CARBON NANOTUBE GRADIENT LAYERS REINFORCED ALUMINUM MATRIX COMPOSITE MATERIALS

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1 General Introduction

In material science functionally graded material (FGM) may be characterized by the variation in composition and structure gradually over volume, resulting in corresponding changes in the properties of the material.[1] The concept of FGM was first considered in Japan in 1984 during a space plane project. Where a combination of materials used would serve the purpose of a thermal barrier capable of withstanding a surface temperature of 2000 K and a temperature gradient of 1000 k across a 10 mm section.[2] However, careful selection of the component materials, particularly the reinforcement, is required to reliably achieve a high performance from the FGM. Carbon nanotubes (CNT), which have a unique combination of excellent mechanical, electrical and thermal properties, have become a hot property in the engineering materials field, since their discovery in Japan in 1991.[3,4] For this reason, CNT is a satisfactory candidate to be a reinforcement material for fabricating high performance FGMs.

In the present study, we attempted to fabricate functionally graded CNT-reinforced metal matrix composite bulk materials by a hot-pressing method and to then characterize these composites. Aluminum (Al) was utilized for the matrix material because its high specific strength and high ductility combined with the CNT offers high performance of structural materials. In particular, extremely different characteristics within the Al-CNT bulk materials (for example, highly strengthened surfaces and highly enhanced ductility inside) can be achieved by the FGM concept. The various Al-CNT composite powders were prepared by a planetary ball milling process and then hot pressed in a layered structure. The FGM bulk obtained was analyzed, with a focus on the microstructural and hardness of each CNT gradient layer.

2 Experimental procedure

Multiwalled CNTs (Baytubes C150P, Bayer material science, purity 99.5%, diameter: 20 nm, length: 30 μm) and gas-atomized pure Al powder (ECKA Granules, purity 99.5%, mean particle size: 63 μm) were used as the starting materials. Homogeneously well dispersed CNT-Al composite powders containing 5, 10, and 15 vol.% CNT were prepared by a planetary ball milling process (Retsch GmbH, PM400) for 3 h under an argon atmosphere; 360 rpm, Ø10mm ball, 10:1 ball to powder weight ratio, and 20 wt.% heptane was used as the process control agent. The Al-CNT composite powders were assembled in a layered structure inside a 30 mm diameter die, with compositions ranging from pure Al to composite containing 15 vol.% CNT, followed by hot-pressing (Walter+bai ag Testing machines, 400kN) consolidating at 500 ^{o}C for 5 min under an uniaxial pressure of 57 MPa. The density of the FGMs were measured according to the Archimedes principle and the micro Vickers hardness (Paar MTH4 microhardness-tester) of the ball milled powders and gradient layers were measured using the loads 0.02 kgf and 20 kgf for at least five measurements per sample. The interlayer microstructure of FGM was observed using optical microscopy (Zeiss Axioplan light microscope), high resolution cold field emission scanning electron microscopy (SEM) (Hitachi, HRCFE-SEM S-4800), and high resolution transmission electron microscopy (TEM) (Jeol, HR TEM JEM-2200FS).

3 Results and Discussion

The raw Al particles had an irregular spherical shape with the size distribution shown in Figure 1a. The CNTs had a curving and twisting shape and contained amorphous impurities (black arrow in Fig. 1d and e) with some unstable graphene structure on the walls (Fig. 1e). Two kinds of CNT tips observed: open and closed-tip, as indicated by the white arrows in Figure 1c and e.

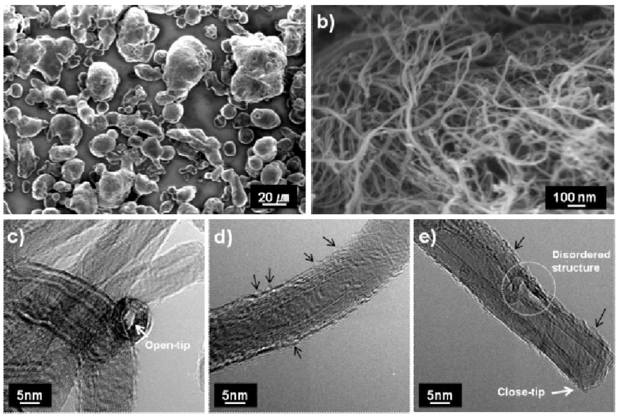

Fig. 1. SEM micrographs of as-received (a) Al and (b) CNT and (c, d, and e) TEM micrographs of the CNT. The white arrows (c and e) indicate open and closed tips on the CNT. The black arrows (d and e) indicate amorphous impurities on the surface of the CNT.[2]

Figure 2 shows SEM micrographs of the Al-CNT composite powders for different amounts of CNT additions. There was no significant size distribution observed in the each Al-CNT composite powders. However, the composite powder particles size was decreased with increasing of the CNT addition. It may be the CNT had acted as lubricant in Al-CNT powder during the ball milling process [2]. Each Al-CNT composite powders were built in layers shape and positioned into the metal mold. The FGM was fully densified regardless of the amount of CNT added at least Archimedes principle level. The FGM was fully densified regardless of the amount of CNT added at least Archimedes principle level.

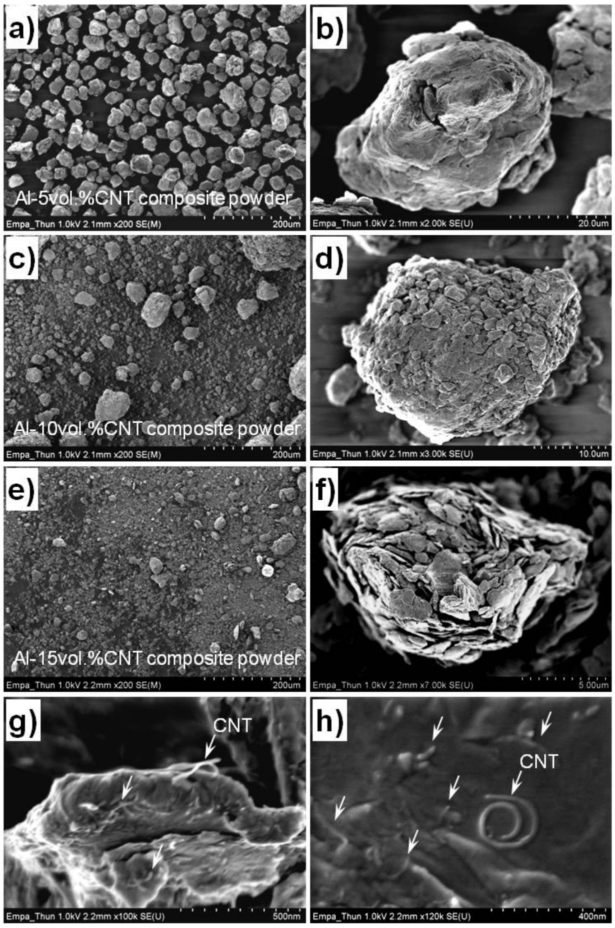

Fig. 2. SEM micrographs of Al-CNT composite powders depending on the amount of CNT additions. (a and b) 5vol.% CNT, (c and d) 10vol.% CNT [2], and (e-h)15vol.% CNT added Al composite powders. The white arrows (g and h) indicate the CNTs.

Digital image of the CNT gradient layer Al matrix composite by hot pressing shows in figure 3. The pure Al side and the 15vol% CNT-Al side are shown in figure 3(a) and (b). There are not serious cracks and open pores were observed onto the composite at least in digital picture lever observation. The obtained composite was fully densified which was measured based on Archimedes principle. The CNT gradient layers were well laminated depending on the design of composition within the FGM composite. However, simple hot pressing process is useful method for fabricating of fully densified CNT gradient Al matrix composite materials.

Table 1 indicates the density of composite layers depending on amount of CNT addition. Every layer in the FGM composite was fully densified regardless of the amount of CNT addition. It is implied that the design of the CNT gradient layer and the amount of CNT addition were not affected to densification parameter. In other words, there is more opportunity to achieve for tailor made characterization by applying for various functionally graded layers and composition in the Al matrix composite materials.

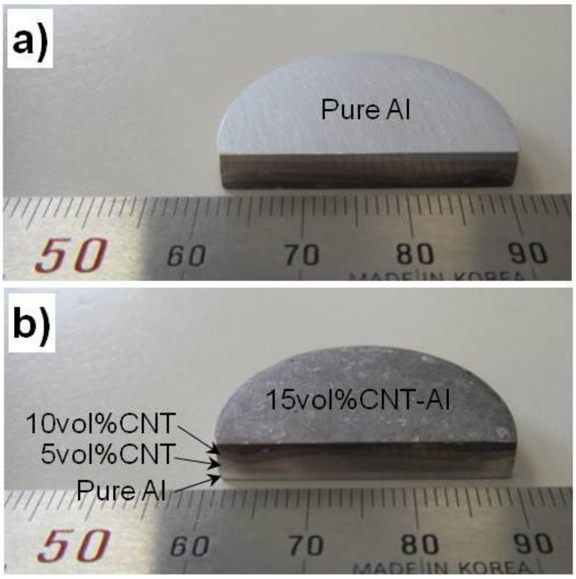

Fig. 3. Digital picture of obtained CNT based Al FGM bulk. (a) The pure Al surface and (b) 15vol% CNT-Al surface.

Table 1. Density of various CNT gradient layers.

CNT contents (vol.%)	Density (g/cm^3)±0.02 Theoretical	Measured
0	2.69	2.69
5	2.65	2.65
10	2.61	2.61
15	2.56	2.56

Figure 4 shows optical micrographs and Vickers hardness values depending on the CNT gradient layers. The higher CNT content layer shows higher dark contrast due to the CNT's own color property. This different contrast depending on the amount of CNT addition can be distinguished at least degree of gradient-lever in within FGM. Vickers hardness was dramatically increased with increasing of the amount of CNT addition.

In particular, Vickers hardness of the 15vol% CNT gradient layer was increased quadruple than that of pure Al. Moreover, any serious pores and cracks were observed into the every layer. However, it is estimated that the CNT had played an important role to increasing of the hardness. In other words, CNT will be good reinforcing material for functionally graded Al composite system.

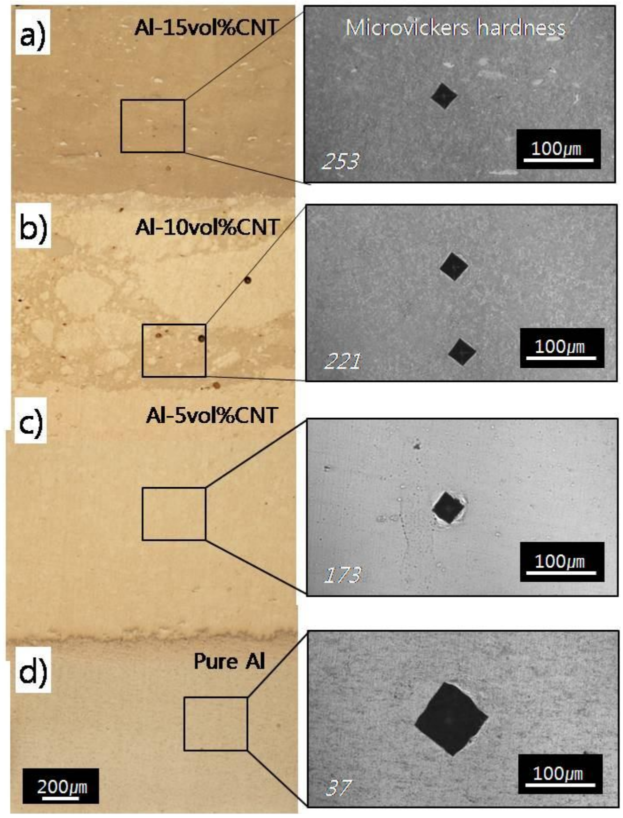

Fig. 4. Optical micrographs of the CNT gradient Al matrix composites with the traces of micro-vickers hardness.

The strengthening mechanism of CNT reinforcement is still unclear but several mechanisms were proposed to solve this matter. For example, Hall-petch relationship [5](grain refinement strengthening), Orowan looping [5] (interruption of dislocation movement), and thermal mismatch[5] (different of coefficient of thermal expansion between the matrix and reinforcement). It is estimated that the CNT gradient layer Al matrix composite was strengthened by not only one of them but also affected by combined complex mechanism. Especially, the obtained FGM in this study was affected by some physical adhesion between the matrix and reinforcement because it was fabricated with large plastic deformation during hot pressing process. Anyhow, it is necessary that deep investigation of the strengthening mechanism by CNT reinforcement for reliability of the Al matrix composite materials.

XRD patterns of the obtained FGM depending on the amount of CNT addition shows in figure 5. The relative intensity of Al peaks were not significantly changed in any layers as shown in figure 5(a). The C peaks were detected with very low relative intensity due to the capacity of used equipment and existing with high volume fraction of the Al. Also, the relative intensity of C peaks was slightly increased with increasing of the amount of CNT addition. According to the XRD phase analysis results, the obtained FGM is consisting of only Al and C phase without any secondary phase.

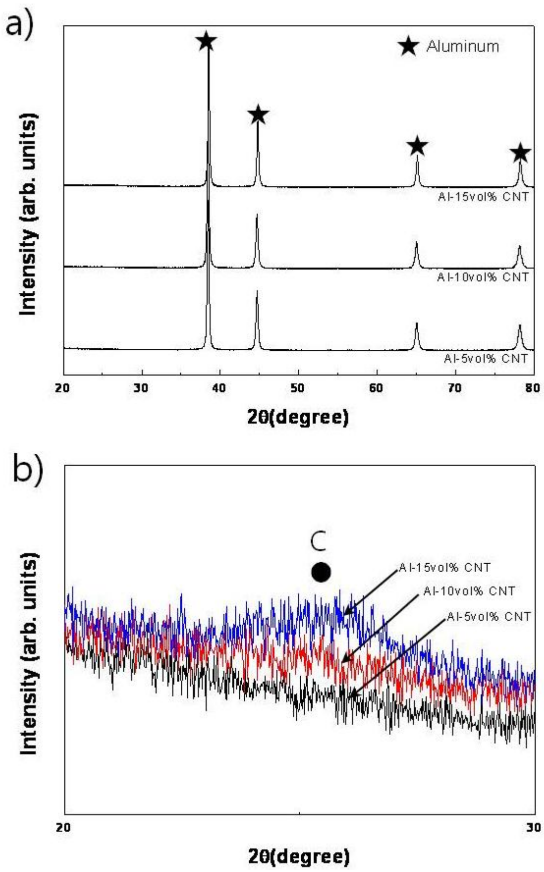

Fig. 5. XRD patterns of (a) the CNT gradient Al matrix composite depending on the amount of CNT addition and (b) high magnification of the 2 theta range of 20 to 30 in (a).

Figure 6 shows TEM microstructure of the 15vol% CNT gradient Al matrix composite. We found around 300 nm Al grain which is smaller than raw Al grain (sub micro). This small grain was created by mechanical ball milling process. It is also estimated that there is not significant grain growth occurred during the hot pressing process due to the mainly relatively short holding time (5min) and pinning effect of the dispersed CNT onto the Al particles. Some amorphous carbon clusters were found and these clusters may be come from pristine CNT and created by during the process (milling and hot pressing).

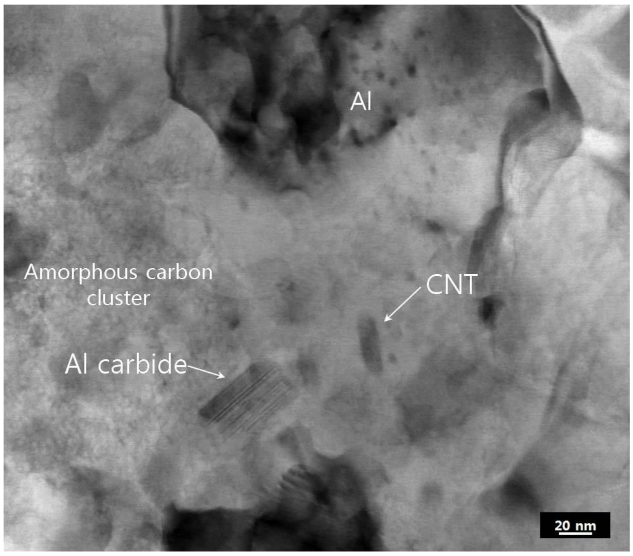

Fig. 6. TEM microstructure of the 15vol% CNT gradient Al matrix composite.

Moreover, implanted fine nanosized (around 30 nm) Al carbide (Al_4C_3) onto the Al matrix was observed which was not detected in XRD analysis. It is estimated that the formed Al carbide in the FGM was very small quantity and size (detection disable range of the used equipment). This nanosized carbide will be not significantly influenced to the properties of FGM but it should be carefully handled due to the brittleness and higroscopicity [6].

4 Conclusions

A well dispersed CNT gradient layer in the CNT-based Al matrix FGM has been successfully fabricated with full density by mechanical ball milling and hot-pressing processes. This CNT gradient layer concept offers high potential for achieving different kinds of FGMs such as those based on ceramics, polymers, and complex materials.

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