (This demonstrates a nearly linear relationship between the weight loss and the increase in the applied load.)

Table 5 The HB hardness of samples No. of 0, 2 and 4. (It is indicated that the hardness of the sample 4 was greater than that of the sample 2 and 0.)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>HB hardness, HB</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>110</td>
</tr>
<tr>
<td>2</td>
<td>118</td>
</tr>
<tr>
<td>4</td>
<td>125</td>
</tr>
</tbody>
</table>

Fig. 7 Vertical section of the Al-Mg-Si equilibrium ternary diagram from Al-20Mg2Si to Si5).

Fig. 8 The solidification curves of sample (a) 0, (b) 2 and (c)4. (These plots indicate that the first in/flection point represented the formation of the primary Mg2Si, and the second point represented a precipitation of the eutectic phases.)

Fig. 9 The relationship between weight loss and applied load of in-situ Mg2Si/Al-Si-Cu composite with different modifiers additions. (This demonstrates a nearly linear relationship between the weight loss and the increase in the applied load.)
2 and also the sample 4, respectively. Therefore, the HB hardness and abrasive resistance data for the samples 1 and 5 were not provided in the present work.

Images obtained from the SEM, demonstrating the wear surfaces of the composite are shown in Fig. 10, where most of the wear surfaces showed abrasion grooves. The sample 0, and the sample 2 were relatively rough due to the presence of distinct craters (see Fig. 10a) and cracks (see Fig. 10b). The experimental results further reveal that the modified composite of the sample 4 had a better wear resistance.

4. Conclusion

The modification effect of Sr+Ce in Mg2Si/Al-Si-Cu composites was investigated for controlling both the microstructure and mechanical properties. The following conclusion can be made.

The rare Ce can change the morphology of primary Mg2Si phase and decreasing its sizes. However, the Sr as well as surplus Sr addition in 0.40Ce modified composites lead to the worse morphologies and the bigger sizes on primary Mg2Si phases. Further increasing the Ce content in Ce+Sr or Ce+surplus-Sr modified composites can transform the morphologies and refining sizes to better direction. Furthermore, the surplus Ce or Sr addition can lead to the transformation of eutectic phases between binary eutectic of Al+Mg2Si and ternary eutectic of Al+Mg2Si+Si. The hardness of modified composites are higher than un-modified composite. As the same, the abrasive resistance property of modified composites are higher than un-modified composite. It demonstrates that the Sr+Ce addition can change the microstructure and enhance the mechanical properties of the material.

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