Using friction stir processing to fabricate Mg based composites with nano fillers

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Abstract. There have been numerous methods in fabricating particulate reinforced metallic matrix composites, including stir casting, squeeze casting, spray forming, powder metallurgy, and mechanical alloying. In this paper, one solid state processing technique, friction stir processing, is applied to incorporate 5-15 vol% nano-sized ceramic particles SiO2 into the AZ61 Mg alloy matrix to form bulk composites, using the characteristic rotating downward and circular material flow around the stir pin. The upper working FSP temperature is controlled to less than 400°C in order to avoid chemical reaction. The fixed pin tool is 6 mm in diameter and 6 mm in length, with a shoulder diameter of 18 mm and a 3° tilt angle. The advancing speed of the rotating pin is kept constant to be 45 mm/min, with rotational speed of the pin from 800 rpm (rotation per min), resulting in a strain rate around 10⁴ s⁻¹. After one-pass FSP, the particle dispersion within the central cross-sectional area of the onion ring regions, measuring nearly 6 mm in diameter, was macroscopically uniform. However, the observed particle size is frequently 0.5-5 µm, much larger than the individual SiO2 size (~20 nm), suggesting the clustering of nano particles. The situation after two FSP passes, with an opposite FSP direction for the second pass, appear to be further improved. Electron microscopy characterizations reveal that the aggregating particles were seen to vary from 10 to 1000 nm in size. Some of the large particles, 1-5 µm in diameter, were identified to be the Mn bearing dispersoids (e.g. Al₄Mn) by the SEM-EDS. The average grain sizes of the composites with 5-15 vol% SiO₂ varied within 0.5-2 µm, and the composites double the hardness as compared with the as-received AZ61 cast billet.

Introduction

After the success and gradually wider applications of the friction stir welding (FSW) technique initially developed by The Welding Institute (TWI) in UK [1] in joining aerospace aluminum alloys, recent modifications into the friction stir processing (FSP) by Mishra et al. [2,3] also attract attention. FSP has been demonstrated to be an effective means in refining grain size of cast or wrought aluminum based alloys via dynamic recrystallization. A fine grain size in the typical range of 0.5-5 µm in the dynamically recrystallized zone of the FSP aluminum and magnesium alloys has been widely reported [2-6]. Exrafine grain sizes in the range of 30-180 nm were also demonstrated [7].

The success in fabrication of various nano-sized powders, wires or tubes has provided the new possibility in modifying existing commercial materials in terms of their functional or structural characteristics. Inorganic nano oxide, nitride or metallic powders may be inserted in polymers, ceramics, metals, or semiconductors by various sorts of simple or sophisticated means. Except for few reports, the majority of achievements were focused on the polymer matrix modified by ceramic nano particles so as to significantly improve its mechanical or physical properties. The addition of nano powders in metallic alloys has been relatively much less addressed.

For most isotropic composites, the micro-sized whiskers or particulates with a reinforcement volume fraction of 15-35% are commonly added into the metallic alloys through casting, liquid infiltration or powder metallurgy. In terms of grain size refinement and particle strengthening, one of the critical microstructure parameter is the particle interspacing Lₛ, which can be roughly estimated from $L = \langle d \rangle [(0.64/V_f)-1]$ [8] where $\langle d \rangle$ is the average particle diameter and $V_f$ is the particle volume fraction.
fraction. With reinforcing particles of Vf=20% and <d>=20 µm in typical aluminum base composites, L will be around 44 µm. The resulting grain size after casting would generally be in this range. Further hot extrusion may refine the grain size down to around 5-10 µm, and the strengthening and toughening effects will only be moderately enhanced. With 20 vol% special fine whiskers or particulates measuring ~0.5 µm in newly developed composites exhibiting high strain rate superplasticity (HSRSP), L will be 1.1 µm. The resulting grain size in HSRSP composites would then be around 1-2 µm [9].

The above mentioned metal based composites, either with reinforcements ~20 µm or ~0.5 µm in dimension, are highly expensive and usually exhibit unsatisfactory tensile ductility less than 3% at room temperature, both limiting their industrial applications [9]. Meanwhile, recent studies on a commercial 6061Al/SiCw composite also showed that the composite was difficult to be fusion welded [10]. With the new development of numerous types of nano inorganic powders, tubes, or wires, it is inspired to study the feasibility in producing modified alloys that are reinforced by a small amount (e.g. 1-5 vol%) of SiO2, Al2O3 or SiC nano-particles measuring around 10-30 nm. According to the above equation, L in the modified alloy with Vf=3% and <d>=20 nm will be 400 nm. Upon subjected to further thermomechanical treatments, the modified alloys might be processed into extrafine grain size less than 100 nm [11]. This also suggests that the addition of 3% nano-powders might be able to stabilize the grain size to less than 400 nm at elevated temperatures and enhance HSRSP in the modified alloy [11].

Dispersion of the nano reinforcements in a uniform manner is a critical and difficult task. Methods in dispersing the nano powders have been limitedly disclosed, mostly still protected by patents. The current paper presents the simple fabrication mean by employing FSP.

**Experimental Methods**

The AZ61A billets used in this study were purchased from the CDN Company, Deltabe, Canada. The chemical composition in mass percent is Mg-6.02%Al-1.01%Zn-0.30%Mn. This alloy is a solution hardened alloy with minimum precipitation. The as-received alloy was fabricated through semi-continuous casting and has the form of extruded billet. The billet possessed nearly equiaxed grains around 75 µm (all grain size hereafter was measured based on the linear line intercept method). The billet was cut as rectangular samples with 60 mm in width, 130 mm in length and 10 mm in thickness. The amorphous SiO2 nanoparticles with an average diameter ~20 nm and purity ~99.9% (Fig. 1) were purchased from the Plasmachem GmbH Company, Germany/Russian. The amorphous SiO2 particles are nearly spherical in shape, with a density of 2.65 Mg/m³.

The simplified FSP machine is a modified form of a horizontal-type miller, with a 5 HP capability, as shown in Fig. 2. The fixed pin tool is 6 mm in diameter and 6 mm in length. The shoulder diameter is 18 mm, and a 3° tilt angle of the fixed pin tool is applied. The pitch distance is 1 mm. The advancing speed of the rotating pin was kept constant in this study to be 45 mm/min, with a fixed pin rotation of the 800 rpm (rotation per min). The plates were fixed by fixture and air cooling was applied. As described in a previous paper [6], the strain rate and the maximum temperature experienced during FSP are around 10¹ s⁻¹ and 400°C, respectively. To insert the nano SiO2 particles, one or two deep and shallow grooves ~6 mm depth and 1.25 mm wide were cut (Fig. 3), in which the nano SiO2 particles to the desired amount were filled before FSP.

The Vickers hardness tests were conducted using a 200 gf load for 10 seconds. The grain structures and the particle distribution of etched or unetched specimens were examined by optical microscopy (OM), scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS) and transmission electron microscopy (TEM).
Results and Discussions

Microstructures. The top and cross-sectional views of the FSP region are shown in Fig. 4. The close-spaced rings on the top view reflect the forward travel distance per rotation of the pin. From the cross-sectional view, there is a characteristic onion ring regime, measuring nearly 6-7 mm in diameter. The nano SiO$_2$ particles are predominantly spread in this regime by the vigorous 3D stirring during FSP at the working temperature around 200-400°C. The volume fractions ($V_f$) of the SiO$_2$ nano particles inserted into the AZ61 Mg alloy are calculated to be around 6.5% and 13% for the one and two deep grooves (1D and 2D), respectively.

After one-pass (1P) FSP, the particle dispersion within the central cross-sectional area of the onion ring regions was macroscopically uniform, as shown in Fig. 5a for the one dip groove (1D1P) and Fig. 6a for the two dip grooves (2D1P). However, the observed particle size is frequently 0.3-1 μm (Table 1), much larger than the individual SiO$_2$ size (~20 nm). The situation after two-pass (2P) FSP, with opposite FSP direction for the second pass, appears to further improved, as shown in Fig. 5b for the one deep groove (1D2P) and Fig. 6b for the two grooves (2D2P). The aggregating particles were seen to vary from 20 to 1000 nm in size (Table 1). Some of the large particles, 1-5 μm in diameter, were identified to be the Mn bearing dispersoids by SEM-EDS, mostly likely the Al$_3$Mn dispersoids formed in the AZ61 billet during semi-continuous casting.

The average grain sizes of the composites with 6.5% and 13% volume fractions varied within 1-2 μm (Table 1). If all of the SiO$_2$ nanoparticles are completely uniformly dispersed, the theoretically estimated grain size should vary within 0.1-0.2 μm.
Fig. 4 Top and cross-sectional views of the FSP regime; the width of FSP nugget is around 7 mm.

Fig. 5 SEM micrographs showing the particle dispersion in the one deep groove specimen (1D, \( V_f \sim 6.5\% \)) after (a) one pass and (b) two passes. Some large Al\(_4\)Mn phase in distinctly white contrast measuring 1-5 \( \mu \)m in diameter can also be seen.

Fig. 6 SEM micrographs showing the inserted particle dispersion in the two deep-groove specimen (2D, \( V_f \sim 13\% \)) after (a) one pass and (b) two passes.

Table 1 Microstructural measurements for the AZ61 alloy with 20 nm SiO\(_2\) nanoparticles

<table>
<thead>
<tr>
<th></th>
<th>1D1P</th>
<th>1D2P</th>
<th>2D1P</th>
<th>2D2P</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2) ( V_f )</td>
<td>6.5%</td>
<td>13%</td>
<td>6.5%</td>
<td>13%</td>
</tr>
<tr>
<td>Average SiO(_2) cluster size</td>
<td>0.5 ( \mu )m</td>
<td>0.2 ( \mu )m</td>
<td>0.5 ( \mu )m</td>
<td>□0.1 ( \mu )m</td>
</tr>
<tr>
<td>Average grain size</td>
<td>3.5 ( \mu )m</td>
<td>2 ( \mu )m</td>
<td>1.5 ( \mu )m</td>
<td>1 ( \mu )m</td>
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**TEM Phase Identification.** Figure 7 presents the typical TEM micrographs of the 2D2P specimens. The average grain size of this specimen is around 1 \( \mu \)m, within the grain interior, tangled dislocations and SiO\(_2\) particles measuring around 20 nm can be seen in Figs. 7a and 7b. The nano SiO\(_2\) particles still maintain to be amorphous in nature, suggesting that they were not transformed to crystalline phase during the elevated temperature FSP. Confirmation experiments have been conducted by thermally annealing the amorphous SiO\(_2\) at 430°C for 10 min, and no crystallization was traced by XRD. Occasionally, the TEM diffraction patterns contain multiple rings, which are identified by the d-spacing to be originated from MgO fine particles measuring around 5 nm (Figs. 7c and 7d). The MgO phase is formed partly during FSP and partly during TEM foil preparation. The dispersion of the SiO\(_2\) nano powders under TEM varies appreciably. Local SiO\(_2\) clusters to a size from 100 nm to 1000 nm have all been observed.

![Fig. 7 TEM micrographs of the 2D2P specimen: (a) fine grains with SiO\(_2\) and dense dislocations, (b) weak amorphous SiO\(_2\) contract in the Mg matrix, (c) diffraction pattern with MgO ring patterns, (d) dark field image of the fine MgO phase measuring ~5 nm.](image)

**Hardness Measurement.** The typical microhardness readings, \( H_v \), in the central cross-sectional zones of the FSP specimens are depicted in Fig. 8. The gray region in the Fig. 8 represents the range which the silica powders added into AZ61 before FSP. Over a double increment was achieved, especially for the specimens with 2 deep grooves, or with 13 vol% SiO\(_2\). After FSP, the scattering of \( H_v \) within the FSP nugget zone is considered to be minor, implying that the pin stirring could efficiently disperse the nano silica powders in a reasonably uniform manner, especially after more than one pass. For the AZ61 alloy with no silica powder, after FSP, the hardness could also increase from ~60 up to ~75 due to grain refinement via dynamic recrystallization.
Fig. 8 Variation of the Hv microhardness distribution in the AZ61 base alloy (no SiO₂) and composites under the 1D1P, 1D2P, 2D1P, and 2D2P conditions. The highest Hv hardness can reach 105, about double increment over the base AZ61 billet.

Conclusions

Friction stir process could successfully fabricate bulk AZ61 Mg based composites with different amounts from 6.5 to 13 vol% of nano SiO₂ particles. The distribution of amorphous SiO₂ nano particles measuring around 20 nm after two FSP passes can result in macroscopically uniform distribution. The amorphous nature of the SiO₂ particles after FSP (with a maximum working temperature up to 400⁰C) is still maintained, implying that no crystallization has occurred. In some cases, fine MgO particles measuring around 5 nm are induced partly during FSP and partly during TEM foil preparation. The hardness of AZ61 Mg composites with nano fillers could be apparently strengthened by a factor of two, as compared with the AZ61 cast billet.

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References