PREPARATION AND PROPERTY OF NANO-SIC\textsubscript{p}/A356 COMPOSITES SYNTHESIZED WITH A NEW PROCESS

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ABSTRACT

Nano-SiC particles reinforced A356 aluminum alloy composites were prepared by molten-metal process, combined with high energy ball milling and ultrasonic vibration methods. The nano particles were $\beta$-SiC\textsubscript{p} with an average diameter of 40nm, and pre-oxidized at about 850$^\circ$C to form an oxide layer with thickness of approximately 4nm. The millimeter sized composite granules containing nano-SiC\textsubscript{p} were firstly produced by milling the mixture of oxidized nano-SiC\textsubscript{p} and pure Al powders, and then were remelted in the matrix-metal melt with mechanical stirring and treated by ultrasonic vibration to prepare the composite. The SEM analysis results show that SiC nanoparticles are dispersed well in the matrix and no serious agglomeration is observed. The tensile strength and elongation of the composites are increased with the increase of reinforcement fraction of SiC\textsubscript{p}, and 2wt.% nano-SiC\textsubscript{p} are improved by 19.5% and 43.5% respectively compared with the A356 alloy

1 INTRODUCTION

Metal matrix composites (MMCs) with ceramic particles as reinforcement have high specific strength, high specific stiffness, superior wear resistance, desirable thermal expansion and better dimensional stability than their matrix\cite{1-4}. It is believed that MMCs with micron-scale particles would have low ductility, and nano-scale particles reinforced MMCs, termed as MMNCs, the ductility would be enhanced considerably even with a very low volume fraction of nano particles\cite{5-7}. Hence MMNCs have gained widespread attention in scientific research and commercial application because of the demands for lightweight, high-modulus, and high-strength materials\cite{7-10}.

MMNCs are generally produced by two major methods, the solid state method and the liquid casting method. Usually the fabrication process of the solid state method has a high cost\cite{7, 11, 12}. In the liquid method the way to produce MMNCs is economical, in which reinforced particles are added directly to liquid alloy by stirring and casting\cite{13}. But the key issues during adding nano-sized ceramic particles into molten metal are wettability and dispersion. The wettability between nano-particles and the molten metal is very poor due to a much higher specific surface area for nano-particles. Therefore it is difficult to add nano-particles into molten metal with common stirring method. Solid-liquid mixed casting is a casting method in which alloy powders with good wettability are added to the melt with mechanical stirring to fabricate high alloy material ingots. This kind of method is proved to be feasible to fabricate MMCs by preparing composite granules which are made of ceramic particles and alloy powders with good wettability through mechanical alloying. Ceramic particles are considered as alloy element when the casting method is applied to the fabrication of MMCs\cite{14} and the weight fraction of reinforcement could reach 5%\cite{15} with micron-sized reinforcement. Su et al.\cite{16} used aluminum powders as the carrier agent to fabricate 0.6%Al$_2$O$_3$/Al2024 composites. Mechanical alloying was achieved by ball-milling of which stearic acid was used as the process control agent(PCA) and resulted in composite granules with diameter...
smaller than 100μm. Then mechanical stirring, which is similar to the fabrication process of the composites reinforced by micron-sized particles, is used to add the composite granules to the melt and fine dispersion of Al₂O₃ particles was achieved. There is a problem when solid-liquid mixed castings works with MMNCs that the size of composite granules would decrease rapidly during the melting process of pure Al and traditional mechanical stirring is useless in dispersing particles in the melt uniformly on the macro level when the size of composite granules becomes too small. As a result, the content of reinforcement in MMNCs is limited and other new process for better dispersion is required.

In this work, Al MMNCs reinforced by dispersed SiC nanoparticles were fabricated by the process combined solid-liquid mixed casting and high-intensity ultrasonic vibration (UV). The mechanical alloying between SiCₚ and pure Al powders was achieved by high energy ball-milling (HBM) without PCA. The millimeter sized composite granules, rather than micron-sized granules, were fabricated, and UV treatment was introduced to disperse the small agglomerations formed by the structures which exists due to the completely melting of composite granules. The microstructure and mechanical properties of SiCₚ/A356 were also studied to understand the effect of nanoparticles in as-cast composites.

2 EXPERIMENTAL PROCEDURES

The matrix material was A356 alloy, with compositions of 7%Si, 0.3%Mg, 0.19%Fe and balanced Al. The reinforcements were β-SiC particles with average diameter of 40nm. Pure aluminum powders for preparing composite granules had an average diameter of 30μm. There were two main procedures of the experiment, HBM for fabrication of nano-SiCₚ/Al composite granules and solid-liquid mixed casting to fabricate MMNCs.

The pretreatment of nano-SiCₚ was calcination at 850°C for 2h, removing the impurities and gas on the surface of nano-SiCₚ and forming a compact oxidation film. Then nano-particles were mixed with pure Al powders with weight fraction of 6% to fabricate nano-SiCₚ/Al composite granules by dry HBM without PCA. The mixture of nano-SiCₚ and pure Al powders was milled in a QM-3SP4 planetary mill filled by stainless steel balls with diameter of 10mm at room temperature after the milling vessels was vacuumized. Rotation speed of the mill was kept about 150 rpm for 5h, 200 rpm for 15h and 300rpm for 5h. Ball-to-powder weight ratio was 5:1.

A balanced amount of Al-24.5Si, pure Al and pure Mg blocks were melted in a graphite crucible. The SiCₚ/Al composite granules were preheated at 250°C before adding into the melt. When the alloy was completely melted, the melt was cooled down to 680°C and mechanical stirring was applied and preheated SiCₚ/Al composite granules were added into the stirring vortex. The stirring speed was 250 rpm and the stirring was kept up for 10min after SiCₚ/Al composite granules were added to the melt completely. When the stirring process was over, the melt was heated up to 720°C and hold for 30min. In order to disperse SiC nano-particles in the melt, ultrasonic vibration with a 20 kHz, maximum 2.8 kW power output and a titanium alloy horn with 20 mm in diameter was introduced into the melt and kept for 3min. After ultrasonic vibration processing, the composite melt was cast into a permanent steel mould which was preheated to 250°C.

The tensile tests for unreinforced A356 and nanocomposites specimens were done with a SHIMATSU AG-iC100KN tester at strain rate of 1 mm/min at room temperature, and the diameter and gauge length of samples are 6 mm and 30 mm, respectively. The distribution of the SiC nanoparticles were investigated with a DMM-480C optical microscopy (OM), a JEOL JSM-7600F scanning electron microscopy (SEM), JEM2100(TEM). The samples were mechanical polished and etched using a solution with 0.5%vol. HF for 10 seconds.

3 RESULTS AND DISCUSSION

3.1 Microstructures of pretreated SiCₚ

High temperature is required for the casting process of composite slurry during the stir-casting. But it would increase the possibility of the reaction between SiCₚ and matrix aluminum to form Al₄C₃, as shown in Fig. 1. It is known that mechanical properties of SiC will be degraded due to the formation of Al₄C₃, and Al₄C₃ is unstable in some environments such as water, methanol, HCl, etc[17-18].
Artificial oxidation of SiC to produce a SiO₂ layer on the surface of SiC has been proven to be effective in preventing the reaction. Investigation on SiCₚ oxidation at elevated temperatures shows that the oxidation increment of SiCₚ, the dependence of the volume fraction and that of the thickness of SiO₂ layer on temperature are both parabolic [19]. Considering the SiCₚ as regular spheres, the thickness of the SiO₂ layer defined as d could be estimated by Equations (1) and (2), where \( R_1 \) is the average radius of SiCₚ before pretreatment, \( R_3 \) is the average radius of SiCₚ after pretreatment, \( R_2 \) is the average radius of a hypothetic sphere formed by the remaining part of pre-treated spheres with the exception of the SiO₂ layer, m and \( m' \) are the weight of SiCₚ before and after pretreatment respectively, and \( \Delta w = m' - m \), d=\( R_3 - R_2 \).

\[
V_{SiO2} = \frac{4}{3} \pi (R_3^3 - R_2^3) \rho_{SiO2} \frac{\Delta w}{\Delta w} = \frac{3 \Delta w}{\rho_{SiO2}}
\]

\[
\frac{4}{3} \pi R_2^3 \rho_{SiC} + \frac{4}{3} \pi (R_3^3 - R_2^3) \rho_{SiO2} = \frac{m'}{m} \pi R_1^3 \rho_{SiC}
\]

The density of β-SiC and amorphous state SiO₂ are 3.16g/cm³ and 2.196g/cm³ respectively. \( R_1 \), the average radius of nano-SiCₚ, is 20nm. The thickness of pre-treated SiCₚ under different pretreatment are shown in the curve of Fig. 2.

When the holding time is 2h at 850°C the thickness of SiO₂ layer is about 4nm, which is consistent with the result of TEM shown in Fig. 3b.

![Fig. 1 SEM microstructures of nano-SiCₚ/A356 composites with Al₄C₃ resulted from reaction of un-pretreated nano-SiCₚ with Al melt](image1)

![Fig. 2 Correlation of oxidation thickness and time of SiCₚ during oxidation at 800, 850, 900°C](image2)

![Fig. 3 TEM images of SiCₚ after pretreatment at low (a) and high (b) magnification](image3)

3.2 Morphologies and microstructures of the SiCₚ/Al composite granules
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Fig. 4 shows the appearance of the composite granules which have an average diameter of 2mm. The ball milling was taken between ductile (pure Al powder) material and brittle material (nano-SiC particles) and consisted of 3 stages[20]. In the first stage micro-forging existed between Al powders and grinding balls. The Al powders were broken into cakes and slices while the nano-SiCp was stable on this ball milling condition. Then lamellar structure would be formed by the slice-shape Al and nano-SiCp while the eaky Al would be transformed and broken further. The distribution of SiCp was concentrated on the junctions between two lamellar structures. The nano-SiCp would adhere to the surfaces of the Al powders during the ball milling gradually in this stage. In the final stage microcosmic routes for diffusion would exist due to the crystal defects produced by plastic deformation and finally the mechanical alloying of nano-SiCp and pure Al was achieved. At the same time repeated welding, fracturing and rewelding of lamellas structures would take place due to the heating effect and bending deformation brought by the plastic deformation.

Fig. 4 Morphologies of the composites granules with 6 wt.% nano-SiCp

Compared with the long work period of mechanical alloying between Al and SiCp, the welding of the Al lamellas conduct much more easily due to the high ductility of pure Al and large heating effect of plastic deformation. As a result that some SiCp were captured by the composite granules in agglomerations, as shown in Fig. 5a. The dispersion of nano-SiCp in the composite granules has significant influence on the dispersion and mechanical properties of the final MMNCs. When one-stage HBM were used to fabricate granules, serious agglomeration occured in composite granules and could hardly be broken up by the UV process afterwards. To solve this problem a three-stages HBM process was choosen to make sure that the process of mechanical alloying and the welding of the Al lamellas complete respectively. The final SiCp were dispersed uniformly in composite granules as shown in Fig. 5b.

Fig. 5 SEM microstructures of the composite granules:(a) one-stage HBM with 300rpm 15h,
(b) three-stages HBM with 150rpm 5h, 200rpm 15h and 300 5h

3.3 Microstructure of the nano-SiCp/A356 composites
After the composite granules added into the melt nano-SiC<sub>p</sub> would diffuse in the melt along with the fusion of composite granules and mechanical stirring. But mechanical stirring would become incapable of dispersing the nanoparticles in the melt since the size of composite granules became smaller during the melting process. A kind of areas, as shown in Fig. 6, occur due to the pre-dispersion effect brought by the HBM. In this kind of areas the orientation and size of the crystalline grains were quite different from the others. The content of SiC<sub>p</sub> was much higher and dispersed well in the areas. But the size of these areas were too small for the whole specimen and were considered as small agglomerations which might lead to the non-uniformity of MMNCs. UV process was taken to broken up these agglomerations by the combination of transient cavitations and acoustic streaming.

![Fig. 6 Agglomeration block of nanocomposite without UV at low (a) and high (b) magnification](image)

The dispersion of SiC nanoparticles of different weight percentage in the aluminum matrix was examined by SEM, as shown in Fig. 7. Microstructural studies conducted on the composites specimens show uniform distribution of SiC particles, and even the small agglomerations mentioned above could not be found in the samples containing different weight percentage of SiC nanoparticles.

![Fig. 7 Microstructure of SiC<sub>p</sub>/A356 with different reinforcement fraction (a)0.5wt%SiC<sub>p</sub>/A356; (b) 1.0wt% SiC<sub>p</sub>/A356;(c) 2wt% SiC<sub>p</sub>/A356](image)
It is generally recognized that most of SiC\(_p\) would be distributed in the eutectic region due to the low wettability between SiC\(_p\) and molten Al [21] except only a small part of SiC\(_p\) can be captured by the growing solid \(\alpha\)-Al phase. As shown in Fig. 8a, SiC\(_p\) distributed in eutectic region spontaneously agglomerate into clusters of 100-200 nm in size due to the long duration of the solidification of eutectic region. The size of the SiC\(_p\) clusters is acceptable and the distribution of SiC\(_p\) is fine as a whole. There are SiC\(_p\) in abundance distributed in \(\alpha\)-Al are found. And this kind of distribution as shown in Fig. 8b may be attributed to the reaction between SiO\(_2\) layer and \(\alpha\)-Al, and further research of TEM is required to confirm the interface combination status.

![Fig. 8 SEM microstructures of MMNCs with UV: (a) eutectic region, (b) inner primary \(\alpha\)-Al phase](image)

### 3.4 Mechanical properties of the nano-SiC\(_p\)/A356 composites

The results of room temperature mechanical properties are given in Table 1. In order to make a comparison, the mechanical properties of the alloy only with ultrasonic processing are also listed in Table 1. It can be seen that SiC nanoparticles bring out good strengthening effects to aluminium alloy except 0.5%SiC/A356 due to the low content of reinforcement led to the non-uniformity of the MMNCs. For unreinforced A356 alloy with UV, the mechanical properties were also improved.

<table>
<thead>
<tr>
<th>Materials</th>
<th>(\sigma_b/\text{MPa})</th>
<th>(\delta/%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A356 alloy (without UV treatment)</td>
<td>189</td>
<td>3.9</td>
</tr>
<tr>
<td>A356 alloy</td>
<td>197</td>
<td>4.2</td>
</tr>
<tr>
<td>0.5%SiC/A356</td>
<td>200</td>
<td>5.0</td>
</tr>
<tr>
<td>1%SiC/A356</td>
<td>213</td>
<td>5.1</td>
</tr>
<tr>
<td>2%SiC/A356</td>
<td>226</td>
<td>5.5</td>
</tr>
</tbody>
</table>

As compared to the A356 aluminium alloy matrix, the tensile strength and elongation of the 2.0wt.%SiC/A356 nanocomposites were improved by 19.5% and 43.5% respectively in permanent mold casting. The higher tensile strength could be attributed to the fact that SiC particles act as obstacles to the motion of dislocation and good distribution of the nano-SiC particles and low degree of porosity lead to effective transfer of applied tensile load to the uniformly distributed SiC particulates. On the other hand, nano-SiC particles have grain-refined strengthening effect, which is improved with increasing weight fraction since they could hinder the growth of \(\alpha\)-Al grains as shown in Fig. 9 clearly, and results in the increase of the tensile strength and ductility of MMNCs.
4 CONCLUSIONS
1. The millimeter sized composite granules containing nano-SiC$_p$ were prepared by HBM, and can be used in a process of solid-liquid mixed casting to fabricate SiC$_p$/A356 composites. These composite granules with good wettability against Al alloy melt are considered as the carrier agent to make sure that nano-SiC$_p$ could be added into Al alloy melt smoothly.
2. SiC nanoparticles are dispersed well in the matrix and no serious agglomeration is observed by cooperation of ultrasonic vibration process for the composite melt.
3. The tensile strength and elongation of the composites are increased with the increase of reinforcement fraction of SiC$_p$, and with 2wt.% nano-SiC$_p$ they are improved by 19.5% and 43.5% respectively compared with the A356 alloy.

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