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Low-temperature solid-state dissolution of carbon atoms into aluminum nanoparticles

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Disintegration of carbon nanotubes (CNTs) into C atoms and dissolution into Al nanoparticles is achieved by mechanically grinding two materials together. This low-temperature solid-state dissolution process involves several steps: (i) mixing CNTs with Al particles; (ii) Al nanoparticle formation; (iii) disintegration of CNTs into C atoms; and (iv) embedding of C atoms into Al nanoparticles. C atom are embedded into Al nanoparticles up to a level of 50 wt.% via the formation of an amorphous phase. This enhances hardness by more than 50%.

Keywords: Mechanical milling; Transmission electron microscopy (TEM); Carbon nanotubes; Amorphous materials; Stress-assisted diffusion

Non-equilibrium processing of materials has attracted much attention as a means to improve their physical and mechanical properties [1]. Non-equilibrium processing of materials can produce a supersaturated solution in the metal matrix which cannot be achieved easily by equilibrium processing [2]. This supersaturated solution blocks the dislocation movements in the matrix and significantly improves the mechanical properties of metals [3]. Due to these reasons intensive researches have been done in order to create non-equilibrium phase via, for example, rapid solidification from the liquid state [4], mechanical alloying [5], plasma processing [6], and vapor deposition [1]. Among these methods, mechanical alloying satisfies both technical performance and industrial processing demands for mass production [5].

Aluminum is a light metal with high corrosion resistance and offers several advantages for vehicles; it has recently attracted attention on energy-saving grounds. It has, however, the serious drawback of low mechanical strength compared to, in particular, iron. This drawback has been ameliorated by forming numerous metal alloys via general equilibrium processing. Recently, carbon materials such as carbon nanotubes (CNTs) [7], carbon fiber [8] and carbon black (CB) [9] have been introduced to improve the mechanical properties of Al metal. Since the C content is restricted by the low solubility of C in Al (e.g. 0.5 weight % at 1500 °C [10]), a high C content is not usually obtained by equilibrium processing. Therefore, non-equilibrium processing is required to incorporate a high C content into the Al matrix, which is an important preliminary step for numerous applications of Al–C alloys.

Here we report a new low-temperature non-equilibrium solid-state dissolution method for creating an Al–C complex with a high concentration of C atoms. Solid-state dissolution is defined as a breakdown of the crystalline lattice into individual atoms and their transport into the medium. Mechanical grinding was used to mix Al and CNTs at room temperature. CNTs were eventually disintegrated into C atoms during the non-equilibrium mixing process and dispersed into the Al matrix to form amorphous Al–C phase. The maximum C solubility was increased up to 50 wt.%, which enhanced the hardness by 50%.

The diameter and length of multiwalled carbon nanotubes (MWCNTs) (CM95, Iljin, Korea) were in the range of 10–30 nm and fewer micrometers, respectively. In order to improve CNT disintegration rate, CNTs were dispersed in ethylene glycol and further treated in
a microwave oven to create defects [11]. Gas-atomized Al powder (Samjeon Chemicals, Korea) was filtered to 200 mesh (<50 μm) and used as a matrix. CB of particle size less than 100 nm (Korea Carbon Black Co. Ltd.) was also used as a reference to compare with MWCNTs. The MWCNTs obtained from microwave treatment plus the Al powder were mechanically ground and dissolved using a planetary ball-miller (Pulverisette 6, Fris tch, German). 5 mm zirconia balls were used as the milling media in a 500 ml carbon steel container (SKD11). The ball/MWCNT/Al mass ratio was fixed to 300/1/1 during the ball-milling processes. Oxygen gas in the jar was removed prior to ball-milling by purging with Ar in order to prevent Al oxidation. The ball-milling times were 1, 3, 6 and 12 h at a fixed 300 rpm.

The morphology of MWCNT–Al complex was characterized by field-emission scanning electron microscopy (SEM) (JEOL 6700F). MWCNT disintegration and dissolution was investigated by high-resolution transmission electron microscopy (TEM) (JEOL 2010F, operating at 200 keV). The amount of embedded C atoms was characterized by thermogravimetric analysis (TGA) (TA Instruments Q500). Microscopic structural changes in the MWCNT–Al complex were further characterized by X-ray diffraction (XRD) (Rigaku Rotafilex D/MAX system, Rigaku, Japan, using Cu $Kα$ radiation with a wavelength of 1.54 Å) and Raman spectroscopy (633 nm laser, Renishaw RM1000). Mechanical properties were measured by a micro-Vickers hardness tester (Mitutoyo HM-211, Japan).

Figure 1 shows a schematic of the low-temperature solid-state dissolution process of MWCNTs into Al particles. Firstly, CNTs are simply mixed with Al particles at the initial stage of mechanical grinding (Fig. 1a). With increasing grinding time, Al particles are fractured into small sizes, blocking coalescence of Al particles, as shown in Figure 1b. During this process, the CNTs are also damaged and fractured by continuous mechanical impact (Fig. 1c). At the final step, the CNT flakes are eventually disintegrated into C atoms, resulting in the dissolution of CNTs into Al nanoparticles, as shown in Figure 1d. Al particles in general experience fracture and coalesce with each other (hence cold welding) during mechanical milling. Cold welding is more dominant among Al particles at longer milling times due to their ductile properties. However, incorporation of CNTs in the milling process prevents Al particles from aggregating together. As a consequence, originally micron-size Al particles are disintegrated into 200–300 nm sized particles. SEM micrographs of the pristine MWCNTs and Al particles used in this experiment are presented in Figure 2a and b. CB was also used as a reference (see Fig. 2c). The MWCNT entanglement can be clearly observed in Figure 2a. A thin amorphous carbon layer is present on the surface of MWCNTs during this synthesis procedure. The sizes of Al particles range widely from 3 to 50 μm. The CB particles were less than 200 nm in size.

After ball-mixing of Al and CNTs for 1 h, Al particles had disintegrated into small particles and reaggregated again to large-size particles, while some of CNTs became incorporated inside the particles during reaggregation. Figure 2d shows the surface of Al aggregate, revealing the presence of CNTs and small Al nanoparticles. Some of the protruded CNTs can be observed in higher magnification image shown in Figure 2e. After mechanical grinding for 3 h, Al particles were further disintegrated into small sizes of 200-300 nm and CNTs were damaged, forming carbonaceous clusters and becoming embedded in Al nanoparticles. No distinct CNTs were visible at the surface of Al nanoparticles. Further treatment to 12 h did not change appreciably the particle morphology, as shown in Figure 2g. CNTs were completely disintegrated, as will be shown by the TGA analysis.

**Figure 1.** Schematic diagram of the solid-state dissolution method: (a) mixture of CNTs and Al particles; (b) nanoparticle formation; (c) disintegration of CNTs into C atoms or clusters; and (d) dissolution of C atoms into Al particles.

**Figure 2.** Morphologies of composite powders after solid-state dissolution. SEM images of (a) pristine CNTs; (b) raw Al powder; (c) raw C black, CNTs and Al particles after mechanical ball-milling for (d) 1 h and (e) protruded CNTs on the surface of Al particles milled for (f) 3 h, (g) 12 h; and (h) carbon black and Al after 12 h ball milling.
examination of the XRD patterns below. Ball-milling of CB with Al powder showed a similar morphology to the case of Al plus CNTs. However, some Al particles were aggregated into particles a few microns in size, as shown in Figure 2h. The role of lubricant to prevent reaggregation of Al particles seems to be less efficient.

Microscopic structural changes in the Al-CNT mixture during ball-milling were investigated by TGA, Raman spectroscopy and XRD. Figure 3a shows the TGA results of burning CNTs located on the surface of Al particles. The mass decrease with increasing temperature is due to the burning of CNTs that are exposed on the surface of Al particles. At 1 h ball-milling, the weight decrease around 400 °C indicates the onset of CNT burning. The rapid decrease of CNT burning slowed down around 650 °C and again near 870 °C. This indicates the existence of different types of C allotropes on the surface of the Al particles. This was clearly visible in the differential TGA shown in Figure 3b. The curve was deconvoluted with a Gaussian function. The first major peak near 495 °C is ascribed to the burning of CNTs exposed on the surface of Al particles. Originally, the pristine MWCNTs were burned around 600 °C [12]. However, the MWCNTs were damaged by microwave treatment and located on the Al particles. This decreases the burning temperature of MWCNTs. The peak near 609 °C indicates oxidized Al particles. Al particles start melting near 650 °C and C allotropes that were embedded inside Al particles become exposed on the surface, leading to further burning. The related peaks appeared near 700 and 890 °C. As the milling times were extended, the mass increase becomes obvious near 609 °C (see Fig. 3a), clearly demonstrating the oxidation of Al particles. At 12 h ball-milling, the CNT burning peak disappeared, as shown in Figure 3c. Instead, a new peak appeared near 657 °C with a peak intensity half that of the maximum peak in Figure 3b, which can be regarded as contribution from the burning of C allotropes near the surface of the Al particles. The weight at the final temperature near 1000 °C shown in Figure 3a simply indicates the final weight of Al particles after the burning of CNTs on the surface of the Al particles. Thus, one can extract the amount of burned CNTs which can be slightly modified by oxidation of Al particles which was indicated in the shaded area near 609°C in Figure 3b and c. By taking account of this factor, one may extract the precise amount of the CNTs on the surface of Al particles and amount of dissolved C atoms inside the Al particles. At 1 h, nearly half the CNTs were exposed on the surface of Al particles (originally 50/50 wt.%) and the other half was embedded inside the Al particles, as shown in Figure 3d. The amount of dissolved C atoms was saturated at 6 h ball-milling. At this stage, 90% of carbons (45 wt.%) CNTs were dissolved into Al particles and the 10% which remained on the surface of the Al particles was burned off.

The damage to the CNTs during ball-milling can be understood by Raman spectroscopy. The G band near 1590 cm⁻¹ and the D band near 1350 cm⁻¹ indicate sp² and sp³ hybridized carbons in MWCNTs, respectively [13]. Raman spectra were compared without normalization to highlight the intensity change of G and D bands from different samples. The intensities of the G and D bands were reduced significantly after 6 h ball-milling, suggesting a substantial portion of CNTs were damaged. The disintegration of MWCNTs is also reflected in the XRD analysis, as shown in Figure 3f. The X-ray diffraction peaks consist of C, Al metal and Al oxide crystal structures, indicated by different symbols in the figure. The C (002) peak at 26° indicates the presence of residual graphitic structures. Al crystal peaks were also observed near 38.5° (111) and 44.7° (200) [14]. A very small quantity of Al oxide (green triangles) was also observed from the native oxide of Al or residual oxygen in the ball milling container. However, Al-related peaks were observed only at 1 h ball milling sample, as shown in Figure 3f (red line). After 3 h ball milling, C and Al lattice diffraction peaks completely disappeared. This phenomenon is also congruent with Raman spectra. The C (002) peak intensity disappeared, implying disintegration of MWCNTs. Al (111) and (200) peaks also disappeared with MWCNT disintegration. This implies that the disintegrated C atoms are dissolved into Al particles, where the crystallinity of Al has vanished and instead amorphous Al–C phase is formed. Intriguingly, aluminum carbide phase (Al₄C₃) is absent in the 12 h ball-milled sample [9].

The crystal structures of the Al–CNT mixture were characterized by TEM and EDS analysis. The TEM image of a sample ball-milled for 1 h is presented in Figure 4a. Al nanoparticles were clearly observed and are surrounded by CNTs (circles). Some of the CNTs were damaged and broken down during this process (inset of Fig. 4a). Figure 4b shows the interface between Al nanoparticles, where CNTs were observed. With increasing ball-milling time (up to 12 h), the graphitic structure of CNTs disappeared (Fig. 4c) and no CNT-like morphology was visible in this case. No distinct
crystal phase of Al was observed by TEM. EDS was performed at the inner position of the Al particle (inset of Fig. 4c). The quantitative analysis suggests that the particle consists of 50 wt.% of Al and 42 wt.% of C, in excellent agreement with the TGA results.

Mechanical properties of the samples were characterized by micro-Vickers hardness measurement. Samples (pure and composites) were prepared by pressing sample powder under 900 MPa for 19 h at room temperature. Table 1 indicates the hardness values of pure Al and 50 wt.% C (from CNT)-dissolved Al which were ball-milled for 12 h. Hardness was averaged over five points of each sample. The hardness of the Al–C mixture was increased by 57% compared to that of pure Al. The hardness of pure Al has been reported to be 22 Hv [15], which is much lower than the 169 Hv indicated in Table 1. This difference arises from the different sample preparation methods. Nanoscale dispersion was used to disperse CNTs in the previous investigation, where Al particles were not deformed and therefore Al grain sizes could remain intact. However, in our method, 12 h of ball-milling induces heavy deformation of Al particles, resulting in small grain sizes. Furthermore, these small grain sizes were retained at low operating temperatures. Due to these reasons a high hardness value of pure Al was observed in our investigation. By incorporating C

Figure 4. Formation of Al nanoparticles and C dissolution observations by TEM. (a) Formation of Al nanoparticles after 1 h ball-milling. Inset: CNT flakes. The scale bar is 10 nm. (b) Interface between Al nanoparticles bridged by CNTs as indicated in the inset. (c) Al–C nanoparticles after 12 h. (d) EDS analysis of Al–C nanoparticles in (c).

Table 1. Hardness measurement of the samples after 12 h ball-milling. Hardness was measured at five points under a 200 g force.

<table>
<thead>
<tr>
<th>Vickers hardness</th>
<th>Average</th>
<th>Error</th>
<th>Increment</th>
</tr>
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<tbody>
<tr>
<td>Pure Al</td>
<td>169</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>50 wt.% C</td>
<td>266</td>
<td>15.9</td>
<td>57%</td>
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atom dissolution in the Al lattice, the Al grains were further destroyed and eventually created an amorphous phase. Therefore, Al–C composite incorporated from solid-state dissolution of C atoms into Al matrix in amorphous phase contributes to the hardness improvement [3].

In summary, a new method for low-temperature solid-state dissolution was introduced in this paper. Dynamic dissolution in this process was systematically studied by SEM, TGA, Raman spectroscopy, XRD and TEM. The SEM results clearly showed the formation of Al nanoparticles and CNT disintegration. TGA indicated that the amount of CNTs that burns decreases with increasing ball-milling time, which implies the presence of a carbon residue inside the Al nanoparticles. XRD analysis also showed the disappearance of C and Al lattice diffraction peaks after 3 h of ball-milling. EDS and TEM observations indicated C atom dissolution into Al particles. Furthermore, Al–C bond increments due to dissolution of C atoms were confirmed by XPS deconvolution. Mechanical properties were also investigated in terms of Vickers hardness, revealing a 57% increase compared to pure Al.

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