1. Introduction

Carbon nanotubes (CNTs) are considered to be the next-generation reinforcement agents for metal matrix composites (MMCs) since they have great potential to improve the physical properties of metals by taking advantage of their high strength and stiffness [1]. Various processing routes, including powder metallurgy [2], casting [3], ball milling [4], severe plastic deformation (SPD) [5,6], and plasma spray forming [7] and friction stirring [8] have been studied to incorporate CNTs into the metal matrix. The critical problems in fabricating the CNTs MMCs are inhomogeneous dispersion of initially entangled CNTs, poor bonding between CNTs and the matrix and unintentional formation of Al₄C₃ due to a reaction of CNTs with the metal matrix during the synthesis of MMCs. Furthermore, mass and economical production of CNTs reinforced MMCs is another challenge for their usage in commercial applications.

It has been shown the SPD such as equal channel angular pressing and high pressure distortion can effectively produce ultrafine grained (UFG) metals and alloys. In this study, we developed a nanocrystalline aluminum matrix composite sheets containing multiwalled CNTs by means of high-ratio differential speed rolling (HRDSR). The HRDSR technique [9,10], which was developed by one of the current authors, has the advantage of being suited to cost-effective mass production of UFG sheets because the process is continuous and requires only a few rolling passes. Scale-up is easy, and no special die is required.

In this study, we examined a possibility of application of HRDSR to produce CNT reinforced aluminum composites.

2. Experimental procedures

The starting material used in this study was the composite aluminum powders with diameters of 5 ~20 µm containing 3 vol.% multi-walled CNTs (MWCNTs), which were supplied from Applied Carbon Nano Co. Ltd. Pure aluminum (99.9%, <150 µm in diameter) and 3 vol.% multi-walled CNTs (MWCNTs with diameter of ~20 nm and length of ~10 µm were mechanically added in an attrition mill to produce the composites powders. Sheath rolling technique was used first to consolidate the composite powders. The composite powders were containerized in a 6061 aluminum tube with an outer diameter of 30 mm and an inner diameter of 28 mm, degassed for 1 hr at 643K and sealed by clamping. The packed tube was held at 673 K for 20 min before being subjected to conventional rolling. Rolling was conducted using a rolling mill with roll diameters of 300 mm. During the rolling, the thickness of the tube was reduced to 5.1 mm by four passes without reheating steps between the passes. In this case, the cold rolls were used. Full powder-compaction was not realized at this stage. To enhance powder compaction in subsequent rolling, the upper and the lower rolls were heated. The roll surfaces were maintained at 473 K throughout the rolling process using heating elements embedded within the rolls. The rolled sample was heated to 673 K for 20 min again and then fed to conventional rolling for the thickness reduction from 5.1 mm to 2.2 mm. Up to
this stage, the degree of sintering densification of powder compact was not high. Finally, HRDSR was applied to produce the sheet with a thickness of 0.7 mm through a two step rolling process. In HRDSR, the speed ratio between the upper and lower rolls was set at 2. The top roll rotated with a speed of 6 rpm in the counterclockwise direction, while the bottom roll rotated with a speed of 3 rpm in the clockwise direction. After rolling, the aluminum can layers were removed through mechanical grinding and polishing with abrasive papers. The schematic illustration of the entire processing described above is presented in Fig. 1. For comparison, pure aluminum powders without CNTs were prepared and then sintered by rolling following the very similar schedules applied to the aluminum powders with CNTs.

Fig. 1. Fabrication procedure for Al-CNTs composites.

Phase analysis was carried out using X-ray diffraction with a Cu Kα radiation source (XRD, Rigaku, ULTIMA IV). Raman spectroscopy was further undertaken to examine any structure change of CNTs during HRDSR. The Raman spectra were acquired in the back-scattering geometry using the 532 nm line of a pumped solid state laser at room temperature in the spectral range from 1100 to 1800 cm$^{-1}$ with a resolution of 0.1 cm$^{-1}$. The surface microstructures of the specimens were observed using a scanning electron microscopy (FESEM, HITACHI S-4300). The sheet planes, i.e., TD-RD planes of the rolled samples, were examined using a field emission TEM (JEM 2001F) operated at 200 kV. Solutions composed of methyl alcohol (CH$_3$OH) and nitric acid (HNO$_3$) ratio of 2:1 was utilized for jet polishing, and a BAL-TEC RES 101 was used for ion milling. The tensile tests were conducted at room temperature at an initial strain rate of $1\times10^{-3}$ s$^{-1}$ operating at a constant rate of cross-head displacement using specimens (gauge length: 5 mm and gauge width: 4 mm) cut out along the rolling direction from the HRDSR sheets. Vickers microhardness was measured using an Akashi MVK-H3. A load of 100 g was applied for 10 s for the measurements.

3. Results and discussion

Fig. 2(a) shows the SEM image of the composite powders. The ball-milled composite powders have irregular shapes and rugged surfaces. CNTs were not easily found on surfaces of the powders. Fig. 2(b) shows the CNTs inside a powder, which were revealed after grinding the green compact powders by abrasive papers. As seen in Fig. 2(a), however, entangled CNT bundles with diameter of 5–10 µm were occasionally seen to interconnect the powders.

Fig. 3. Optical micrograph of the cross section of the HRDSR processed composite sheet.

Fig. 3 shows the longitudinal section of the HRDSR processed sheet with CNTs observed by SEM. The composite layer takes about a half of the total volume and the top and bottom 6061 aluminum layers take a quarter, respectively. The interface between the composite and aluminum can layer was wavy. Observation using SEM verified that neither pores nor microcracks were visible in the composite layer, indicating that full densification of the composite powders was achieved during the HRDSR process. The Vickers microhardness was measured on
the longitudinal sections of the HRDSR processed samples with and without CNTs and the results are summarized in Table 1. The average hardness of the HRDSR processed sample with CNTs was 120 Hv. This value is significantly higher than that of the HRDSR processed sample without CNTs (41 Hv). The difference in hardness of the 6061 Al can be significantly increased after HRDSR when the rolling temperature was low (xxx K). This result implies that the rolling temperature used in the current experiments was so high that the grain refining efficiency almost vanished.

Table 1. The vickers microhardness on cross-sectional planes for HRDSR processed samples.

<table>
<thead>
<tr>
<th>specimen</th>
<th>6061 can powder</th>
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<tbody>
<tr>
<td>Al without CNTs</td>
<td>51</td>
</tr>
<tr>
<td>Al-CNTs composite</td>
<td>54</td>
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</tbody>
</table>

Raman spectrographs of the initial MWNTs, the composite powders and the HRDSR processed composite shown in Fig. 4(a). The two peaks are distinct in each sample. The peaks associated with 1580 cm\(^{-1}\) and 1340 cm\(^{-1}\) represent a G-line (from graphite) and a D-line (from defects). The peak intensity ratio between the D- and G- bands of the initial MWNTs was 0.7, while those of the composite powders and HRDSR processed composite were similar as 1.3 and 1.2, respectively. The results imply that 1) the D-band became pronounced during the ball mill for the composite powder production due to breaking and bending of the CNTs during ball milling and 2) further damage of CNTs, however, did not occur during the rolling processes. The XRD patterns of the composite powders and the HRDSR processed composite are shown in Fig. 4(b). Very small carbon peaks appeared in the HRDSR processed composite, whereas they could not be seen in the composite powders. The appearance of the carbon peaks in the former is thought due to the surface treatment done before the XRD testing, where the surface was polished and then the surface layer was removed my chemical etching for CNTs embedded beneath the surface of the particles to be exposed to the surfaces. This result indicates that most CNTs in the composite powders exist inside the powders, which is in agreement with the SEM observation where CNTs were not easy to be found on the surfaces of the powders. No peaks for Al\(_4\)C\(_3\) appeared in the composite powders and the HRDSR processed composite. This result indicates that the reaction between the CNTs and aluminum did not occur during the ball-mill process as well as during the rolling process.

Fig. 4. (a) Raman spectra of MWCNTs, the Al-3vol.% of MWCNTs milled powders and the HRDSR processed sheet (b) XRD patterns of the Al-CNTs composite powders and the HRDSR processed sheet.

Fig. 5(a) and (b) shows bright field TEM images for the HRDSR processed sample without CNTs and the HRDSR processed sample with CNTs, respectively. In the case without CNTs, it is apparent that dynamic recrystallization fully took place. Equiaxed grains with low dislocation density in their interiors comprised the microstructure. In contrast, the sample with CNTs shows the bamboo-like microstructure composed of elongated grains that were divided to rectangular domains by the short boundaries that perpendicularly intersected the boundaries of elongated grains. The widths of
elongated grains were in a narrow range between 100 and 200 nm. Some equiaxed grains evolved from the rectangular domains were occasionally seen. Fig. 5(c) shows the STEM image of the HRDSR processed sample with CNTs. Many CNTs are aligned to the rolling direction.

![Fig. 5](image)

Fig. 5. TEM images of the HRDSR processed sample (a) without CNTs (b) with CNTs, (c) STEM image with CNTs and (d) agglomerated CNTs.

Macroscopically, the distribution of CNTs appears uniform. Closer examination, however, indicates that most of CNTs are located along the grain boundaries of the elongated grains that lie parallel to the rolling direction. CNTs are hard to be cut by dislocations and thus they can act as effective obstacles to dislocation motion. The CNTs became distributed to be densely dispersed in the CNT bands narrowly spaced with a spacing of 0.1~0.2 µm by shear plastic flow during HRDSR. The CNTs in bands provides good sites for dislocation accumulation. The dislocation accumulation then leads to the formation of grain boundaries of elongated grains. In the case of the HRDSR processed sample without CNTs, where obstacles to dislocation motion are absent, coarse grains with equiaxed morphology has formed. This result implies that CNTs played a important role of refining the grain size of matrix. It is believed that Fig. 5(d) captured the moment that CNT dispersion was taking place in tangled CNTs agglomerates such as the CNT bundles seen in Fig. 2(a). The present TEM observations suggest that HRDSR is useful in enhancing uniform dispersion of CNTs and detangling of CNTs agglomerates.

Fig. 6 shows the engineering stress-strain curves of the HRDSR processed with and without CNTs. The sample with CNTs exhibit the yield stress (YS) of 250 MPa, which is higher than that of the sample without CNTs by about 5 times. This large strengthening in the sample with CNTs compared to the sample without CNTs can be attributed to formation of much smaller (sub)grains and presence of CNTs. The tensile elongation of the sample with CNTs is, however, only 2.5%, which is considerably smaller than that of the sample without CNTs (29.5%).

It is generally accepted that the mechanical properties of the composites are dominated not only by the reinforcement and the matrix but also by the interfacial bonding status between them. Improvements in the strength of CNT/Al matrix composites are largely attributable to sufficient load transfer from the matrix to carbon nanotubes through the interface. To ensure a good load transfer, the composite must maintain a medium strong interfacial bonding.

![Fig. 6](image)

Fig. 6. The engineering stress-strain curves of the HRDSR processed with and without CNTs.

![Fig. 7](image)

Fig. 7. FESEM image of fractured surface of the HRDSR processed sample after tensile test.
Fig. 7 shows the fractured surface of the HRDSR processed composite after the tensile test. Many carbon nanotubes were pulled-out on the tensile fracture surfaces, being parallel to the rolling direction. The pits on the fracture surface, however, indicate that the length of the carbon nanotubes pulled-out are short, suggesting a strong interfacial bonding between carbon nanotubes and the Al matrix.

4. Conclusions

We demonstrated the possibility of fabricating the CNTs reinforced aluminum CNTs composites with high strength by combining sheath rolling and high-ratio differential speed rolling (HRSDR) in sequence. HRDSR has a good potential for producing a high performance CNTs reinforced metal matrix composites in sheet form.

5. References