Effect of Sintered Reinforcement on Characteristics of MWCNT-Reinforced Aluminum Alloy Composite via Friction Stir Processing

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In order to enhance the strength of 5083 Al alloy, fabrication of multi-walled carbon nanotubes (MWCNTs) reinforced 5083 Al alloy by the use of friction stir processing (FSP) was investigated. The MWCNT-reinforced Al alloy composites using sintered sheets of 5083 Al alloy-8%MWCNT were successfully fabricated. Grain refinement and many minute aluminum carbides (Al₄C₃) were observed in the composites fabricated. The proof stress of the composites fabricated with the 550°C sintered sheets considerably increased by 153 percent and the tensile strength increased by 55 percent compared with that of the base material.

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1. Introduction

Carbon nanotubes1-2) (CNTs) have been expected as a prospective reinforcement for composite materials due to their outstandingly high Young’s modulus of above 1 TPa and strength of a few tens of GPa as well as good thermal and electrical properties.3,4) The employment of CNT reinforcements has been primarily restricted to polymer matrix composites, because the uniform distribution of CNTs in a metal matrix is quite difficult and the agglomeration of CNTs reduces their effectiveness.3,5) Many studies, however, have been devoted to the development of metal matrix composites reinforced with CNTs.6-9)

Friction stir processing (FSP) has evolved as an alternative technique of fabricating metal matrix composites in the past decade.10,11) FSP is a microstructural modification process based on friction stir welding (FSW), where a rotating tool with a specially designed probe and shoulder is thrust into the material surface and traversed along its surface. The rotating tool generates frictional heat and produces a severely plastically deformed zone (stir zone).12,13) When a reinforcement is introduced into the path of the tool during FSP, it is dispersed throughout the stir zone.

Morisada et al. successfully dispersed multi-walled carbon nanotubes (MWCNTs) into the magnesium alloy via FSP.14) The grain refinement of less than 500 nm and the increase in hardness were obtained, but the tensile strengths were not reported. Izadi et al. fabricated MWCNT/aluminum alloy composites with MWCNT content as high as 50 vol% via FSP.15) It was found that after three pass the distribution of CNTs are uniform which restricted the size of the grains and enhanced the microhardness.

In our previous study,16) MWCNT-reinforced 5083Al alloy composites made by FSP were successfully fabricated. The use of 5083Al alloy-8%MWCNT composite powder via ball milling as a reinforcement contributed to uniform distribution of MWCNTs. The strength of the composite made by FSP increased, but the tensile strength, for instance, stood at approximately 350 MPa, which was superior to that of the base material (5083Al alloy) but represented an increase of only 15 percent. It is difficult to compound a large amount of the composite powder within the base material. Because it is difficult to pack the composite powder densely into the groove with compressing pores among the composite powder. Thus, in order to increase the amount of reinforcement instead of using the composite powder, a sintered sheet fabricated with the composite powder was adopted. In this study, further research proceeded to improve the strength of the stir zone of the Al matrix composite. This study also focuses on a fabrication process via FSP for producing Al alloy composites reinforced with MWCNTs (hereinafter referred to as FSP composite). MWCNT-reinforcement structure and the mechanical properties of the resulting FSP composites are investigated.

2. Experimental Procedure

2.1 Materials

The base material used was the same 5083-O aluminum alloy (4.6%Mg-0.6%Mn-0.3%Fe-0.2%Si-0.1%Cr-bal Al in mass%) as in the previous study,16) which has gained wide acceptance in automobile and rolling stock industries attributed to its high strength to weight ratio and corrosion resistance. The CNTs used were high purity and high crystalline MWCNTs, prepared by the catalytic chemical vapor deposition method2,17) and were produced by Showa Denko K.K. (Vapor growth carbon fiber, VGCF).

Since the use of 5083 Al alloy-8%MWCNT composite powder by ball milling (hereinafter referred to as 8% composite powder) contributed to the uniform distribution of WMCNTs, the 8% composite powder was similarly used in this research. The process for producing the 8% composite powder was described in the previous report.16)

The high purity graphite sheet-lined mold which was contained in a vacuum below 200 Pa was filled up with the above-mentioned composite powder. The powder was then hot-pressed at 200°C and 550°C for 3.6 ks under a pressure of 280 MPa and 140 MPa, respectively. The sintered plates of 8%MWCNT-reinforced Al alloy matrix composites were finally obtained in the form of a plate 40 mm ×
The 200°C and 550°C sintered plates are shown in Fig. 1. The reasons why the sintering temperature was controlled to two levels of 200°C and 550°C are as follows. The temperature of 200°C was intended to obtain a bulk plate material which could withstand mechanical cutting and milling while preventing the formation of aluminum carbide by reaction between the base material powder and MWCNTs. On the other hand, the formation of aluminum carbide was inevitable at the temperature of 550°C. Still, it was intended to easily obtain a mechanically durable and dense bulk plate material without causing a phenomenon in which the raw material powder was excessively softened and leaked out through the gaps of the metal mold set. Additionally, a 550°C sintered sheet fabricated from base material powder (BM-sheet) was prepared in the same manner.

### 2.2 Fabrication of FSP composites

Figure 2 shows the schematic illustration of the fabrication process of FSP composites by means of FSP. The above-mentioned sintered plate was cut into a sheet 40 mm × 4 mm (hereinafter referred to as sintered sheet). The sintered sheet was put in a long narrow slit on a side face of one base material, and the two base materials were butted tightly together. A rotating tool with no probe and a shoulder (φ16 mm) came into contact with the surface of the base materials and was moved along the butt line. Then, a rotating tool with a threaded probe (3.5 × φ4 mm, pitch 0.7 mm) and a shoulder (φ16 mm) was inserted into the butt line at its probe and was moved along the butt line. The rotating tool is made of SKD61 tool steel and was hardened to 45 HRC. The FSP conditions are shown in Table 1. When the FSP condition changes, the amount of heat input into the object material fluctuates, which sometimes causes defects. If the amount of heat input is too much, the stir zone is softened and melted. If the amount of heat input is too little, defects such as voids are generated. In consideration of these factors and our experimental studies, appropriate FSP conditions as shown in Table 1 were determined.

### 2.3 Evaluation

The microstructural characterization of the FSP composites fabricated was carried out by means of optical microscopy (OM), field emission scanning electron microscopy (FES-EM), energy dispersive spectroscopy (EDS), electron backscattered diffraction (EBSD), and transmission electron microscopy (TEM) measurements. Furthermore, the phase constituents in the composite powder and the FSP 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. Tensile test specimens were cut out by wire electrical discharge machining to evaluate the strength of the stir zones. The configuration and size of the specimens were the same as in the previous report. The tensile tests were carried out at room temperature 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 sintered plate

The FESEM and the XRD observations of both MWCNTs and the 8% composite powder have been reported in our previous study. Furthermore, MWCNTs having a high aspect ratio were seldom observed in the 8% composite powder dissolved in aqua regia, whereas the nanoparticles of MWCNTs were observed.

Figure 3 shows the XRD pattern of the sintered plate which was sintered at 200°C for 3.6 ks along with that of the 8% composite powder. The Al phase was detected both in the 200°C sintered plate and in the 8% composite powder. The peaks of MWCNTs were not detected. This is because the diffraction peak intensity of a light element of MWCNTs was

<table>
<thead>
<tr>
<th>Rotating speed (N/min⁻¹)</th>
<th>Travel speed (v/mm·min⁻¹)</th>
<th>Downward force (F/kN)</th>
<th>Travel length (L/mm)</th>
<th>Tool tilt angle (θ°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>880</td>
<td>25</td>
<td>3.9–4.0</td>
<td>90</td>
<td>3</td>
</tr>
</tbody>
</table>
weak and the content of MWCNTs was fairly lower than the content of aluminum.

Figure 4(a) shows the FESEM image of the bending fracture surface of the 550°C sintered plate. The fracture surface turned out reasonably smooth and flat but had many pores. It appears that the pores resulted from defects at grain boundaries after powder sintering. River patterns on the fracture surface were observed, thus the sintered plate broke in a brittle manner. The XRD pattern of the 550°C sintered plate revealed both the Al phase and the Al₄C₃ phase as in Fig. 4(b). Since only the Al phase was detected in the 200°C sintered plate, it turns out that MWCNTs react with aluminum in the matrix to form Al₄C₃, when the sintering temperature rises to 550°C.

Figure 5 shows EDS elemental maps and the corresponding EDS spectrum of the fracture surface of the 550°C sintered plate. Al, Mg, C, and O were detected by the EDS spectrum and the elemental maps of the four elements revealed nearly uniform distribution for each, as shown in Fig. 5(b)–(e). Al₄C₃ and Al₃Mg₂ as well as the segregation of the elements were not detected. Since the sizes of the precipitates were less than 1 µm as will be discussed later in
the TEM observation in Fig. 9, it is understandable that the EDS detector could not identify the characteristic X-ray excited from a precipitate region and could not detect the precipitate.

### 3.2 FSP composite

Figure 6 shows the top surface of the friction stir processed base material. Traces of an insufficient stir and surface flaws were not observed. Figure 7 shows optical micrographs of the cross sections of the stir zones and the corresponding hardness distributions in the horizontal direction along the dotted line in Fig. 7(a) and (b). Figure 7(a) illustrates the stir zone which was friction-stirred without a reinforcement (only stirred base material) and Fig. 7(b) illustrates the stir zone which was friction-stirred with the 550°C sintered sheet of a 1.6 mm thickness. The shapes of both stir zones were inverted trapezoids. The upper stir zone expanded horizontally along the tool shoulder and the bottom stir zone was analogous to a movable scope of the tool probe. The linear, deep gray region (shown by an arrow) in the top stir zone in Fig. 7(b) was not a cavity, but a part of an insufficiently stirred reinforcement. The only stirred base material had almost uniform hardness distributions as in Fig. 7(c)–(e), with the hardness values of the only stirred base material being nearly the same as that of the base material. In this regard, Sato et al.\(^{18}\) reported that the hardness could not be explained by the grain size refining (Hall-Petch relationship) in friction stir welded 5083-O Al alloy which contains a high density of small particles. In addition, it was revealed that the hardness profiles are mainly governed by the particle distribution (Orowan mechanism) in the friction stir welded 5083-O Al alloy according to the detailed TEM observations, etc. The hardness values of the stir zone containing the sintered sheet increased to 160–180 HV, which shows the effect of the introduction of MWCNTs. As for the top stir zone, the hardness values increased to 140–160 HV (Fig. 7(c)). The traces in the top stir zone showing the insufficient stirring give evidence that the improvement of the stirring and/or of the process for mixing the base material with the sintered sheet is necessary to achieve a uniform distribution.

Figure 8 shows EBSD (IPF) maps of the cross sections of the base material and the stir zones. The grain structure of the base material was a coarse, flattened rolling texture as in Fig. 8(a). The rolling texture disappeared and grain refinement occurred after FSP. On the basis of the EBSD analyses, the most frequent grain diameters of the base material, the stir zone fabricated with a sintered sheet of base material powder (BM-sheet) (Fig. 8(b)), the stir zone fabricated with the 200°C sintered sheet (Fig. 8(c)), and the stir zone fabricated with the 550°C sintered sheet (Fig. 8(d)) were 7–8 μm, 3–4 μm, 2–3 μm, and 2–3 μm, respectively. The BM-sheet was produced in the same way as the 550°C sintered sheet, but without MWCNTs. FSP repeatedly caused strong plastic deformation in the base material which resulted in 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.\(^{19}\) This is why the addition of MWCNTs contributed to further grain refinement.

Figure 9 shows XRD patterns of the only stirred base material and stir zones which were fabricated with the 200°C sintered sheet and the 550°C sintered sheet. All XRD patterns
revealed the strong peaks corresponding to base material (Al phase) as a first phase. The peaks of Al₄C₃ were detected in both stir zones. However, the peaks of Al₄C₃ in the stir zone fabricated with the 200°C sintered sheet were weaker than in the stir zone fabricated with the 550°C sintered sheet. The appearance of Al₄C₃ phase in the stir zone fabricated with the 200°C sintered sheet must be due to the heat generated by FSP, since the carbide Al₄C₃ was not detected in the 200°C sintered plate as in Fig. 3(b). Specifically, for instance, Okamura et al.²⁰ reported that the temperature generated by FSW reached a maximum of 508°C.

Figure 10(a) is the bright-field TEM image of the FSP composite fabricated with the 550°C sintered sheet of a 1.6 mm thickness. Minute intricate shapes of less than 100 nm were observed. Furthermore, adjacent to them, acicular shapes of less than tens of nanometers were observed as in Fig. 10(b). This means that minute phases and/or defects of less than 100 nm which were different from the Al phase existed in the matrix. In other words, this demonstrates the mechanism by which MWCNTs are broken up and folded in the matrix and then distributed in the stir zone through the process of ball milling and of FSP.

Figure 10(c) shows the selected-area electron diffraction pattern from the composite matrix of Fig. 10(a) and exhibits the strong diffraction spots from the Al phase (base material) and the weak diffraction spots from other phases. The diffraction rings in the pattern (c) are sequentially numbered from the center and then are illustrated in Fig. 10(d). The analysis results from the diffraction rings are shown in Table 2. According to the lattice spacing and the lattice parameter calculated by the radius of each diffraction ring,
phases were determined within an error range of ±1%. Consequently, Al₄C₃ was identified as a second phase. In addition, there seems to be a diffraction ring corresponding to Al₃Mg₂. Since it also corresponds to Al₄C₃, we cannot determine the existence of Al₃Mg₂. Diffraction rings corresponding to MWCNTs were not observed. A plate-like crystal having a lattice spacing of approximately 0.8 nm, a length of approx. 30 nm, and a width of approx. 4 nm was observed in Fig. 10(b). This lattice spacing nearly corresponds to that of the Al₄C₃ (003) plane. Besides this, crystals having lattice spacings of 0.8 nm or less were observed throughout the composite matrix. It is necessary to conduct detailed studies, but the sizes of crystals having such lattice spacings are a few tens of nanometers at most. It is certain that extremely fine Al₄C₃ below a submicron order are produced throughout the composite.

### 3.3 Tensile test behavior

Figure 11(a) shows typical stress-strain curves for the base material, the only stirred base material, the composite fabricated with a BM-sheet, and two FSP composites. In addition, Fig. 11(b) and (c) summarize values of 0.2% proof stress, tensile strength, and Young’s modulus for the following conditions: the base material, the only stirred base

<table>
<thead>
<tr>
<th>Diffraction ring</th>
<th>Spacing d/ nm</th>
<th>Corresponding phase and crystal plane</th>
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<tbody>
<tr>
<td>①</td>
<td>0.415</td>
<td>Al₄C₃ (006)</td>
</tr>
<tr>
<td>②</td>
<td>0.283</td>
<td>Al₄C₃ (101), Al₃C₃ (012)</td>
</tr>
<tr>
<td>③</td>
<td>0.249</td>
<td>Al₄C₃ (015), Al₃Mg₂ (020)</td>
</tr>
<tr>
<td>④</td>
<td>0.243</td>
<td>Al (111)</td>
</tr>
<tr>
<td>⑤</td>
<td>0.202</td>
<td>Al (200)</td>
</tr>
<tr>
<td>⑥</td>
<td>0.166</td>
<td>Al₄C₃ (110), Al₃C₃ (0015)</td>
</tr>
<tr>
<td>⑦</td>
<td>0.143</td>
<td>Al (220)</td>
</tr>
</tbody>
</table>

Fig. 10 TEM micrographs of the composite produced by FSP of 1.6 mm thick 5083Al–8 mass%MWCNT plate with the matrix alloy. (a) bright field image; (b) higher magnification image for area E on (a); (c) electron diffraction pattern for (a); (d) phase analysis on the pattern (c).
material, the composite fabricated with a BM-sheet, the composite fabricated with a 200°C sintered sheet of a 1.6 mm thickness, and the composite fabricated with a 550°C sintered sheet of a 1.6 mm thickness.

The yield strength increases as grain size reduces according to the Hall-Petch relation in the conventional polycrystalline range (micrometer and larger sized grains).\(^{21}\) Incidentally, research on a variety of materials suggests that the deviation from the Hall-Petch relation occurs at approximately 20 nm mean grain size or less.\(^{22}\) The proof stress and the tensile strength of the only stirred base material decreased to some degree. As is comprehensible from the hardness values of the only stirred base material as in Fig. 7(c)–(e), the effect of stirring itself on the natural character of brittleness deteriorate the ductility of the composite. Therefore, the control of the additive amount of MWCNTs seems to be of importance in order to improve the mechanical properties where the strength and the ductility are well-balanced.

4. Conclusion

By the use of sintered sheets and friction stir processing, MWCNT-reinforced 5083Al matrix composites were successfully fabricated. The microstructure and the mechanical properties of the FSP composites were evaluated. The main conclusions drawn are shown as follows:

1. The sintered sheet fabricated with 5083Al-8%MWCNT composite powder is adopted as a reinforcement, which is the fundamental factor in obtaining the high strength of the FSP composite.
2. The grain size of the only stirred base material was refined compared with that of the base material, but the influence on improving the mechanical properties was minimal.
3. Many minute Al\(_4\)C\(_3\) particles formed in the FSP composite and then the grain size of the composite was significantly refined compared with that of the base material. The proof stress of the composites fabricated with the 550°C sintered sheets considerably increased by 153 percent and the tensile strength increased by 55 percent compared with that of the base material, while the breaking elongation dropped compared with that of the base material.

In order to enhance the mechanical strength of the matrix, MWCNTs with their excellent strength or graphene sheets which may be caused by pulverizing MWCNTs by a ball mill are needed. Even if MWCNTs and/or graphene sheets are present, strengthening does not take place in principle. It is necessary that MWCNTs or graphene sheets connect with the matrix alloy for the sake of conveying the force between the matrix alloy and them. Therefore, it is considered that MWCNTs or graphene sheets reacted with the aluminum alloy matrix to form Al\(_4\)C\(_3\) etc., which leads to the strengthening of the matrix alloy. Ci et al.\(^{23}\) also reported that aluminum carbide (Al\(_4\)C\(_3\)) was formed at the interface between the Al and CNT layers in the composite films fabricated by sputtering; the Al\(_4\)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. In this research, Al\(_4\)C\(_3\) formed in the composite certainly contributes to the strengthening. On the other hand, carbides having the natural character of brittleness deteriorate the ductility of the composite. Therefore, the control of the additive amount of MWCNTs seems to be of importance in order to improve the mechanical properties where the strength and the ductility are well-balanced.
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