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# Strategies to suppress grain growth of nanocrystalline aluminum

Gowoon JEONG, Jooyoung PARK, Singon KANG, Hyunjoo CHOI

School of Advanced Materials Engineering, Kookmin University,
77 Jeongneung-ro, Seongbuk-gu, Seoul, 136-702, Korea

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**Abstract:** The grain growth behaviors of nanocrystalline aluminum, alloy and composite are compared. First, nanocrystalline aluminum is fabricated by consolidation of ball-milled powder. Second, nanocrystalline aluminum alloy is designed to have elements such as Mn, Zr, and Misch metals, which can form thermally stable second phases at grain boundaries and also drag the movement of grain boundaries. Third, nanocrystalline aluminum-based composites containing multi-walled carbon nanotubes (MWCNTs) are also prepared because MWCNTs are expected to be located at grain boundaries and to suppress the grain growth of nanocrystalline aluminum. These three types of samples are annealed at 550 °C for up to 5 d and the effect of annealing time on Vickers hardness of the samples is compared. As a result, MWCNTs are found to be most effective to impede grain growth of nanocrystalline aluminum.

**Key words:** aluminum (Al); carbon nanotubes (CNTs); composites; nanocrystalline; grain growth

## 1 Introduction

Aluminum ranks second as the most frequently used metal after steel, possibly stemming from its economic saving and lightweight natures [1−3]. However, its inherit poor mechanical properties such as low specific stiffness and strength have restricted its usages as structural parts in a variety of industries.

Nano-structured materials, whose structural elements, clusters, crystallites or molecules, have dimensions ranging below 100 nm, have attracted a great deal of attention due to the remarkable progresses in fundamental mechanical properties [4−9]. Numerous studies have so far been conducted to investigate the effects of grain size on the mechanical behavior of aluminum as well as to develop nanocrystalline aluminum [10−22]. In this grain size regime, plastic deformation by means of intragranular slip becomes to lose its significance and hence nanocrystalline aluminum shows significantly different deformation behavior from that of ultrafine crystalline (grain sizes in the range from 100 to 500 nm) or microcrystalline (grain sizes larger than 500 nm) aluminum [10−18]. This implies that the superior strength, positively deviated from Hall−Petch relation, can be achieved as the grain size of aluminum is reduced down to tens of nanometers [18,19]. Hence, a number of techniques have so far been introduced to produce nanocrystalline aluminum, by means of top-down methods such as severe plastic deformation [20] and mechanical milling [18,19] as well as bottom-up methods including gas condensation [21] and crystallization of amorphous alloys [22].

Despite considerable progress in the field of nanocrystalline aluminum, the thermally unstable structure is one of major challenges to be overcome; the large volume fraction of grain boundaries comes with an inherent instability. Hence, grain growth commonly induces significant softening of metals even at elevated temperatures. With this scope, attention has currently shifted to the problem of stabilizing nanocrystalline structures. Researchers have recently reported that the proper alloying design may lower the kinetic energy for grain growth, providing thermodynamically stabilized grain boundaries [23−27]; the grain boundary energy can be lowered by the segregation of alloying elements. However, it has not been well attended for nanocrystalline aluminum.

In the present work, we employ two strategies to impede grain growth of nanocrystalline aluminum at high temperatures: 1) precipitation of thermally stable second phases at grain boundaries; 2) reinforcement of

**Corresponding author:** Hyunjoo CHOI; Tel: +82-2-910-4287; Fax: +82-2-910-5647; E-mail: hyunjoo@kookmin.ac.kr
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the aluminum matrix using thermally stable multi-walled carbon nanotubes (MWCNTs). Three types of samples including nanocrystalline aluminum, alloy and composite were annealed at 550 °C for up to 5 d and Vickers hardness was measured at every time step to indirectly compare the grain growth behaviors of the samples.

## 2 Experimental

### 2.1 Powder process

A ball-milling process via an attrition mill (KMC Co. Ltd., KMC-1BV, Korea) was utilized for 1) grain size refinement of aluminum, 2) mechanical alloying and 3) dispersion of multi-walled CNTs (MWCNTs) in aluminum powder, in order to finally produce three different powders of nanocrystalline aluminum, alloy and composite.

Nanocrystalline aluminum powder was fabricated by ball-milling of the starting aluminum powder for 24 h. Gas-atomized aluminum powder (150 μm, 99.5% in purity, Changsung Co. Ltd.) was charged in a stainless steel chamber with stainless steel balls of 5 mm in diameter at a mass ratio of 1:15. 1% (mass fraction) stearic acid ($CH_3(CH_2)16COOH$) was added as a process control agent to prevent excessive cold welding among powders. The powder and balls were stirred by horizontal impellers attached to a vertical shaft rotating at 500 r/min. The milling process was performed under argon atmosphere to prevent the oxidation of powder.

To fabricate the nanocrystalline Al−11.9%Cu−3.5%Ce−0.3%Zr−0.1%Mn (mass fraction) alloy, all element powders were ball-milled together for 24 h under the same condition with nanocrystalline aluminum. Cerium (165 μm, 99.9% in purity, Sigma Aldrich Korea Co. Ltd.) and copper (180 μm, 99.9% in purity, High Purity Chemicals Co. Ltd.) are expected to form $Al_8CeCu_4$ precipitates to impede the grain growth of aluminum. Further, zirconium (700 μm, 99.5% in purity, Sigma Aldrich Korea Co. Ltd.) and manganese (75 μm, 99% in purity, Sigma Aldrich Korea Co. Ltd.) are added with a purpose of solid solution strengthening and further grain refinement.

Nanocrystalline aluminum matrix composite powder containing 7.5% (volume fraction) of MWCNTs was produced through two-step ball-milling processes: monolithic aluminum powder was solely ball-milled for 18 h; then the aluminum powder was further ball-milled with MWCNTs (~20 nm in diameter, and ~5 μm in length, supplied from Applied Carbon Nano Co. Ltd.) for 6 h; hence, the total milling time was kept to be 24 h. Milling was conducted under the same condition with nanocrystalline aluminum or alloy although, in the second step, the composite powder was ball-milled at a 600 r/min to induce sufficient energy on MWCNTs so that MWCNTs can be uniformly dispersed in aluminum powder.

The powder size is significantly reduced during the attrition milling process, resulting in difficulties in consolidation. Therefore, planetary milling was utilized to increase the powder size by cold welding of the attrition-milled powder. Stainless steel bowls (500 mL) were filled with the milled powder (50 g) and stainless steel balls (~5 mm in diameter, 750 g) without any process control agents. Planetary milling was performed with a rotation speed of 200 r/min for 1.5 h.

### 2.2 Sintering

To obtain fully dense specimens, hot rolling was utilized. Prior to hot rolling, stearic acid was removed by heat treatment of ball-milled powder at 500 °C for 30 min. Then, powder was packed in a one-end-sealed copper tube (outer diameter: 45 mm, length: 150 mm, and thickness: 1.2 mm), compacted with pressure of ~200 MPa at room temperature. Then, the other end of the copper tube was also sealed. The sample was heated to a predetermined temperature of 480 °C; it required ~40 min upon heating the sample. Rolling was conducted with every 12% reduction. After 19 passes, the sample thickness was reduced to be ~1.7 mm. The copper container was mechanically peeled off.

### 2.3 Microstructure observation

The morphology of powder was observed using scanning electron microscope (SEM, JEOL, JSM 2001F, Japan). Specimens were attached to a carbon tape for SEM analysis. The microstructure with a high magnification of as-rolled specimens was examined by high-resolution transmission electron microscopy (HRTEM, JEOL 2100FX). The operating voltage was 200 keV in JEOL 2100FX. Thin foil specimens from the composite sheets were carefully prepared by polishing and an ion beam milling method (Gatan, PIPS 691, Oxford, U.K.) by double-sided $Ar^+$ ion-beam etching at acceleration voltage of 2.0−3.5 kV. The angle between the ion beam and the surface of specimens was set at approximately from 4° to 8°. The presence of MWCNTs was confirmed by Raman spectroscopy (LabRam Aramis, Horiba Jobin Yvon, France). The spectra were collected under the ambient conditions using the 514.5 nm line of an argon-ion laser.

### 2.4 Heat-treatment and grain size measurement

The grain growth behavior of three different samples were examined by heat-treatment of samples at 550 °C for up to 120 h. The grain size and the composition of the samples were analyzed using X-ray diffraction (XRD, Rigaku, CN2301) with a Cu $K_\alpha$