Original Article

Simultaneous refinement and modification of the eutectic Si in hypoeutectic Al–Si alloys achieved via the addition of SiC nanoparticles

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ABSTRACT

This paper reports that the addition of SiC<sub>nps</sub> is demonstrated to induce the simultaneous modification and refinement of the eutectic Si in the SiC<sub>nps</sub>/A356 samples, which becomes increasingly significant with increasing SiC<sub>nps</sub> addition. The effect of SiC<sub>nps</sub> addition is primarily investigated via the results obtained from differential scanning calorimetry and high resolution transmission electron microscopy. The modification and refinement of the eutectic Si are closely related to the interaction between the SiC<sub>nps</sub> and the solidification front (SF). When the particle size of the SiC<sub>nps</sub> is greater than the critical size, the SiC<sub>nps</sub> tend to move ahead of the SF, while smaller SiC<sub>nps</sub> tend to be engulfed. Here, SiC<sub>nps</sub> distributed at the interface between the eutectic Si/Al phase hinder the growth of the eutectic Si. Meanwhile, SiC<sub>nps</sub> are observed to act as heterogeneous nucleation sites for the eutectic Si. Hence, the simultaneous modification and refinement of the eutectic Si is mainly facilitated by a combination of the above two individual effects of SiC<sub>nps</sub> addition. Furthermore, SiC<sub>nps</sub> distributed in the eutectic Si leads to the formation of multiple Si crystal twin variants.

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1. Introduction

The low density, good castability, and excellent mechanical properties of the A356 Al–Si alloy make it well suited for wide use as a structural material in various fields such as transportation and aerospace [1,2]. The A356 alloy is characterized by Al dendrites surrounded by an Al–Si eutectic system (i.e., a eutectic Si). However, the microstructure of the eutectic Si phase has a substantial influence on the mechanical properties of A356. Here, ensuring good mechanical properties for the alloy requires that the eutectic Si phase be modified from its originally coarse flake-like microstructure and refined to obtain a finer fibrous microstructure. Therefore, developing strategies for the effective modification and refinement of the eutectic Si microstructure in Al–Si alloys is of significant importance.

The conventional strategy for modifying the microstructure of the eutectic Si phase in Al–Si alloys employs the addition of a variety of alloying elements, such as Na, Sr, and Eu [3–5]. Several studies have observed that high density twin crystal growth is related to the modification of
eutectic Si microstructures in Al-Si alloys [6–8]. Presently, a few widely accepted mechanisms have been adopted for explaining the modification of eutectic Si microstructures in Al-Si alloys, such as the impurity induced twinning (ITI) and twin plane reentrant edge (TPRE) growth mechanisms, as well as poisoning of the TPRE [9,10]. The formation of Al2Si5Sr within the eutectic Si has a negligible effect on the modification of the eutectic Si structure in Al-Si alloys [11]. However, recent investigation has shown that Al2Si5Sr and NaAlSi5 clusters formed at the Si/liquid interface exert a significant influence on the modification of the eutectic Si microstructure by altering the eutectic Si growth process [12]. In addition, other elements, such as Yb, Ca, and P, have been added into Al-Si alloys for refining the eutectic Si microstructure [13–15]. For example, the addition of Yb was shown to lead to the refinement of the eutectic Si microstructure rather than the modification of the eutectic Si microstructure during the eutectic Si growth process [10]. In addition, the combined addition of Ca and P was shown to lead to a deactivation of the AlP impurity particles, resulting in the poisoning of AlP nucleation sites for the eutectic Si, which promoted refinement via an increased recalescence undercooling of the eutectic Si [16,17].

Compared with the conventional modification and refinement strategy discussed above, the modification and refinement of not only the eutectic Si phase in Al-Si alloys can be achieved simultaneously but also the failure of the modification is avoided via the addition of nanoparticles. Numerous investigations have shown that nanoparticles can control the eutectic Si phase growth during solidification [18–20]. Nanoparticles, such as Al2O3 and TiCN, have been shown to hinder the growth of the eutectic Si phase by distributing on the Al/Si interface, and thereby lead to the refinement of the eutectic phase [21,22]. In addition, the refinement of the eutectic Si phase in Al-Si alloys has also been shown to be related to the heterogeneous nucleation of TiCN nanoparticles and pre-nucleation clusters during solidification [23,24]. It has also been reported that the addition of AlN nanoparticles in Al-Si alloys modified the eutectic Si from a flake-like microstructure to a block-like microstructure [25]. However, the role played by SiC nanoparticles in the modification and refinement of the eutectic Si in Al-Si alloys remains poorly understood. Therefore, additional research focused on this very important strategy is required.

To address these issues, the present study prepares A356 Al-Si alloys with the addition of 0.5–2.0 wt% SiC nanoparticles (SiCnps) by a solidification process combined with ultrasonic treatment. The effect of SiCnps addition on the modification and refinement of the eutectic Si in Al-Si alloys is systematically studied primarily via differential scanning calorimetry (DSC) and high resolution transmission electron microscopy (HRTEM). The simultaneous modification and refinement of the eutectic Si is shown to be mainly facilitated by a combination of the two effects of SiCnps addition that are closely related to the distribution of the SiCnps. These include the following. (1) The effect of SiCnps distributed at the interface between the eutectic Si and Al phase for hindering the growth and promoting the fragmentation of the eutectic Si. (2) The effect of SiCnps to act as heterogeneous nucleation sites for the eutectic Si. Furthermore, the effect of SiCnps distributed in the eutectic Si for promoting the formation of multiple Si twin crystal variants.

### 2. Experimental procedure

The chemical composition of A356 is listed in Table 1. The A356 samples were melted in an alumina crucible using an electric resistance furnace, and SiCnps (purchased from Shanghai Yao Tian Nano Material Co. Ltd.) were added into the molten A356 with varying additions of 0.5, 1.0, and 2.0 wt%. The particle sizes of the added SiCnps are presented in detail in Section 3. The apparatus and solidification process combined with ultrasonic treatment employed for preparing SiCnps/A356 materials are described in detail elsewhere [26]. The melt was cast using a cast iron cylindrical mold preheated to 400°C. For comparison, A356 samples without the addition of SiCnps were also prepared by an equivalent process.

Metallographic samples were sectioned 51 mm from the bottom of the casting, and then ground with 400 grit, 800 grit, and 1200 grit emery papers in turn. Subsequently, the samples were polished and lightly etched using a 0.5% aqueous HF solution. In addition, samples were also deeply etched for 1, 2, or 3 h to reveal the three-dimensional (3D) morphology of the eutectic Si.

The morphology of the eutectic Si was characterized using optical microscopy (OM; Olympus MPG4, Tokyo, Japan) and scanning electron microscopy (SEM; FEI Nova NanoSEM 450, Hillsboro, USA) with energy dispersive X-ray spectroscopy (EDS; INCA X-Max, Oxford, UK). The dimensions of the distributed eutectic Si phase and the particle sizes of the SiCnps were evaluated from micrographs using Image-Pro Plus (6.0, Media Cybernetics, Rockville, MD, USA). X-ray diffraction (XRD; PANalytical X’Pert PRO, Almelo, The Netherlands) was used to analyze the crystalline phases of A356 and SiCnps/A356. Moreover, the interfaces between the SiCnps and the eutectic Si, and the distributions of SiCnps in the eutectic Si and primary α-Al regions were investigated using HRTEM (Tecani F30 G’, FEI, USA). Finally, DSC (STA 449F3, NETZSCH, Germany) was used to investigate the nucleation behavior of SiCnps/A356 samples processed by the droplet emulsion technique [27].

### 3. Results

Transmission electron microscopy (TEM) bright field images and the size distribution of the SiCnps are shown in Fig. 1(a) and (b), respectively. As such, the diameters of the SiCnps mainly ranged from 10 nm to 80 nm with an average diameter of about 40 nm.

The XRD patterns obtained for A356 and 2.0 wt% SiCnps/A356 samples are shown in Fig. 2(a) and (b), respectively. As can be seen from Fig. 2(a), the SiCnps/A356 sample includes three crystalline phases, namely Al, Si, and SiC.
Cross-sectional SEM micrographs were captured to more clearly reveal the morphology of the eutectic Si, as shown in Fig. 4. Here, Fig. 4 presents the overall cross-sectional morphologies of the A356 sample and the SiC<sub>nps</sub>/A356 samples with 0.5, 1.0, and 2.0 wt% SiC<sub>nps</sub>. These figures clearly reveal that the lengths of the eutectic Si microstructures are greatly decreased with increasing SiC<sub>nps</sub> content and the shapes of the eutectic Si are also modified significantly and approach an equiaxed microstructure. We note that the lengths of the eutectic Si in the 0.5 wt% SiC<sub>nps</sub>/A356 sample are reduced relative to those of the A356 sample, and the morphology of some of the eutectic Si have changed from a flake-like microstructure to a polygonal microstructure. However, most of the eutectic Si in the 0.5 wt% SiC<sub>nps</sub>/A356 sample retain a flake-like microstructure. With increasing SiC<sub>nps</sub> content from 0.5 wt% to 1.0 wt%, we note that the eutectic Si microstructure lengths become substantially reduced, and their length-to-width ratios (i.e., the aspect ratios) are also reduced. With further increase in the SiC<sub>nps</sub> content to 2.0 wt%, the lengths of eutectic Si microstructures are further reduced, and the shapes become nearly equiaxed. As such, the addition of SiC<sub>nps</sub> both refines and modifies the microstructure of the eutectic Si in A356.

The eutectic Si microstructure length and aspect ratio distributions of the A356 and SiC<sub>nps</sub>/A356 samples are presented in Fig. 5. We note that the average lengths of the eutectic Si microstructures are reduced slightly from 15 μm to 13.7 μm when introducing 0.5 wt% SiC<sub>nps</sub> into the A356 alloy, and that the change in the aspect ratio distribution of the eutectic Si microstructures is also slight. However, the addition of 1.0 wt% SiC<sub>nps</sub> into the A356 alloy substantially decreases the average eutectic Si microstructure length to 1.36 μm (Fig. 5(e)), and the aspect ratio distribution (Fig. 5(f)) is skewed to smaller values characteristic of a polygonal microstructure. Finally, we note from Fig. 5(g) that the refinement of the eutectic Si is very significant with the addition of 2.0 wt% SiC<sub>nps</sub>, where approximately 97% of the measured eutectic Si microstructures are less than 2 μm in length and their average length is 0.85 μm. Furthermore, the aspect ratio distribution (Fig. 5(h)) is further skewed to smaller values characteristic of a near-equiaxed microstructure.
SEM micrographs of samples etched for 3 h are presented in Fig. 6. We note that the 3D morphology of the eutectic Si in A356 is characterized by a large plate-like microstructure. Furthermore, some step-like formations are observed on the parallel platelets of the eutectic Si. These formations are representative of the layer growth behavior of the eutectic Si in A356 [6]. Comparing Fig. 6(a) and (b), we note that the morphology of a portion of the eutectic Si has transformed from platelets to block-like microstructures. However, the addition of 1.0 wt% SiC nanoparticles into the A356 alloy substantially alters the 3D morphology of the eutectic Si from relatively coarse platelets and blocks to a dendritic microstructure with some fine platelets (Fig. 6(c)). Finally, as can be seen from Fig. 6(d), the addition of 2.0 wt% SiC nanoparticles into the A356 alloy produces the eutectic Si phase with a strongly dendritic microstructure that is nearly characteristic of a fibrous morphology. The effect of the addition of SiC nanoparticles on the eutectic Si morphology may be related to a modification of the local diffusion behavior of the solute during crystal growth with the increasing addition of SiC nanoparticles. Hence, SiC nanoparticles make a difference in the growth of the eutectic Si.

To investigate the effect of SiC nanoparticles on the microstructure of the eutectic Si, we present SEM micrographs of 2.0 wt% SiC nanoparticles/A356 samples etched for 1 h and 2 h in Fig. 7(a) and (c), respectively. From Fig. 7(a) and (b), we note that layers of SiC nanoparticles are observable on the surfaces of the eutectic Si. The SiC nanoparticles on the surface of the eutectic Si can be distinguished clearly in Fig. 7(b), and the average particle size is about 100 nm. As such, the average particle size of SiC nanoparticles distributed on the surface of the eutectic Si is much greater than the average particle size of the original SiC nanoparticles (i.e., 40 nm [Fig. 1(b)]). Therefore, we confirmed the composition of the SiC nanoparticles layer by applying EDS analysis to the area marked “+” in Fig. 7(b), and the results are shown in Fig. 7(d). The EDS results indicate the presence of C, Mg, Si, and Al. Here, we note that Al and Mg are detected because the A356 alloy material is not completely dissolved during etching and C mainly derives from SiC nanoparticles. It confirms that the nanoparticles are SiC. This indicates that the SiC nanoparticles.
Fig. 4 – SEM micrographs of A356 with different SiC<sub>nps</sub> additions: (a) A356; (c) 0.5 wt% SiC<sub>nps</sub>/A356; (e) 1.0 wt% SiC<sub>nps</sub>/A356; (g) 2.0 wt% SiC<sub>nps</sub>/A356. In addition, (b), (d), (f), and (h) represent the areas marked in subfigures (a), (c), (e), and (g), respectively, at greater magnification.
Fig. 5 – Eutectic Si particle length distributions for A356 with different SiC<sub>nps</sub> additions: (a) A356; (c) 0.5 wt% SiC<sub>nps</sub>/A356; (e) 1.0 wt% SiC<sub>nps</sub>/A356; (g) 2.0 wt% SiC<sub>nps</sub>/A356. In addition, (b), (d), (f), and (h) represent the aspect ratio distributions of A356, 0.5 wt% SiC<sub>nps</sub>/A356, 1.0 wt% SiC<sub>nps</sub>/A356, and 2.0 wt% SiC<sub>nps</sub>/A356, respectively.
are not homogeneously distributed according to particle size throughout the matrix, and that SiC_{nps} with a much larger average particle size tend to reside at the interface between the eutectic Al and Si phase. This is an important finding that is discussed at much greater length in Section 4. Fig. 7(e) presents a high-magnification SEM micrograph of the edge of a eutectic Si, and the vicinity of the eutectic Si in the sample etched in short time. Here, we note that SiC_{nps} are adhered to the eutectic Si, and the cross-sectional morphology of the eutectic Si becomes nearly equiaxed. In addition, some SiC_{nps} are distributed in the vicinity of the eutectic Si. These results further suggest that SiC_{nps} distributed at the surface of the eutectic Si block the local diffusion of the solute, and lead to the modification and refinement of the eutectic Si.

Fig. 8 presents DSC solidification curves obtained at a cooling rate of 10 °C/min for the A356 and 2.0 wt% SiC_{nps}/A356 samples. Here, the observed extrema for the A356 sample are marked A, B, and C and those for the 2.0 wt% SiC_{nps}/A356 sample are marked A1, B1, and C1. As can be seen from the figure, no obvious endothermic and exothermic extrema occurred in two DSC curves below 540 °C. For the A356 sample, the onset temperature of the first exothermic peak A was 610 °C, the onset temperature, peak temperature, and ending temperature of peak B were 569.9 °C, 563 °C, and 552.1 °C, respectively, and the onset temperature, peak temperature, and ending temperature of peak C were 543 °C, 540.5 °C, and 538 °C, respectively. For the 2.0 wt% SiC_{nps}/A356 sample, the first exothermic peak A1 occurred with an onset temperature of 607.2 °C, which was followed by peaks B1 and C1, with peak temperatures of 555.6 °C and 535.5 °C, respectively. The onset and ending temperatures of peak B1 were 562.5 °C and 549.4 °C, respectively, while the onset and ending temperature of peak C1 was 540.4 °C and 533 °C, respectively.

The temperature ranges and peak features for the two samples given in Fig. 8 indicate that the extrema given by A and A1 correspond with the solidification of α-Al, while the extrema
Fig. 7 – (a) and (c) are SEM images of the eutectic microstructures in 2 wt% SiC<sub>nps</sub>/A356 samples deep-etched for 1 h and 2 h respectively. (b) Magnified from the area marked as the rectangle in (a) shows the morphology of the eutectic microstructures. (d) The EDS results of the area marked with “+” in (b). (e) The SEM image of the eutectic Si edge and the vicinity of the eutectic Si in 2 wt% SiC<sub>nps</sub>/Al composites etched in short time.
Fig. 8 – DSC solidification curves obtained at a cooling rate of 10 °C/min for the A356 alloy (with extrema marked A, B, and C) and the A356 alloy with the addition of 2.0 wt% SiC\textsubscript{nps} (with extrema marked A1, B1, and C1). The extrema marked A and A1 represent the solidification of primary Al dendrites. The extrema marked B and B1 represent the solidification of the binary Al–Si eutectic at the α-Al grain boundaries. The extrema marked C and C1 represent the solidification of binary Al–Si eutectic droplets in the interior of α-Al grains.

given by B, C and B1, C1 correspond with the solidification of the Al–Si eutectic. Here, the extrema given by B and B1 correspond with the solidification of the binary Al–Si eutectic at the α-Al grain boundaries, while the extrema given by C and C1 correspond with the solidification of Al–Si eutectic droplets in the interiors of the α-Al grains. A comparison of the DSC curves of the two samples indicate that the onset, peak, and ending temperatures of extremum B1 for the 2.0 wt% SiC\textsubscript{nps}/A356 sample were less than those of extremum B for the A356 sample. In addition, the onset, peak, and ending temperatures of extremum C1 for the 2.0 wt% SiC\textsubscript{nps}/A356 sample were also less than those of extremum C for the A356 sample. Undercooling (ΔT) is defined as the difference between the onset temperatures corresponding with the solidification of the Al–Si eutectic at the α-Al grain boundaries and the solidification of Al–Si eutectic droplets in the interiors of the α-Al grains. As such, ΔT represents the extent of undercooling required to nucleate the eutectic Si microstructure during solidification. Accordingly, we obtain ΔT values of 26.9 °C for the A356 alloy and 22.1 °C for the 2.0 wt% SiC\textsubscript{nps}/A356 sample. As such, the value of ΔT for the SiC\textsubscript{nps}/A356 sample is considerably less than that of the A356 alloy. This indicates that the addition of SiC\textsubscript{nps} leads to a decreased extent of undercooling required to nucleate the eutectic Si microstructure in the 2.0 wt% SiC\textsubscript{nps}/A356 sample.

HRTEM analyses were applied to further evaluate the effect of SiC\textsubscript{nps} on the microstructure of the eutectic Si. Fig. 9 shows a series of HRTEM images obtained from A356 with the addition of 2.0 wt% SiC\textsubscript{nps}. Fig. 9(a) shows that SiC\textsubscript{nps} are distributed uniformly in the α-Al and eutectic area, and that the particle sizes of SiC\textsubscript{nps} distributed in the α-Al are smaller than those in the eutectic area. These results contrast sharply with average particle size of SiC\textsubscript{nps} at the eutectic Si/Al interface, which serves as another important finding that is discussed at much greater length in Section 4. As can be seen from Fig. 9(b), a significant number of multiple Si twin crystals are formed within the eutectic Si. And nanoparticles are distributed at the eutectic Si/Al interface and in the eutectic Si. This is further illustrated by the magnified image of the eutectic Si shown in Fig. 9(c), where a number of SiC\textsubscript{nps} and Si micro-twin crystals are observed. The high-density Si micro-twin crystals are parallel to each other and grow along the <112> growth direction of Si, which is marked with white arrows in Fig. 9(c). The SiC\textsubscript{nps} are distributed along the <112> growth direction of Si, which is marked by white dashed lines with the growth direction indicated by the arrow in Fig. 9(c). Furthermore, some SiC\textsubscript{nps} give rise to line defects within the eutectic Si. The role played by SiC\textsubscript{nps} in the eutectic Si can be further evaluated by the HRTEM image in Fig. 9(d) of the area marked by the white box in Fig. 9(c). Here, we note that the Si micro-twin crystals originate at, or very near, the interface between the nanoparticle and the eutectic Si. These micro-twins are parallel to each other and grow along the <112> growth direction of Si. The EDS analysis of SiC\textsubscript{nps} in the eutectic Si is shown in Fig. 9(e). Accordingly, we note the presence of only C and Si in the area. In combination with the HRTEM images, these results indicate that the C signal mainly derives from SiC\textsubscript{nps} in the eutectic Si.

4. Discussion

The results presented indicate that the addition of SiC\textsubscript{nps} has a vital effect on the nucleation and growth of the eutectic Si. However, to understand this effect, we must first discuss the factors affecting the distribution of SiC\textsubscript{nps} based on the interaction mechanism between SiC\textsubscript{nps} and the solidification front (SF) of the alloy.

The impact of Brownian motion on the distribution of particles becomes increasingly significant as the size of the particles approaches the nanoscale, and a critical size is eventually reached where nanoparticles are dominated by Brownian motion, which then maintains a uniform distribution of nanoparticles within a molten alloy. Therefore, determining the critical size of nanoparticles is essential for evaluating the distribution of SiC\textsubscript{nps}. Based on a consideration of both Stokes’ law and Brownian motion in the settling of nanoparticles in molten alloys, Schultz et al. [28] developed the following expression for the critical radius of nanoparticles (R\textsuperscript{*}):

\[
R^* = \left[ \frac{27}{8\pi \mu m_p v_p} \right]^{1/5} \left( \frac{\rho_p \rho_f}{\rho_f - \rho_p} \right) \frac{1}{g} \text{.}
\]

Here, C is a shape-dependent constant that is assumed typically to be C = 1, \( \rho_p \) and \( \rho_f \) are the densities of the SiC\textsubscript{nps} and the molten alloy respectively, \( \mu \) is the viscosity of the molten alloy, \( m_p \) is the mass of the molten alloy particles, \( v_p \) is the velocity of the molten alloy particles based on the temperature \( T \) and Boltzmann’s constant \( k_B \) (i.e., \( v_p = \sqrt{2k_B T/m_p} \)), and \( g \) is the constant of gravitational acceleration. These parameters for the SiC\textsubscript{nps}/A356 system are listed in Table 2, and the value of R\textsuperscript{*} can be calculated accordingly from Eq. (1). For SiC\textsubscript{nps} in
Fig. 9—HRTEM bright field images of the 2.0 wt% SiC<sub>nps</sub>/A356 sample showing the distribution of SiC<sub>nps</sub> on the α-Al and eutectic area (a), multiple twinned Si crystals and SiC<sub>nps</sub> (b), and SiC<sub>nps</sub> within a micro-twinned Si crystal (c). (d) HRTEM image and (e) EDS analysis of the area marked by the white box in (c).

where \(v\) and \(R\) are the velocity and radius of the nanoparticle, respectively. The repulsive force exerted by the SF on nanoparticles can be expressed as follows [30]:

\[
F_{vdw} = \frac{|A|}{3} \frac{2R^3}{D^2(D + 2R)^2},
\]

(3)
Table 2 – Parameters for the calculation of the critical nanoparticle radius based on Eq. (1) [28,31,32].

<table>
<thead>
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<th>Unit</th>
<th>Value</th>
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<td>μ</td>
<td>Pa s</td>
<td>(1 \times 10^{-7}) (Al); (5 \times 10^{-4}) (Si)</td>
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<tr>
<td>(m_p)</td>
<td>kg</td>
<td>(4.48 \times 10^{-26}) (Al); (4.68 \times 10^{-26}) (Si)</td>
</tr>
<tr>
<td>(\rho_v)</td>
<td>kg/m³</td>
<td>3220</td>
</tr>
<tr>
<td>(\rho_f)</td>
<td>kg/m³</td>
<td>2700 (Al); 2320 (Si)</td>
</tr>
<tr>
<td>(\kappa)</td>
<td>J/K</td>
<td>1.38054 \times 10^{21}</td>
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<tr>
<td>γ</td>
<td>kg m/s²</td>
<td>9.8</td>
</tr>
<tr>
<td>T</td>
<td>K</td>
<td>1023</td>
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</table>

Table 3 – Parameters for the calculation of the critical nanoparticle velocity based on Eqs. (4) and (5) [31,32].

<table>
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<th>Unit</th>
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<th>Value (Si)</th>
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<tr>
<td>A</td>
<td>(J)</td>
<td>(-1.09 \times 10^{-21})</td>
<td>(-1.22 \times 10^{-21})</td>
</tr>
<tr>
<td>(D_{v})</td>
<td>nm</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>D</td>
<td>nm</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(a_0)</td>
<td>nm</td>
<td>0.286</td>
<td>0.117</td>
</tr>
<tr>
<td>α</td>
<td></td>
<td>0.35</td>
<td>0.56</td>
</tr>
<tr>
<td>(A_{\gamma 0})</td>
<td>J/m²</td>
<td>0.85</td>
<td>2.02</td>
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</table>

where \(\Delta \gamma_0\) is the interfacial energy between the solid and liquid phase in the molten alloy, \(a_0\) is the atomic diameter of the matrix, and \(\alpha\) is the thermal conductivity ratio between the nanoparticle and the solid-liquid interface. These parameters for the SiC\(_{nps}/\)Al–Si system are listed in Table 3, and the values of \(v_c\) can be calculated accordingly from Eqs. (4) and (5).

Fig. 10(a) and (b) shows the dependence of \(v_c\) on \(R\) for SiC\(_{nps}\) based on the parameters listed in Table 3 for \(\alpha\)-Al and the eutectic Si, respectively. For \(R < R^*\), \(v_c\) increases with increasing \(R\). However, for \(R \geq R^*\), \(v_c\) decreases with increasing \(R\). For the current work, the velocity of a dendrite (\(V_D\)) is determined to be \(0.38 \text{ mm/s} [20]\), which is shown by the dashed line in Fig. 10(a). Accordingly, SiC\(_{nps}\) with radii resulting in \(v_c\) values less than \(V_D\) tend to be trapped within the \(\alpha\)-Al area by the SF. From the HRTEM results shown in Fig. 9, we know that the value of \(R\) for SiC\(_{nps}\) in the \(\alpha\)-Al about 10 nm, which is consistent with this theoretical analysis. In contrast, SiC\(_{nps}\) with larger radii resulting in \(v_c\) values greater than \(V_D\) tend to move ahead of the SF, and therefore tend to move into the eutectic area, owing to its lower solidification temperature, or become trapped at the \(\alpha\)-Al/eutectic interface upon complete solidification. This is consistent with the observation in Fig. 9 that the average particle size of SiC\(_{nps}\) in the eutectic area was greater than that in the \(\alpha\)-Al. We must also consider the interface velocity during eutectic solidification, which can be calculated for unmodified hypoeutectic Al–Si alloys based on the extent of undercooling (\(\Delta T\)) as follows [33]:

\[
v_c (\mu \text{m/s}) = 0.041 \Delta T^4.
\] (6)

According to the results in Fig. 8, the measured value of \(\Delta T\) for the 2.0 wt% SiC\(_{nps}/\)Al–Si sample in this study was 4.8 K, and \(v_c\) varies accordingly 21.76 \(\mu\)m/s. Wang [22] reported that the interactions between nanoparticles and the SF in Al–Si alloys are equally applicable in the case of eutectic growth. Therefore, Fig. 10(b) shows the dependence of \(v_c\) on \(R\) for the eutectic Si, where \(V_c\) is represented by the dashed line in the figure. The basic trends of the curve are similar to that shown in Fig. 10(a) for the \(\alpha\)-Al. According to the inset in Fig. 10(b) showing the variation in \(v_c\) over small \(R\), nanoparticles with a value of \(R\) less than about 25 nm have a value of \(v_c\) that is less than or equal to \(V_c\). Therefore, these nanoparticles will tend to be engulfed in the eutectic Si. From the HRTEM results shown in Fig. 9, we know that the value of \(R\) for SiC\(_{nps}\) in the eutectic Si area ranges from 5 nm to 20 nm, which is consistent with this theoretical analysis. Finally, Fig. 10(a) and (b) indicate that nanoparticles...
with R values around 30–60 nm tend to move ahead of both the SF in the α-Al phase and the eutectic Si phase, and therefore become trapped at the eutectic Si/Al interface after solidification, which is consistent with the results presented in Fig. 7.

According to the results given and the above discussion, we can analyze the process by which SiC\textsubscript{nps} bring about the modification and refinement of the eutectic Si microstructure by inhibiting the growth and stimulating the nucleation of the eutectic Si according to the illustration given in Fig. 11. The distribution of SiC\textsubscript{nps} in the illustration is closely related to the evolution of the morphology of the eutectic Si. Beginning with the fully distributed SiC\textsubscript{nps}/the eutectic Si system in Fig. 11(a), the effects of SiC\textsubscript{nps} on the nucleation and growth of the eutectic Si are accordingly discussed separately as follows.

4.1 Effect of SiC nanoparticles on the nucleation of the eutectic Si

Considering the reduced nucleation undercooling of the eutectic after the addition of SiC\textsubscript{nps} (Fig. 8) and the distribution of SiC\textsubscript{nps} in the eutectic Si (Fig. 9), SiC\textsubscript{nps} at the center of the eutectic Si are likely to act as nucleation sites, as shown in Fig. 11(b). According to the free growth model [23], the undercooling required for grain initiation can be given as follows:

$$\Delta T_{fg} = \frac{4\sigma_b}{\Delta S_v d},$$

where the solid–liquid interfacial energy is given as $\sigma_b = 0.352$ J/m$^2$, the entropy of fusion per unit volume is given as $\Delta S_v = 7.3 \times 10^6$ J/K m$^3$ [23], and $d$ is the particle diameter. Therefore, $\Delta T_{fg} = 4.8$ K when $d = 40$ nm. This result is consistent with the value of $\Delta T$ measured by DSC in the present work. Furthermore, good crystallographic matching between nanoparticles and the eutectic Si is a necessary condition for nanoparticles serving as nucleation sites. The crystallographic matching at an Si/SiC interface of the 2.0 wt% SiC\textsubscript{nps}/A356 sample is examined in Fig. 12(a). In addition, the selected area diffraction pattern of the interface is shown in the inset of Fig. 12(a), where the SiC\textsubscript{nps} and eutectic Si lattices are identified using white and red lines, respectively. The results demonstrate a cube-on-cube orientation relationship between the eutectic Si and SiC\textsubscript{nps} lattices, with an orientation relationship of $\langle 111 \rangle_{Si}[011]_{Si}/\langle 111 \rangle_{SiC}[2 \ 1 \ 3]_{SiC}$. The lattice spacing mismatch between $<011>_{Si}$ on $\langle 111 \rangle_{Si}$ and $<213>_{SiC}$ on $\langle 111 \rangle_{SiC}$ is $\delta = 10.4\%$. This small value of $\delta$ demonstrates that SiC\textsubscript{nps} have excellent potential for serving as heterogeneous nucleation sites for the eutectic Si during eutectic solidification. In addition, the absence of an interfacial product in Fig. 12(a) indicates that very good bonding occurs between SiC\textsubscript{nps} and the eutectic Si. Finally, Fig. 12(b) indicates that the lattice mismatch between SiC\textsubscript{nps} and the eutectic Si is alleviated by the generation of dislocations at the Si/SiC\textsubscript{nps} interface.

4.2 Effect of SiC nanoparticles on the growth of the eutectic Si

As discussed previously, relatively large SiC\textsubscript{nps} that move ahead of the SF tend to be distributed in either the eutectic Al or at the eutectic Si/Al interface during the solidification of the eutectic microstructure. When the SiC\textsubscript{nps} are distributed in the eutectic Al, the Gibbs free energy is given as:

$$\Delta G_1 = S_{SiC-Al},$$

(8)

where $S$ is the surface area of the SiC\textsubscript{nps} and $\sigma_{SiC-Al}$ is the interfacial energy between SiC\textsubscript{nps} and Al, which is given as 0.81 J/m$^2$ [32]. When the SiC\textsubscript{nps} are distributed at the eutectic Si/Al interface, the Gibbs free energy is given as:

$$\Delta G_2 = S_{Si-\text{SiC}}\sigma_{Si-Al} + S_{Si-\text{SiC}}\sigma_{Si-C} - S_{Si}\sigma_{Si-Al},$$

(9)

where $\sigma_{Si-Al}$ and $\sigma_{Si-C}$ are the contact areas between the SiC\textsubscript{nps} and Al and between the SiC\textsubscript{nps} and Si, respectively, and $\sigma_{Si-C}$ and $\sigma_{Si-Al}$ are the interfacial energies between SiC\textsubscript{nps} and Si (i.e., 1.26 J/m$^2$ [33]) and between Si and Al (i.e., 0.479 J/m$^2$ [34]), respectively. Based on the above parameters, we note that the calculated value of $\Delta G_2$ is less than that of $\Delta G_1$, indicating that the system is more stable if the SiC\textsubscript{nps} are
distributed at the eutectic Si/Al interface. As such, the relatively large SiC\textsubscript{nps} that move ahead of the SF would tend to distribute at the eutectic Si/Al interface, and thereby hinder the diffusion of the solute atoms and inhibit the growth of the eutectic Si, as illustrated in Fig. 11(c). The factor would then lead to a transformation of the microstructure of the eutectic Si from a flake-like to a near-equiaxed microstructure (Fig. 4) and the refinement of the eutectic Si (Fig. 5).

Accordingly, SiC\textsubscript{nps} lead to the modification and refinement of the eutectic Si by the processes of eutectic Si growth blockage and the nucleation of the eutectic Si on SiC nanoparticles. In addition, some SiC\textsubscript{nps} are engulfed by the SF and distributed in the eutectic Si, as shown in Fig. 11(c). The eutectic Si crystals are extended in the $<112>$ direction only. However, SiC\textsubscript{nps} engulfed by the SF alter the stacking sequence of Si atoms during crystal growth, and a new stacking fault is formed with an equivalent $<112>$ direction to restore the original stacking sequence. Hence, multiple Si micro-twin variants are observed, which are parallel to each other in the growth direction of the eutectic Si. This analysis is consistent with the restricted TPRE growth mechanism. These Si micro-twin variants may be related to the morphology of the eutectic Si shifting from flake-like to block-like, and finally to a fibrous microstructure.

5. Conclusions

The present work demonstrated that the addition of 0.5–2.0 wt\% SiC\textsubscript{nps} can induce the modification and refinement of the eutectic Si in Al–Si alloys, and that the effect becomes increasingly significant with an increasing concentration of SiC\textsubscript{nps}. The results and the analysis presented verified that the modification and refinement of the eutectic Si is closely related to the interaction between the SiC\textsubscript{nps} and the SF. When the particle size of the SiC\textsubscript{nps} is greater than the critical size, the SiC\textsubscript{nps} tend to move ahead of the SF, while smaller SiC\textsubscript{nps} tend to be engulfed. The SiC\textsubscript{nps} moving ahead of the SF hinder the growth of the eutectic Si by the formation of an SiC\textsubscript{nps} layer coating its surface. In addition, the SiC\textsubscript{nps} can act as heterogeneous nucleation sites for the eutectic Si. Ultimately, the modification and refinement of the eutectic Si is caused collaboratively by a combination of the above two effects of SiC\textsubscript{nps} addition. Furthermore, the SiC\textsubscript{nps} engulfed by the SF cause the formation of Si crystal twins in the eutectic Si.

Data availability

The raw data required to reproduce these findings are available to download from https://doi.org/10.17632/nmj7d4j9d8.1.

Conflicts of interest

The authors declare no conflicts of interest.

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