Effect of SiC particle addition on microstructure of Mg$_2$Si/Al composite

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Abstract: In the present study, by adding SiC particles into Al-Si-Mg melt, Mg$_2$Si and SiC particles hybrid reinforced Al matrix composites were fabricated through the Mg$_2$Si in situ synthesis in melt combined with the SiC ex situ stir casting. The as-cast microstructure containing primary Mg$_2$Si and SiC particles that distribute homogeneously in Al matrix was successfully achieved. The effects of SiC particle addition on the microstructure of Mg$_2$Si/Al composites were investigated by using scanning electron microscopy (SEM) and XRD. The results show that, with increasing the fraction of the SiC particles from 5wt.% to 10wt.%, the morphologies of the primary Mg$_2$Si particulates in the prepared samples remain polygonal, but the size of the primary phase decreases slightly. However, when the SiC particle addition reaches 15wt.%, the morphologies of the primary Mg$_2$Si particulates change partially from polygonal to quadrangular with a decrease in size from 50 μm to 30 μm. The size of primary Al dendrites decreases with increasing fraction of the SiC particles from 0wt.% to 15wt.%. The morphology of the eutectic Mg$_2$Si phase changes from a fiber-form to a short fiber-form and/or a dot-like shape with increasing fraction of the SiC particles. Furthermore, no significant change in dendrite arm spacing (DAS) was observed in the presence of SiC particles.

Key words: Mg$_2$Si/Al matrix composite; SiC particles; microstructure; solidification

Conceivable efforts have been devoted to the development of novel, lightweight materials in automobile and other industries during the last decades. Aluminium metal matrix composite is one of the competitive lightweight automobile materials. Hypereutectic Al-Si alloys with high Mg content are in fact an in situ aluminum matrix composite containing a large amount of hard Mg$_2$Si particles. The Mg$_2$Si/Al composite has a potential as a material for automobile brake discs because the intermetallic compound of Mg$_2$Si exhibits high melting temperature, low density, appropriate hardness, low thermal expansion coefficient and reasonably high elastic modulus [1-4]. In addition, an in situ process of fabricating Mg$_2$Si/Al composite possesses some merits, such as even distribution of reinforcement, well matched matrix-reinforcement interface, thermodynamically stable system and much lower costs of production compared with their counterparts from ex situ processes [5]. However, the Mg$_2$Si/Al composite has low temperature brittleness and deficient wear resistance, which limit its application.

SiC is also the most commonly used reinforcement phase in aluminum matrix composites [6-12]. Since 1970, SiC reinforced Al matrix composites have been investigated for automobile applications, such as diesel engine pistons, connecting rods, drive shafts, brake discs, cylinder liners, etc., owing to their excellent mechanical properties (such as good wear resistance) and light weight [13]. However, various conventional ex situ processes of fabricating SiC/Al composites have some of the inherent problems, such as poor wettability of the reinforcement, reaction of matrix-reinforcement interface, and inhomogeneous distribution of SiC particles in the matrix [14]. Furthermore, SiC/Al composite has poor machinability and difficulty in recovery.

Some previous studies have been conducted on the microstructure evolution of SiC/Al composites [15-16]. Dutta et al. [15] studied the solidification behavior of Al-Cu-SiC$_p$ composite under multidirectional solidification conditions. It was reported that SiC particles promoted grain refinement in the matrix in the absence of convection, and matrix dendrite arm spacing (DAS)
was not significantly altered by the presence of SiC particles. Nagarajan et al. [16] reported that an increase in SiC volume fraction led to a reduction in the size of eutectic Si and also changed its morphology from needle-like to equiaxed, and that SiC particles were found to have negligible influence on DAS. However, there is limited experimental study on the effects of SiC particle addition on the microstructure of Mg2Si/Al composites.

In the present research, by adding oxidized SiC particles into Al-Si-Mg melt, Mg2Si and SiC particles hybrid reinforced Al matrix composites were fabricated through the Mg2Si in situ synthesis in melt combined with the SiC ex situ stir casting. This would improve not only the deficient wear resistance of Mg2Si/Al composite, but also the machinability of SiC/Al composite. In addition, according to previous studies, the SiO2 layer on the surface of SiC reacts with the Al matrix and Mg that segregates on the interface to form MgAl2O4 and Si[17-22], which prevents the formation of Al4C3 and results in the improvement of wettability of the SiC/Al system. In the present work, an as-cast microstructure containing primary Mg2Si and SiC particles distributing homogeneously in the Al matrix has been obtained. The effects of SiC particle addition on primary Al dendrite, primary Mg2Si, secondary dendrite arm spacing and eutectic phases have also been studied. It is expected these investigations could help achieve a better understanding of solidification behavior of composites, and serve as a more practical reference.

1 Experimental procedure

Commercial Al-25Si master alloy (ingot), magnesium (ingot, >98.0% purity) and SiC particle (>99% purity, 10–15 μm) were used as starting materials. The SiC particles were pre-oxidized at 900 ℃ for 3 h to obtain a better wettability [17, 18]. The mass fractions of SiC particle addition were set at 0wt.%, 5wt.%, 10wt.% and 15wt.%, respectively. About 700 g of Al-Si alloy was melted in a graphite crucible in an electric resistance furnace. About 103 g of magnesium was added into the Al-Si melt at 680–700 ℃. The designed content of Mg2Si was 20wt.%. After 10 min, the 0.5wt.% of P via a Cu-14wt.%P master alloy were added into the melts at 800 ℃. After holding for 15 min, the 600 ℃ pre-heated SiC particles were added into the Al-Si-Mg melt at 700 ℃ with a stirring action, in which the stirring condition for the fabrication of (Mg2Si + SiCp)/Al composite was: stirring speed of 500 r·min⁻¹ and stirring time of 30 min. Subsequently, after holding for 15 min, the composite melts were reheated to 720 ℃, and poured into steel die to produce ingots of 200 mm × 150 mm × 12 mm.

Metallographic specimens were polished through standard routines and examined using optical microscopy to observe the features of the Mg2Si phase and SiC particles in the composites. A 0.5% hydrofluoric acid (HF) water solution was used as etchant on the polished samples. A 25% NaOH water solution was used as reagent to carry out the extraction test to get the stereoscopic features of Mg2Si and SiC particles. The microstructure characteristics of the etched specimens were examined with a scanning electron microscopy (JSM-5310, Japan), while the grain size and volume fraction were analyzed by a quantitative analysis system (Omnimet imaging systems-Buehler, USA). The phase constituents were analyzed using X-ray diffraction (XRD) (D/Max 2500 PC Rigaku, Japan).

Hardness value was determined with a hardness tester (Brinell Hardness Tester HB-3000B, Laizhou Huayin Testing Instrument Co., Ltd., China) using 7,355 N load (indenter diameter of 5 mm) and 30 s holding time, and from the average value of at least five hardness readings on each sample.

2 Results

2.1 As-cast microstructure of composite

Figure 1 shows the as-cast microstructure of the (Mg2Si + 15wt.%SiCp)/Al composite modified by phosphorus with stirring speed of 500 r·min⁻¹ and stirring time of 30 min. It is apparent that the relatively homogenous distribution of Mg2Si and SiC reinforcement particles was obtained in the Al matrix after stir casting.

![Fig. 1: As-cast microstructure of (Mg2Si + 15wt.% SiCp)/Al](image)

According to the phase diagram [23] in Fig. 2, the solidification process of Mg2Si/Al composites is as follows:

\[ L \rightarrow L1 + Mg_Si_b \rightarrow L2 + (Al + Mg_Si)_b + Mg_Si_b \rightarrow (Al + Si + Mg_Si)_b + (Al + Mg_Si)_b + Mg_Si_p \]  
where, the subscript P represents the primary phase and e represents the eutectic phase. Because of non-equilibrium in the solidification process, other phases, such as eutectic Si phase, appeared. According to previous study [24], the morphology of primary Mg2Si phase should be dendritic in the as-cast microstructure of the composite. When the composite was modified with phosphorus, the morphology of primary Mg2Si changed to polygon, as shown in Fig. 3. It was reported that the changes of the morphology and size of primary Mg2Si particles may be caused by the effect of heterogeneous nucleation [25].
Figure 2: Calculated vertical section of Al-20Mg$_2$Si to Si in equilibrium Al-Mg-Si phase diagram\textsuperscript{[23]}

Figure 4 shows the XRD patterns of (Mg$_2$Si + SiC$_p$)/Al composites. The XRD result reveals that the constitutions of the Mg$_2$Si/Al composite consist of Al, Mg$_2$Si, CuAl$_2$, and Si phases. When SiC particles are present in the composites, the constitutions of (Mg$_2$Si + SiC$_p$)/Al composites contain not only phases mentioned above, but also SiC and MgAl$_2$O$_4$ phases.

2.2 Morphological change of primary Mg$_2$Si

Figure 3 shows the microstructures of (Mg$_2$Si + SiC$_p$)/Al composites modified by phosphorus. The primary Mg$_2$Si phase was changed to irregular polygon and equiaxed grain with an average particle size of 50 μm, as shown in Fig. 3(a). From Fig. 3(a) through Fig. 3(d), microstructural changes could be observed: (I) when 5wt.% and 10wt.% SiC particles were added into Al-Si-Mg melt, the morphologies of primary Mg$_2$Si particulates in the prepared samples remained polygonal, and the shape was relatively regular and the size decreased slightly, as shown in Fig. 3(b) and Fig. 3(c); (II) with increasing fraction of the SiC particles from 10wt.% to 15wt.%, the morphology of primary Mg$_2$Si particulates was changed to quadrangular with a decrease in size from 50 μm to 30 μm, as shown in Fig. 3(d); (III) SiC and Mg$_2$Si particles distributed more uniformly in the matrix. It can be concluded that an increase in SiC particle content can lead to grain refinement of primary Mg$_2$Si.

2.3 Morphological changes of primary Al dendrites

The morphological changes of primary Al dendrites are shown in Fig. 3 and Fig. 5. According to previous study, the $\alpha$-Al is
identified as dendritic. The primary Al dendrites are coarse, with an average size of about 100 μm, as shown in Fig. 5(a). However, the sizes of primary Al dendrites changed with the addition of SiC particles. It can be observed that an increase in SiC fraction leads to a decrease in matrix grain size. With increasing fraction of the SiC particles from 0wt.% to 15wt.% [from Fig. 5(a) to Fig. 5(d)], its morphology remained dendritic, while its size decreased obviously. When 15wt.% SiC particles were added into Al-Si-Mg melt, the size was refined to a size of about 40 μm, as shown in Fig. 5(d). Clearly, the presence of SiC reinforcement has caused a significant refinement of primary Al dendrites. However, the secondary dendrite arm spacing (DAS) does not seem to have any marked changes in the presence of SiC particles.

3 Discussion

3.1 Effect of SiC particle addition on size and morphology of primary Mg2Si

In the Al-Si-Mg melt, the primary Mg2Si begins to precipitate and grow up with the decreasing of temperature, leading to the gradual decrease of Mg and Si contents. Accordingly, the Al content gradually increases. It is very obvious that the primary Mg2Si forms in the melt with a lower content of Mg and Si and a higher content of Al. As a result, there are Al dendrites surrounding the primary Mg2Si, as shown in Fig. 3(a).

When SiC particles were added into the Al-Si-Mg melt, the size and morphology of primary Mg2Si changed. Guo et al. [21] found that there was enrichment of Mg element at the Al/SiC interface. In the present study, SiC was oxidized in air at 900 °C, and the SiC reacted with the oxygen to form a thin layer of SiO2 on the surface of SiC. Furthermore, the SiO2 layer reacted with Al and Mg within the matrix alloy, forming MgAl2O4 and Si at the expense of the SiO2 layer, according to the reaction given by Eq. (2) [17, 18].

$$2\text{SiO}_2 + 2\text{Al} + \text{Mg} = \text{MgAl}_2\text{O}_4 + 2\text{Si}$$  \hspace{1cm} (2)

MgAl2O4 crystal formed as a result of this interfacial reaction is face-centered cubic structure with lattice constant of $a = 0.8085 \text{ nm}$ [26]. Lee et al. [18] reported that the resultant interface formed as a result of the interfacial reaction could act as the protective barrier which prevents the formation of Al4C3. Lee et al. [20] studied and confirmed that MgAl2O4 crystals were present in SiC/2014Al composite. It was reported that the bonding...
strength of SiO₂ interface was close to that of Al₄C₃ interface, while the bonding strength of MgAl₂O₄ interface was 2.5 times greater than those of the former two. Guo et al. [21] found that there was only 2.93% Mg in the matrix, but as high as 24.52% Mg segregated on the interface of SiC/Al composite, namely, there were elemental segregations on the interface of SiC/Al composite. Additionally, according to the results of XRD, the MgAl₂O₄ phase was identified in (Mg₂Si + SiC₃p)/Al composites, as shown in Fig. 4.

According to the interface lattice mismatch theory, when the atomic arrangement and inter-atomic distance on the surface of solid phase substrate are close to that of newly formed crystal nucleus, the solid-liquid interfacial free energy is very low, and the external solid phase has a very strong capability to serve as site for heterogeneous nucleation. It means that coherent interface can be formed with lattice mismatch at smaller range. The lattice mismatch is defined [27] as:

\[ \delta = \left| \frac{a_\alpha - a_\beta}{a_\alpha} \right| \]  

where \( a_\alpha \) and \( a_\beta \) are lattice constants of the substrate phase and newly formed phase, respectively. In general, when \( \delta \leq 0.05 \), coherent interface can be formed; when \( 0.05 \leq \delta \leq 0.25 \), semi-coherent interface can be formed; and when \( \delta > 0.25 \), incoherent interface can be formed [23]. Mg₂Si is face-centered cubic structure with lattice constant of \( a = 0.6338 \) nm. The calculation values of planar mismatch \( \delta \) between Mg₂Si and MgAl₂O₄ are shown in Table 1. It indicates that the calculation value of planar mismatch \( \delta \) between [110] \( \text{MgAl}_2\text{O}_4 \) and [010] \( \text{Mg}_2\text{Si} \) is 0.109, namely the interfacial-bonding mode between MgAl₂O₄ and Mg₂Si is semi-coherent, and so MgAl₂O₄ formed at the SiC surface may serve as favorable sites for the heterogenous nucleation of primary Mg₂Si phase. As a result, some primary Mg₂Si particles cling to SiC particles and grow up, and others nucleate independently and grow up in the liquid phase. The morphologies of Mg₂Si and SiC particles extracted from (Mg₂Si + SiC₃p)/Al composite are shown in Fig. 6. It is obvious that primary Mg₂Si particles cling to SiC particles. Thus, with the increasing of the number of SiC particles, more nucleation sites can be provided for the primary Mg₂Si phase, essentially leading to refinement of grain size. In addition, quantitative analysis shows that the volume fraction of the primary Mg₂Si phase in the composites of Mg₂Si/Al, (Mg₂Si + 5wt.%SiC₃p)/Al, (Mg₂Si + 10wt.%SiC₃p)/Al and (Mg₂Si + 15wt.%SiC₃p)/Al is 22%, 22.9%, 23.4% and 23.4%, respectively. This indicates that the SiC addition does not affect the volume fraction of primary Mg₂Si phase. At a constant volume, a decrease in the size of particles means an increase in the number of particles. This implies an increase in the number of nuclei for the primary Mg₂Si particles during the initial stage of the solidification and thereby is responsible for the grain refinement of primary Mg₂Si particulates. On the other hand, the presence of SiC particles restricts the growth of primary Mg₂Si due to their mechanical obstruction. In short, it is the factors discussed above that cause the changes of the size and morphology of primary Mg₂Si.

3.2 Effect of SiC particle addition on size of primary Al dendrites

According to reference [15], the role of ceramic reinforcements on the matrix grain size during solidification of composite slurry can be analyzed based on following mechanisms: (I)

Table 1: Calculation values of planar mismatch \( \delta \) between Mg₂Si and MgAl₂O₄

<table>
<thead>
<tr>
<th>Matching interface</th>
<th>(010) ( \text{MgAl}_2\text{O}_4 )//(010) ( \text{Mg}_2\text{Si} )</th>
<th>(110) ( \text{MgAl}_2\text{O}_4 )//(110) ( \text{Mg}_2\text{Si} )</th>
<th>(110) ( \text{MgAl}_2\text{O}_4 )//(010) ( \text{Mg}_2\text{Si} )</th>
<th>(010) ( \text{MgAl}_2\text{O}_4 )//(110) ( \text{Mg}_2\text{Si} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[uvw] ( \text{MgAl}_2\text{O}_4 )</td>
<td>[010]</td>
<td>[110]</td>
<td>[110]</td>
<td>[010]</td>
</tr>
<tr>
<td>[hkl] ( \text{Mg}_2\text{Si} )</td>
<td>[010]</td>
<td>[110]</td>
<td>[110]</td>
<td>[110]</td>
</tr>
<tr>
<td>( d_{[uvw]} ) ( \text{MgAl}_2\text{O}_4 ) (nm)</td>
<td>0.8085</td>
<td>0.5716</td>
<td>0.5716</td>
<td>0.8085</td>
</tr>
<tr>
<td>( d_{[hkl]} ) ( \text{Mg}_2\text{Si} ) (nm)</td>
<td>0.6338</td>
<td>0.4481</td>
<td>0.6338</td>
<td>0.4481</td>
</tr>
<tr>
<td>( \theta )</td>
<td>0°</td>
<td>0°</td>
<td>45°</td>
<td>45°</td>
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<tr>
<td>( \delta )</td>
<td>0.216</td>
<td>0.216</td>
<td>0.109</td>
<td>0.446</td>
</tr>
</tbody>
</table>

Fig. 6: Morphologies of primary Mg₂Si and SiC particles: (a) Mg₂Si/Al composite and (b) extracted from Mg₂Si/Al composite
heterogeneous nucleation of the matrix phase on the ceramic reinforcements; (II) convection during solidification of the slurry; (III) particle restricted grain growth[9]. It is well known that SiC does not act as a heterogeneous nucleation site for $\alpha$-Al[15], and any role of heterogeneous nucleation on grain size evolution in composites is ruled out. Hence, results of the present investigation can be explained with the help of mechanisms (II) and (III).

The addition of SiC particles to Al melt increases its viscosity. An increase in viscosity due to an increase in the volume fraction of particles will reduce the degree of convection in composites, and this in turn will tend to promote coarser grain size with increasing SiC content. On the other hand, during the solidification of (Mg$_2$Si + SiC$_p$)/Al composite, SiC particles suspended in the melt interact with the advancing solid-liquid interface. In the case of Al-Si-Mg melt, SiC particles impose a physical barrier to the diffusing solute flux, which further slows down the interface movement, namely the velocity of the solidification front. This provides time for more nuclei to form and thus leads to a refinement of grain size in the composite castings. Clearly, the mechanisms (II) and (III) are counteracting, and the final grain size will be decided by the dominating mechanism. In the present study, the presence of SiC reinforcements has caused a significant refinement of primary Al dendrites. Considering the above two mechanisms and the obtained results from the present investigation, it can be concluded that mechanism (III), i.e. particle restricted grain growth, which overshadows convection effects, seems to be playing the deciding role and thus refines the size of primary Al dendrites in the (Mg$_2$Si + SiC$_p$)/Al composites. Dutta et al. [15] had reported a similar influence of SiC particles on matrix grain size. It was reported that the presence of SiC particles was found to decrease the matrix grain size as a result of particle restricted growth. The present study has shown that, with increasing fraction of the SiC particles, the restriction effect strengthens.

In addition, matrix dendrite arm spacing (DAS) does not seem to show any marked changes in the presence of SiC particles. This can be attributed to the larger interparticle spacing compared to the characteristic diffusion length in the present experiments [15].

3.3 Effect of SiC particle addition on morphologies of eutectic phases

The present study shows that the morphology of eutectic Mg$_2$Si phase changes from fiber-form to short fiber-form and/or dot-like with increasing the fraction of the SiC particles. The refining mechanism of eutectic Mg$_2$Si phase and ternary eutectic (Al + Si + Mg$_2$Si) phase may be related to the mechanical obstruction of SiC particles. As discussed above, the presence of SiC particles restricts the growth of matrix phase. Accordingly, it may restrict the growth of eutectic Mg$_2$Si phase according to mechanism of “particle restricted grain growth”, leading to the above morphological changes of eutectic Mg$_2$Si phase. However, the detailed refining mechanism of eutectic Mg$_2$Si phase is still not very clear at present, and needs further study.

Nevertheless, the size of Al dendrites, the size and morphologies of primary Mg$_2$Si and the morphologies of eutectic phases change with increasing the fraction of the SiC particles from 0wt.% to 15wt.%, and consequently, the properties of (Mg$_2$Si + SiC$_p$)/Al composites are improved, such as HB hardness, as shown in Table 2.

<table>
<thead>
<tr>
<th>SiC content (wt.%)</th>
<th>HB</th>
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<tr>
<td>0</td>
<td>116</td>
</tr>
<tr>
<td>5</td>
<td>128</td>
</tr>
<tr>
<td>10</td>
<td>135</td>
</tr>
<tr>
<td>15</td>
<td>150</td>
</tr>
</tbody>
</table>

4 Conclusions

(1) By adding SiC particles into Al-Si-Mg melt, Mg$_2$Si and SiC particles hybrid reinforced Al matrix composites with relatively homogenous distribution of the reinforcement Mg$_2$Si and SiC particles can be obtained through Mg$_2$Si in situ synthesis in melt combined with SiC ex situ stir casting.

(2) With increasing the fraction of the SiC particles from 5wt.% to 10wt.%, the morphologies of the primary Mg$_2$Si particulates in the prepared samples remain polygonal, but the size of the primary phase decreases slightly. However, the morphologies of the primary Mg$_2$Si particulates change to quadrangular with a decrease in size from 50 μm to 30 μm when the SiC particle addition reaches 15wt.%. (3) With increasing the fraction of the SiC particles from 0wt.% to 15wt.%, the size of primary Al dendrite decreases. But, no significant change in secondary dendrite arm spacing (DAS) has been observed in the presence of SiC particles.

(4) With increasing the fraction of the SiC particles from 0wt.% to 15wt.%, the morphologies of the eutectic Mg$_2$Si phase change from fiber-form to short fiber-form and/or dot-like. Some primary Mg$_2$Si particles appear, cling to SiC particles and grow up.

References


The research was financially supported by the National Natural Science Foundation of China (No. 50671044) and the Sci-tech Development Project of Jilin Province of China (No. 20070506).