

Development of Al/C₆₀ Composites with Nano-Network Structures

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Abstract

It has been challenging for metals to synthesize optimal nano-structures with a desirable performance. Herein, we propose a new idea for the development of nano-network structures in Al/C₆₀ composites by the self-assembly of Al-C phases. Carbon atoms, dissembled from the individually dispersed C₆₀-fullerenes, are intercalated into the interstitials of aluminum, producing Al-C phases with artificially moderated lattice structures. The isolated Al-C phases grow with a strong anisotropy derived from lattice mismatch, meet neighbor Al-C phases, and then self-assemble into network structures. The novel nano-structures, extremely stable at high temperatures, offer significant potential for the development of thermally-stable high-strength structural aluminum. The controlled lattice provides a new paradigm for atomic level design of crystalline materials.

Introduction

The desire for the development of crystalline metals with a high performance has inspired researchers to design optimal nano-structures through nano-scale boundaries [1, 2], solute atoms [3], and second-phase particles [4]. Furthermore, amorphous [5] or quasi-crystalline [6] phases have occasionally been employed for exotic mechanical properties. However, these structures are obtained only under the specific thermal-dynamic conditions and hence the stability of the structures is extremely low. In this context, composites incorporating nano-scale non-metallic materials have captured a great deal of attention due to their stable and easily formable nano-structures [7-14]. In particular, carbon-based nano-materials, including fullerenes and nano-tubes, have been considered as a key material for the development of nano-structured composites, due to their exceptional properties and stable molecular structures induced by the strong sp² C-C bonds [10, 11]. They can also effectively impede diffusion of metal atoms at high temperatures, suppressing changes in the nano-structures of the metal matrix (e.g. grain growth) during hot working processes. However, there has not been much remarkable progress reported in structural applications for the composites; poor dispersion of the nano-materials [12, 13] and carbide formation [14] are critical factors.

Despite a long journey, the synthesis of optimal metal nano-structures with a desirable performance is still challenging. Furthermore, the poor stability of nano-structures is also a crucial problem; grain growth, precipitate coarsening, and unfavorable chemical reactions commonly destroy the original structures, leading to significant softening of metals at high temperatures. In research fields, therefore, a new scheme is urgently required. One possible strategy in fabricating nano-structured materials is the incorporation of self-assembling materials into an accessible manufacturing process to achieve atomic-level design [15]. Block copolymers are well-known examples of self-assembling systems, in which chemically distinct blocks separate into nano-scale periodic domains [16, 17]. Contrary to organic molecules,

however, there have been no reports on self-assembling systems in densely packed solid crystals such as metals.

In this study, nano-network structures in Al/C₆₀ composites are constructed by the self-assembly of Al-C phases, which are derived from elastic energy associated with the lattice mismatch. Carbon atoms, dissembled from individually dispersed fullerene, occupy the interstitial sites of aluminum and form Al-C nano-phases, distorting the aluminum lattice structures during annealing at high temperatures ($\sim 0.8 T_m$, T_m is the melting point of aluminum).

Experimental

C₆₀-fullerenes (99.95% purity), supplied from Nano-C Co., LTD., are synthesized using the 2nd generation combustion process; a continuous high-flow of hydrocarbon is burned at low pressure in a 3-dimensional chamber. Although individual fullerene molecules are about 1 nm in diameter, these molecules come together to form particles ($\sim 200 \mu\text{m}$ in diameter) with the long-range periodicity of the FCC (face-centered cubic) crystalline structure during manufacture (Fig.1 (a)). Scanning electron microscopy (SEM) observation of the as-milled fullerenes (Fig.1 (b)) exhibits a size reduction of the particles from $\sim 200 \mu\text{m}$ at the beginning to less than $1 \mu\text{m}$ after mechanical milling, where the small (less than $1 \mu\text{m}$) particles aggregate by a weak Van der Waals force. The solely milled fullerenes (2 vol%) are further milled with aluminum powders. During the milling process, ductile aluminum powders get flattened by the ball-powder-ball collisions, whereas fullerenes are further fragmented. The fullerene aggregates, embedded in the aluminum powders, are gradually separated and located deeper through plastic deformation of the matrix. Flattened large aluminum powders ($200\text{--}300 \mu\text{m}$ in diameter) are fractured, and then the refined powders again are cold-welded to each other. After milling for a certain length of time, therefore, a balance is achieved between the rate of welding and fracturing, with an overall tendency to drive most powders toward an intermediate size (i.e., $30\text{--}40 \mu\text{m}$ in diameter). During the process, most fullerenes are individually dispersed inside the aluminum powders, exhibiting fewer fullerenes on the surface of the aluminum powders (Fig.1 (c)). To fabricate a dense composite sheet, hot-rolling is employed. The ball-milled powder is containerized in a copper tube, compacted under high pressure, sealed by welding, and is then hot-rolled at 480°C . After rolling, the Al/C₆₀ composite was annealed at 500°C ($\sim 0.8 T_m$) for up to 24 h.

Changes in microstructures of composites are observed using HRTEM (JEOL 2100FX). The operating voltage was 200 keV in JEOL 2100FX. Thin foil specimens from the composite sheets were carefully prepared by an ion beam milling method (Gatan, PIPS 691, Oxford, U.K.) by double-sided Ar⁺ ion-beam etching at $2.0\text{--}3.5 \text{ kV}$ acceleration voltage. Quasi-static compression and tension tests are carried out using an Instron-type machine at an initial strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. Rectangular specimens with 2:1 of height-to-width ratio were prepared for compression tests.

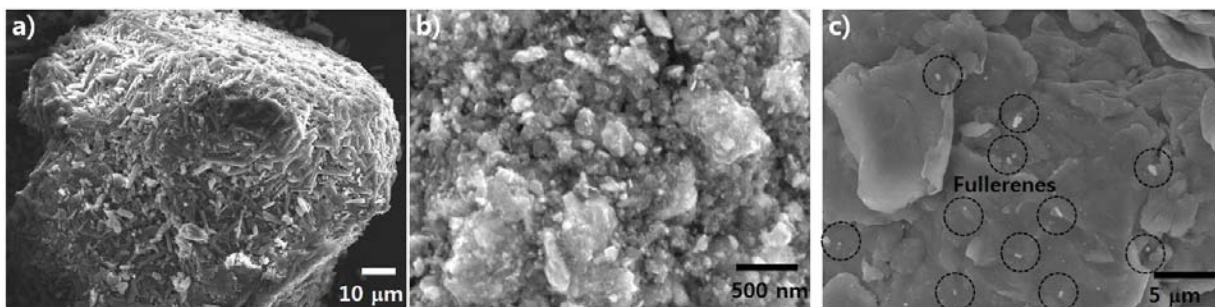


Figure 1 SEM images of **a)** as-received fullerene particles, **b)** solely-milled fullerene aggregates, and **c)** as-milled Al-C₆₀ powder

Results and discussion

Figure 2 (a) shows TEM image of the composite containing 2 vol% fullerenes. Although, to a great extent, large fullerene clusters (~200 μm) become fragmented, and some of fullerenes are individually dispersed during the process, short-range periodicity (tens of nano-meters) remains in the FCC lattice of fullerenes for some clusters in the composite, exhibiting a giant fullerene aggregate with a size of ~20 nm. Figure 2 (b) shows the microstructure of the composite after 24-h-annealing. As noticed in the previous report [18], during annealing at 500°C, carbon atoms from the individually dispersed C₆₀-fullerenes are intercalated into the interstitials of aluminum, producing Al-C phases with the increased volume of the unit lattice. The Al-C phase, which forms a coherent or semi-coherent interface with the aluminum matrix, reveals a mixed moiré resulting from the interference of possibly two different crystals. In Fig. 2 (b), aluminum fringes with a spacing of ~0.28 nm for the matrix and extended fringes with a spacing of ~0.30 nm in the (111) plane, where fast Fourier Transform (FFT) patterns are also evident in the lattice parameters. The extension of the lattice parameters may come from the intercalation of carbon atoms into the interstitial sites of aluminum. Carbon atoms, dissembled from the severely deformed fullerenes, attempt to form aluminum carbides due to the high annealing temperature and high local strain energy; hence, the C-C bonds in the fullerenes will be broken. However, thermal energy is not sufficient for long-range diffusion to form carbides, which have an enormous rhombohedral lattice structure with a lattice parameter of $a = 0.334$ nm and $c = 2.5$ nm. Carbon atoms from the individual fullerenes fail to form carbides due to the lack of carbon contents and the limited diffusion capacities. It might offer potential for the intercalation of carbon atoms into the interstitials of aluminum. Carbon atoms may diffuse to other interstitials as the composite is further annealed. The isolated Al-C phases grow with a strong anisotropy derived from lattice mismatch, meet neighbor Al-C phases, and then self-assemble into network structures. The localized lattice distortion at the interface between the phases and the matrix, as shown in Fig. 2 (b), may act like a driving force for self-assembly among the phases into a networked nano-band structure.

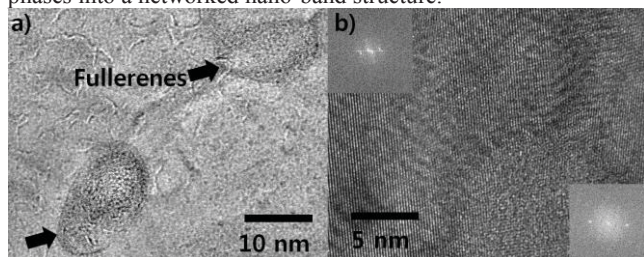


Figure 2 **(a)** HRTEM image of Al-2vol% fullerenes composite and **(b)** of the lattice distortion at the interface between the Al-C phases and the matrix, annealing at 500°C for 24 h.

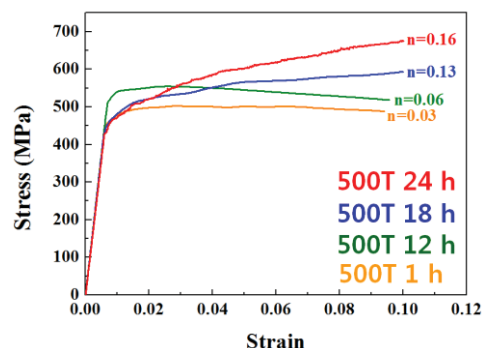


Figure 3 Compressive stress-strain curves for Al-2vol% fullerenes composite, after annealing at 500°C for 1 (orange-colored), 12 (green-colored), 18 (blue-colored), and 24 h (red-colored).

Figure 3 shows compressive stress-strain curves for Al-2vol% fullerenes composite, varied by annealing time. The yield strength of the composite increases after annealing at 500°C for 12 h and then decreases after further annealing. This softening originates from grain growth and thermal recovery processes, similar to conventional metals. As annealing time increases, however, work hardening rate increases significantly and the deterioration of the yield strength is negligible.

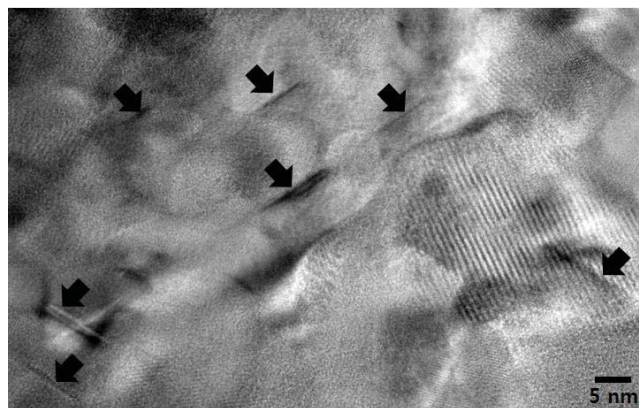


Figure 4 HRTEM macrographs of twins, observed after ~5% plastic deformation for the composite with 2 vol% of fullerenes, which was annealed at 500°C for 18 h.

A number of twins are observed in the matrix of composite, which is annealed for 18 h, after the compression test (Fig. 4). The composites with less than 5 vol. % of fullerenes comprise binominal micro structures; the networked nano-bands cannot be developed throughout the composite due to the low volume

fraction of fullerenes [18]. Therefore, plastic deformation, including twinning, occurs mostly in the matrix, where the networks are not yet developed and where particle-type nano-phases are observed. The twinning seems to occur preferentially in smaller grains (~5 nm in size) and propagates across the whole grain. The deformation twins could be generated by the dynamic overlapping of two extended partial dislocations with stacking faults on adjacent slip planes. Although there have been reports of deformation twins in aluminum under highly localized abnormal stress concentrations, this is the first observation of deformation twins for homogeneously deformed aluminum using a conventional compression test.

Conclusions

The present study introduces a couple of important findings in aluminum matrix composites. The interstitial sites of aluminum can be occupied by carbon atoms by distorting the aluminum lattice, despite the negligible solubility; carbon atoms, dissembled from individually dispersed fullerenes, fail to form carbide due to the short supply of carbon atoms and settle down on the interstitial sites of aluminum, forming the isolated Al-C nano-phases. The Al-C phases grow with a strong anisotropy, meet other Al-C phases, and then self-assemble into network structures to reduce lattice misfit energy, providing extremely stable nano-structures. Deformation twins are observed in grains below 10 nm in diameter for the homogeneously deformed composite. With the self-assembled network nano-structures, the composite with an incorporation of just 2 vol% (i.e. ~3 wt. %) fullerenes exhibits a yield strength of ~500 MPa, which is very stable even at 500°C. Therefore, the investigation opens up a research area of both fundamental and applied importance.

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