Fabrication and Strength Behavior of MWCNT-Reinforced 5083 Aluminum Alloy Composite via Friction Stir Processing

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In order to improve the strength of 5083 Al alloy used in a wide range of industries, incorporation of multi-walled carbon nanotubes (MWCNTs) into 5083 Al alloy by the use of friction stir processing (FSP) was investigated. The MWCNT-reinforced Al alloy composites via FSP were successfully fabricated. The composites have no voids and other defects with the optimized conditions of FSP. The grain refining and uniform distribution of MWCNTs were achieved because the composite powder comprised of MWCNTs and 5083 Al alloy via ball milling was used as a reinforcement. Nanoparticles of MWCNTs and submicron particles were observed in the composite. The proof stresses of the composites increased by ranging from 53 to 61 percent compared with that of the base material and the tensile strengths increased by ranging from 13 to 16 percent. [doi:10.2320/matertrans.M2018191]

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1. Introduction

Carbon nanotubes (CNTs) are nanomaterials made up of entirely carbon and described as seamless cylinders of one or more layers of graphene (denoted single-walled, SWCNT, or multi-walled, MWCNT).¹ CNTs are endowed with exceptionally high material properties, very close to their theoretical limits, such as electrical and thermal conductivity, strength, stiffness, and toughness.² For example, MWCNTs exhibit exceptional strength and stiffness as manifested by a Young’s modulus of above 1 TPa and strength of a few tens of GPa.³ Therefore, CNTs are of special interest for the industry and will be the subject of this paper as a reinforcement.

CNT-based composites form a new class of lightweight super strong functional materials, so that the composites have gained popularity in the realm of aerospace, energy storage, and biomedical industries.⁴ However, employment of CNT reinforcements has been primarily restricted polymer-based composites, because the uniform distribution of CNTs in metal is quite difficult and aggregation of the CNTs reduces their effectiveness.⁵,⁶ In the case of melt mixing that is preferred method of CNT-polymer composite preparation, chemical reactions with the molten metal easily occurred.⁷

Recently, friction-stir processing (FSP), a variation of friction-stir welding (FSW), has been used for microstructural modification and homogenization of precipitate particles in aluminum alloy and magnesium alloy matrices for specific property enhancement.⁸,⁹ In addition, FSP technique seems to have the potential to produce surface composite on metal matrix.⁶,¹⁰ FSW uses a rotating tool consisting of a threaded probe and shoulder to apply frictional heating and severe plastic deformation to the base material and produce a strong joint.¹¹,¹²

This study focuses on using FSP as a fabrication method for producing aluminum alloy composites reinforced with MWCNTs (hereinafter referred to as MWCNT/Al composite). Furthermore, MWCNT reinforcement morphology and FSP conditions without a defect, and the mechanical properties of the resulting MWCNT/Al composites are investigated.

2. Experimental Procedure

2.1 Materials

The base material used in this study was a 5083-O Al alloy due to its wide acceptance in automobile and rolling stock industries attributed to their high strength to weight ratio and corrosion resistance. Table 1 shows the nominal composition of the 5083 Al alloy.

The CNTs used were high purity and high crystalline MWCNTs, prepared by the catalytic chemical vapor deposition method,¹³,¹⁴ and were produced by Showa Denko K.K. (Vapor growth carbon fiber, VGCF). 5083 Al alloy composite powder reinforced with 8 mass%MWCNT (hereinafter referred to as composite powder) was adopted as a reinforcement so that MWCNTs were uniformly dispersed into the base material. The composite powder was produced as follows. The Al alloy flaky chips which were generated from milling the base material under dry condition and the MWCNTs (8 mass%) were physically blended with SUS balls in a SUS container using a tri-axial vibrating-type ball miller (TKMAC-1200L, Topologic Systems Co., Ltd.). The ball milling was performed with a rotational frequency of

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Nominal composition of 5083Al alloy (mass%).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>&lt;0.40</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0.40</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Mn</td>
<td>0.4–1.0</td>
</tr>
<tr>
<td>Mg</td>
<td>4.0–4.9</td>
</tr>
<tr>
<td>Cr</td>
<td>0.05–0.25</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;0.15</td>
</tr>
<tr>
<td>Al</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
800 rpm for 5 hours in N₂ gas. The obtained composite powder was put through a sieve so as to control the size to ≤90 µm.

2.2 Fabrication of MWCNT/Al composites

Figure 1 shows the schematic illustration of the fabrication process of MWCNT/Al composites by means of FSP.

The above-mentioned composite powder was put into a side face groove (2.5 mm in width, 1.6 mm in depth, and 60 mm in length) of one base material, and the machined ends of the two base materials were butted tightly together. A rotating tool with a threaded probe (φ4 mm) and a shoulder (φ16 mm) was inserted into the butt line and was moved along the butt line. The rotating tool is made of SKD61 tool steel and is hardened to 45 HRC. The FSP conditions are shown in Table 2.

2.3 Evaluation

The microstructural characterization of the MWCNT/Al composites fabricated was carried out by means of optical microscopy (OM), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), electron backscattered diffraction (EBSD), and transmission electron microscopy (TEM) measurements. Furthermore, the phase constituents in the composite powder and the MWCNT/Al composite were characterized by X-ray diffraction (XRD) measurements using Cu-Kα radiation.

The hardness of the stir zones was measured by a Vickers microhardness tester with 490 mN load and 10 s holding time.

The tensile test specimens were cut out by wire electrical discharge machining to evaluate the strength of the stir zones. The configuration and size of a tensile test specimen are illustrated in Fig. 2. The tensile tests were carried out at room temperature at a crosshead speed of 1 mm/min (at a strain rate of 1.2 × 10⁻³ s⁻¹) using a computer-controlled tensile test machine. In addition, strain values were measured using a strain gauge attached on the parallel part of the specimen in order to obtain a modulus of longitudinal elasticity.

3. Results and Discussions

3.1 Microstructure of composite powder

Figure 3 shows a FESEM image and a XRD pattern of MWCNTs. It was found that MWCNTs give a diameter of approximately 150 nm and a length of 5–20 µm. Moreover, MWCNTs got entangled in part and had some knobby joints. The XRD analysis revealed that the MWCNTs have clear crystalline structure and the sharp (002) diffraction peak.

<table>
<thead>
<tr>
<th>Rotating speed</th>
<th>Travel speed</th>
<th>Downward force</th>
<th>Travel length</th>
<th>Tool tilt angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/min⁻¹</td>
<td>mm/min⁻¹</td>
<td>kN</td>
<td>mm</td>
<td>°</td>
</tr>
<tr>
<td>880</td>
<td>25</td>
<td>3.9–4.0</td>
<td>90</td>
<td>3</td>
</tr>
</tbody>
</table>
It is acceptable that the XRD profile of the MWCNTs are dominated by this reflection.\textsuperscript{15,16)

Figure 4 shows FESEM images of 5083 Al alloy-8\%MWCNT composite powder by ball milling. The size of the composite powder is approximately 100 µm or smaller. The enlarged view of the composite powder illustrated a few fiber-like MWCNTs. It is presumed that most MWCNTs were broken into pieces and caught in the powder during the ball milling. No peaks corresponding to MWCNTs were observed in the XRD, but strong peaks corresponding to base material (Al phase) were observed. Possible reasons for this are as follows: a small quantity of MWCNTs compared to a quantity of the base material, weak XRD intensity for MWCNTs of a light element, and broad diffraction line due to crushing MWCNTs during ball milling.

Figure 5 shows FESEM images and elemental maps for 5083Al-8\%MWCNT composite powder dissolved in aqua regia in order to investigate the disposition of MWCNTs inside the composite powder. The constituents of the residues were 94 at\% carbon, 3 at\% oxygen, and others by the EDS analysis, as shown in Fig. 5(c). MWCNTs having high aspect ratio were seldom observed in the dissolved composite powder as in Fig. 5(a), while nanoparticles and graphene-shaped substances were observed as in Fig. 5(b). The nanoparticles look like torn-off MWCNTs.

3.2 Microstructure of MWCNT/Al composite

First, the stir zone produced with a reinforcement not of composite powder but of intact MWCNTs are illustrated. Figure 6 shows optical micrographs of the cross section of the stir zone using intact MWCNTs (10 mg). Four horizontal layers were observed in the stir zone and the width of the layers appears to correspond to the distance between the two thread crests on the tool probe. The stir zone revealed a strong contrast between the layers and the interlayers in Fig. 6(a), and traces of agglomeration were distinctly observed within the layer in the enlarged view (Fig. 6(b)). In other words, the stir zone revealed an uneven microstructure. Further FESEM observation unveiled that the traces were an agglomeration of holes at the size of sub-half micron in which MWCNTs might have stayed. Consequently, uniform dispersion of MWCNTs was not accomplished in this method.

Next, Fig. 7 shows an optical micrograph of the cross section of the stir zone which was produced with the composite powder of 170 mg. The stir zone mainly featured two layers comprised of upper and lower stir zones and each layer revealed comparatively uniform distribution of the composite powder. Agglomeration and bundling are the major obstacles for utilizing the properties of CNTs, but MWCNTs were not agglomerated and bundled. Furthermore, any flaws such as voids and cracks were not observed in the stir zone. Figure 7(b) shows the hardness distribution of the upper layer (open circle) and the lower layer (closed circle) in a horizontal direction. Open square symbols (denoted by “only stirred”) indicate the hardness values in the stir zone without a reinforcement. The hardness values of MWCNT/Al composite (stir zone) were comparatively stable and were higher than those of only stirred. The hardness values of the lower stir zone exhibiting gray color in appearance were slightly higher than those of the periphery of the stir zone. On the other hand, the hardening of the upper stir zone was not apparent.

EBSD (IPF) maps of the cross section of the base material and the stir zones are shown in Fig. 8. The grain structure of the base material was coarse, flattened rolling texture as in Fig. 8(a). The rolling texture disappeared and grain refinement occurred after FSP. The average grain diameters of the base material, the only stirred base material (Fig. 8(b)), and the stir zone produced with the composite powder of 170 mg (Fig. 8(c)) were found to be 7.2 µm, 2.7 µm, and 1.2 µm, respectively.

FSP repeatedly gave strong plastic deformation to the base material and performed crystal grain refining. It can be deduced that the recombination of adjacent crystal grains was interrupted due to the existence of MWCNTs between them, because MWCNTs have poor joinability to aluminum by nature.\textsuperscript{17}) This is why the addition of MWCNTs contributed to further grain refinement.
Figure 9 shows results of EDS and XRD analysis of the cross section of the stir zone which was produced with the composite powder of 170 mg. The EDS analysis revealed that the constitution of area A was almost equal to that of area B, and these stir zones contained 1–2% carbon as in Fig. 9(b). Similarly, the EDS analysis revealed that the constitution of area C is almost equal to that of area D, and these stir zones contained 2–4% carbon. The XRD analysis revealed that the strong peaks corresponding to base material (Al phase) were observed.
It was found that the stir zone illustrated uniform distribution of the elements aluminum, magnesium, carbon, and oxygen by the EDS elemental mapping, except fine particles of a sub-micron order were observed as shown in Fig. 10. These fine particles consisted mainly of aluminum, carbon, and oxygen and existed only in the lower stir zone. The stir zone produced with the composite powder of 200 mg exhibited a similar tendency in structure.

The presence of aluminum, carbon, and oxygen on the particle is assumed as follows: The carbide Al₄C₃ is the only intermediate compound reported in Al–C phase diagram through the following reaction:

\[ 4\text{Al} + 3\text{C} \rightarrow \text{Al}_4\text{C}_3 \]

It has been also reported that the Al₄C₃ was formed at the interface between the Al and CNT layers, because the nano-sized CNTs are precursors for carbide formation. Thus, the nano-sized Al₄C₃ were possibly generated at the interface between the Al and MWCNTs in the composite powder and some carbides appear to be developed with the assistance of the heat which was generated during the ball milling and FSP. Thereafter the carbides were spread over the stir zone by FSP.

From the time of the formation of the composite powder, the carbide Al₄C₃ gradually reacts with oxygen, carbon dioxide, and carbon monoxide in the air to form alumina according to the following reactions:

\[ \text{Al}_4\text{C}_3 + 9\text{O}_2 = 4\text{Al}_2\text{O}_3 + 6\text{CO} \]
\[ \text{Al}_4\text{C}_3 + 3\text{CO}_2 = 2\text{Al}_2\text{O}_3 + 6\text{C} \]
\[ \text{Al}_4\text{C}_3 + 6\text{CO} = 2\text{Al}_2\text{O}_3 + 9\text{C} \]

Therefore, aluminum, carbon, and oxygen are detected as shown in Fig. 10.

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**Table 1**

<table>
<thead>
<tr>
<th>Element (mass%)</th>
<th>Al</th>
<th>Mg</th>
<th>C</th>
<th>O</th>
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<tbody>
<tr>
<td>Area A</td>
<td>92.5</td>
<td>4.6</td>
<td>1.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Area B</td>
<td>92.8</td>
<td>4.7</td>
<td>1.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Area C</td>
<td>90.8</td>
<td>4.7</td>
<td>2.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Area D</td>
<td>89.7</td>
<td>4.7</td>
<td>3.3</td>
<td>2.3</td>
</tr>
</tbody>
</table>

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**Fig. 8** EBSD (IPF) maps showing cross section of the specimens: (a) Base material, (b) only stirred base material, (c) stir zone produced with 8% MWCNT composite powder.

**Fig. 9** (a) Optical micrograph of stir zone produced with composite powder of 170 mg, (b) results of quantitative analysis, and (c) XRD pattern of stir zone.
The TEM image of MWCNT/Al composite shows dispersed MWCNTs in the Al based composite matrix and MWCNTs were found to have a length less than several tens of nanometers, as in Fig. 11.

3.3 Tensile test behavior

Figure 12(a) shows stress-strain curves for the base material, the only stirred base material, and the stir zones using reinforcements of 170 and 200 mg. In addition, Fig. 12(b) and (c) summarize values of 0.2% proof stresses, tensile strengths, and Young’s modulus for the following conditions: the base material, the only stirred base material, the stir zone using reinforcements of 120 mg, of 170 mg, and of 200 mg. Tensile tests were performed ranging from 3 times to 5 times for each condition.

Classically, the yield strength increases as grain size decreases according to the Hall-Petch equation. Thus, the proof stresses of the only stirred base material increased considerably: by 44 percent when compared with that of the base material. However, the tensile strength of the only stirred base material increased slightly: by 6 percent. In the case of the stir zones using reinforcements, the proof stresses increased by ranging from 53 percent to 61 percent and the tensile strengths increased by ranging from 13 percent to 16 percent, which exceeded the values of the only stirred base material. Judging from these values, MWCNT addition has effect on strengthening. The volume of the groove in where the composite powder was packed was 240 mm³ (2.5 × 1.6 ×
60 mm). Assuming that the shape of the cross section of the stir zone is a trapezoid, the volume of the stir zone was approximately 2310 mm$^3$ (38.5 × 60 mm) due to simple geometric calculation. Therefore, the stirring region expanded approximately ten fold in volume and the effect of MWCNT addition reduced to one tenth. Regardless of the small MWCNT addition, the rise in proof stress and tensile strength was achieved. Amounts of reinforcements varying from 120 mg to 200 mg have no influence on the proof strength and tensile strength. In respect of Young’s modulus, as shown in Fig. 12(c), the values of the only stirred base material and of the stir zones using reinforcements were nearly equivalent to that of the base material. The value of the stir zone using the reinforcement of 200 mg, however, eventually increased by 7 percent compared with that of the base material.

Considering all the above observations of Figs. 4-12, the mechanism of strengthening by compounding MWCNTs is presumed as follows. Firstly, FSW and FSP admittedly produce ultrafine grain microstructures in stir zones$^{21,22}$ and Sato et al.$^{23}$ for instance, reported that the friction stir welding on 5083Al plates created fine recrystallized grains with an average grain size of 4 µm in the stir zone. Similarly, microstructures with fine grain sizes were observed in the present research. Secondly, Ci et al.$^{19}$ reported that aluminum carbide (Al$_2$C$_3$) was formed at the interface between the Al and CNT layers in the composite films fabricated by sputtering. The Al$_2$C$_3$ formed on the surface as well as on the tips of the CNTs improves the interfacial interaction between the CNTs and the Al layers. Thus, the Al$_2$C$_3$ possibly improves the interfacial strength between matrices of the base material. Thirdly, recrystallization and grain growth involve the movement of grain boundaries, but the motion will be inhibited by second phase particles, in our case the nanoparticles of MWCNTs.$^{24,25}$ On the basis of microstructural observations, MWCNTs seem to be uniformly distributed in the stir zones containing the composite powder of 120 mg and 170 mg. In addition, the concentration of WMCNTs increases with an increase in the amount of the composite powder. In the case of 200 mg, however, part of MWCNTs were agglomerated and bundled due to insufficient stirring. The EBPD analysis revealed that the average grain diameters of the stir zone containing the composite powder of 120 mg, 170 mg, and 200 mg were 2.0 µm, 1.2 µm, and 1.1 µm, respectively. As mentioned above, the effect of MWCNT addition reduced to one tenth due to the expansion of the stirring region, which seems to result in similar grain sizes. While the additive amount of the composite powder had less influence in this research, the distribution of MWCNTs almost certainly contributes to grain refinement.

4. Conclusion

MWCNT-reinforced 5083 Al alloy composites using friction stir processing were successfully fabricated. The microstructure and the mechanical properties of the MWCNT/Al composite were evaluated. Main conclusions obtained are shown as follows:

1) It is capable to produce MWCNT/Al composites having no agglomerations of MWCNTs and no macroscopic defects such as voids.

2) As a reinforcement, MWCNT-reinforced 5083 Al alloy composite powder via ball milling is the key factor in uniform distribution of MWCNTs.

3) The grain size of the MWCNT/Al composite was significantly refined compared with that of the base material. The MWCNTs in the composite were shortened compared to the as-received ones.

4) The proof stresses of MWCNT/Al composites increased by ranging from 53 to 61 percent compared with that of the base material and the tensile strengths increased by ranging from 13 to 16 percent, which exceeded the values of the only stirred base material.

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REFERENCES