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Powder metallurgy routes toward aluminum boron nitride nanotube composites, their morphologies, structures and mechanical properties

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ABSTRACT

Aluminum/boron nitride nanotube (BNNT) composites with up to 5 wt% (i.e., 9.7 vol%) nanotube fractions were prepared via spark plasma sintering (SPS) and high-pressure torsion (HPT) methods. Various microscopy techniques, X-ray diffraction, and energy dispersive X-ray analysis confirmed the integration of the two phases into decently dense and compact composites. No other phases, like Al borides or nitrides, formed in the Al–BNNTs macrocomposites of the two series. The BNNTs were found to be preferentially located along Al grain boundaries in SPS samples (grain size was 10–20 μm) creating micro-discontinuities and pores which were found to be detrimental for the sample hardness, whereas in HPT samples, the tubes were rather evenly distributed within a fine-grained Al matrix (grain size of several hundred nm). Therefore, the hardness of HPT samples was drastically increased with increasing BNNTs content in Al pellets. The value for Al–BNNT 3.0 wt% sample was more than doubled (190 MPa) compared to a pure Al–HPT compact (90 MPa). And the room temperature ultimate tensile strength of Al–BNNTs HPT samples containing 3.0 wt% BNNT (~300 MPa) became ~1.5 times larger than that of a BNNT-free HPT–Al compact (~200 MPa).

1. Introduction

Light metal matrix composites (MMCs) reinforced with nanophases became a popular direction in Materials Science of the 21st century. To date, as a strengthening nanophase, most typically, carbon nanotubes (CNT) have been used. Most of the MMC–CNT composites have been produced by powder metallurgy techniques, such as mechanical alloying, sintering, hot pressing and compacting [1]. To do so, after the initial mixing step, a blend of CNTs and a metal must be consolidated to a high density. A wide range of compaction processes has been applied to reach a sufficient densification, among those spark plasma sintering (SPS) and high-pressure torsion (HPT) are particularly notable. SPS was used for the CNT–MMC studies (mostly for Al [2] and Cu–CNT systems [3,4]). For example, Kwon et al. [5] and Kurita et al. [6] found that CNTs may be well dispersed within an Al matrix by using a hetero-agglomeration principle. And 5.0 vol% CNTs addition could elevate the strength to about thrice of that of pure Al [5]. This improvement was attributed to particular strengthening by CNTs, which are strongly bonded with the matrix through the crystallized Al carbide phase [5]. A fully dense 1.0 vol% MWCNT–Al matrix composite has documented a 40% improved tensile strength with respect to pure Al, whereas an elongation to failure has become of 27.3%, nearly similar to that of cast pure Al [6]. Other than the mechanical property studies, thermal properties were also one of the most important topics in regard to the MMC–CNTs research [7–9].

HPT is one of the severe plastic deformation (SPD) techniques that allows one to achieve very large deformations without heating, under vacuum sintering conditions. Typically, a HPT method has frequently been applied for the grain refinement in bulk coarse-grained metals [10,11], but it is also fully capable of consolidating pure metallic powders [11] or their blends with CNTs [12,13]. Due to a very high applied pressure and imposed shear strain, ultrafine-grained (UFG) or nanocrystalline microstructures are formed in the consolidated samples, even if the initial powders consist of coarse grains. Grain refinement is important for increasing hardness according to the Hall–Petch relationship [14]. For the MMC–CNT works by a HPT method, Al [15–17] and Cu [18–20] were the main metal candidates, similar to SPS studies. For example, Tokunaga

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et al. [15], Joo et al. [16] and Janei et al. [18] analyzed the difference of hardness depending on the area from the center of the HPT samples, because the torsion under high pressure may differently affect the sample center and its edge.

We have been long looking for reinforcing agents other than CNTs for making lightweight and strong Al matrices through a powder metallurgy route. And multi-walled boron nitride nanotubes (BNNTs) have drawn our prime attention [21,22]. These nanotubes possess the crystal geometry identical to those of CNTs (in which each C atom is replaced by alternating B and N atoms), but their properties are totally different. The perfectly straight and peculiar de-bundled appearance of BNNT makes their placement in a given metal matrix more technological compared to CNTs. It is also worth noting that BNNTs are far more chemically and thermally stable compared to CNTs, while having nearly the same huge values of Young's modulus ($\sim$1 TPa) and ultimate tensile strength ($>$30 GPa) [23].

It is worth mentioning that decent successes have already been achieved by us using BNNTs for improving conventional polymers or ceramics over the past decade [24,25]. By contrast, metal/BNNT composites are almost entirely unstudied materials. Only a few reports globally, including ours, have been published with respect to these new composites. For instance, Singhal et al. [26] while using powder sintering route observed an increase of compressive strength and microhardness of Al/BNNT samples compared to non-doped Al compacts. Agarwal's group has explored the Al/BNNT chemical interfacial reactions [27]. Most recently this group has made an initial attempt to make Al/BNNT composites using a SPS technique [28], i.e., Lahiri et al. stated that BNNT had survived high pressure and temperature over prolonged time needed for SPS. Performed micro-pillar compressive tests showed 50% improvement in both yield and compressive strength with 5.0 vol% BNNT addition into an Al matrix.

But it is important to note that multi-walled BNNTs that Singhal et al. [26] and Lahiri et al. [27,28] utilized in their studies were not of preferred morphologies. They possessed so-called bamboo-like structures formed under a ball milling synthesis [29]. According to our comparative in situ TEM direct tensile tests on individual BN tubes of different morphologies, such nanostructures are several times weaker (having strength below 8 GPa [30]), compared to well crystallized nested and long (up to 10–20 μm) BN tubular cylinders or polygons routinely produced by us [23].

Over the past two years, using these perfectly shaped and well-structured BNNTs we successfully fabricated various metal–matrix composites made of Al and BNNTs using ion-implantation [31], magnetron sputtering [32] and melt-spinning [33], and analyzed their tensile and bending properties at the nano- and micro-scales. Drastic improvement of the Al mechanical performance was documented on nano- and micro-samples. However, while addressing the issues of future mass production of light and strong MMCs, one essentially needs to move toward the powder metallurgy route which is able to produce macro-samples at high yields.

Therefore, this paper was planned as to fabricate bulky Al–BNNT composites using two selected and efficient compacting procedures, namely, SPS and HPT, and to comparatively analyze structural peculiarities and mechanical properties of the fabricated composites toward their further possible technological implementations.

2. Experimental procedure

2.1. Powder preparation and consolidation

Multi-walled BNNTs were synthesized by the boron oxide-assisted CVD (BOCVD) method [21,22]. After subsequent high-temperature purification in argon atmosphere, they were dispersed in ethanol using ultrasonic agitator for about an hour. An Al powder (20 μm, 99.9%, Kojundo Chemicals, Japan) was added into the BNNTs–ethanol solvent and mixed with a stirrer for about 2 h. Ethanol was evaporated after the sample preparation. The starting Al–BNNTs powders were loaded with 1.0–5.0 wt% (i.e., $\sim$2–9.7 vol%) of BNNTs. The dried powder mixtures were consolidated by SPS ('Dr. Sinter' SPS-511 S apparatus, Sumitomo Coal Mining Co., Japan) in vacuum at 550–600 °C and 50 MPa pressure for 15–20 min in a graphite die, the heating rate was 60 °C/min. The same Al–BNNT powder mixtures were used for HPT fabrication. The dried powder mixtures were compacted by a REP-HPT-60-05 apparatus, Riken Enterprise Co., Ltd., Japan. Approximately 0.1 g of the powder mixture was put in a circular shallow hole 10 mm in diameter located at the center on the lower anvil of the HPT machine. The lower anvil was lifted to contact the upper anvil as the former was rotated with respect to the upper one at a rotation speed of 1 rpm. Compacting was undertaken at room temperature with an applied pressure of 2.5 GPa. The rotation was initiated 10 s after the load application and terminated after 10 turns. The resultant pellet thickness was $\sim$0.5 mm.

2.2. Structural analysis

The phase compositions of SPS and HPT compacts were identified by X-ray diffraction (XRD; RINT2000 Ultima III, Rigaku Corporation, Japan) using Cu Kα radiation. The morphologies of the polished and fractured surfaces of the samples were investigated by scanning electron microscopy (SEM; S4800, Hitachi Ltd., Japan) and high-resolution transmission electron microscopy (TEM; JEM-2100 F (200 kV), JEM-3000 F (300 kV) and JEM-3100FEF (Omega filter) instruments, JEOL Ltd., Japan). TEM samples were prepared by using focused ion beam (FIB) polishing. Energy dispersive X-ray spectrometry under SEM and TEM investigations (EMAX EX-220, Horiba Ltd., Kyoto, Japan; JEM-3100FEF microscopes) at accelerating voltages of 10 kV (SEM) and 300 kV (TEM), respectively, were employed to identify the composite chemistry and to spatially map the constituting species.

2.3. Mechanical property measurements

Microhardness was measured by Vickers indentation using a diamond indenter (Durascan 70, EMCO-TEST Prüfmaschinen GmbH, Austria) under a load of HV0.2 for 10 s. The tensile strength was measured at room temperature on HPT samples by using a tensile test machine (AUTOGRAPH AGS-10KNJ, Shimadzu, Japan) at a strain rate of 2.0×10^{-3} s^{-1}. The displacements were measured by a video extensometer with a 3 μm resolution. The samples were cut to 'dog

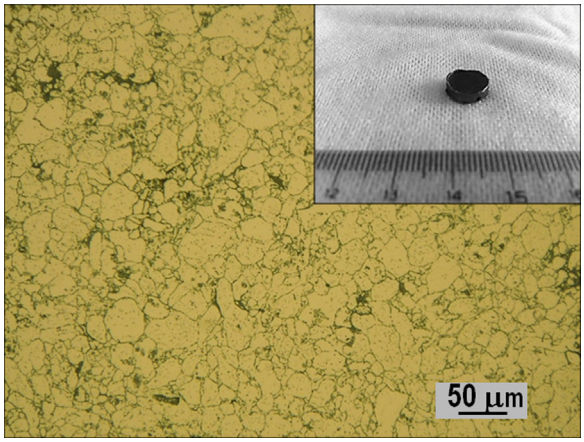

Fig. 1. An optical microscopy image of a polished and etched Al-based SPS sample with 1 wt% of BNNT. The average grain size is 10–20 μm. The inset shows the appearance of the actual SPS pellet. It measures around 1 cm in diameter and $\sim$3 mm in thickness.