

科学研究費助成事業 研究成果報告書

平成 26 年 6 月 23 日現在

機関番号：82108

研究種目：基盤研究(B)

研究期間：2011～2013

課題番号：23310082

研究課題名(和文)自動車・航空機応用のためのBNナノチューブと低密度金属による超軽量高強度材料開発

研究課題名(英文)Development of novel ultralight and superstrong hybrid materials made of low density metals/alloys reinforced with boron nitride nanotubes for automobile and aerospace applications

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交付決定額(研究期間全体)：(直接経費) 9,600,000円、(間接経費) 2,880,000円

研究成果の概要(和文)：放電プラズマ焼結(SPS)法や高圧ねじり加工(HPT)法と呼ばれる粉末焼結法により、ナノチューブの含有率を5 wt%(すなわち9.7 vol%)に上昇させたアルミニウム(Al)/窒化ホウ素ナノチューブ(BNNT)複合材料を作製した。

3.0 wt%のBNNTを含有したAl-BNNT試料の値は、HPT法で作製した純粋なAlの試料の90 MPaに比較して、2倍以上の190 MPaに達した。また、本試料の室温における最大引張強度が、BNNTを含有しないHPT法で作製したAl試料の~200 MPaに比較して、1.5倍の~300 MPaに達することが分かった。

研究成果の概要(英文)：Aluminum/Boron nitride nanotube (BNNT) composites with up to 5 wt% (i.e. 9.7 vol%) nanotube fractions were prepared via various powder metallurgy routes, namely, Spark Plasma Sintering (SPS) and High Pressure Torsion (HPT) methods. Optical microscopy, transmission electron microscopy, scanning electron microscopy, 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, form in the Al-BNNTs macrocomposites of the two series. 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 double d (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).

研究分野：複合新領域

科研費の分科・細目：ナノマイクロ科学・ナノ材料・ナノバイオサイエンス

キーワード：複合材料 低密度金属 電子顕微鏡 ナノチューブ 機能的機能

1. 研究開始当初の背景

Nowadays, it is becoming more and more important to provide “superlight” and “superstrong” materials for vehicles to make them lighter and reduce the amount of carbon dioxide or fuel cost. Metal matrix composites (MMC) made of aluminum and carbon nanotubes (CNTs) have become of great interest with respect to utilization in automotive, aircraft and aerospace industries [1]. However, CNTs have drawbacks for those applications such as absorption of light, and thus heating, and ease in bundling and buckling. Boron nitride nanotubes (BNNTs), while having quite similar structures to CNTs, are particularly known for their remarkable mechanical properties, no absorption of visible light, high thermal, chemical and oxidation stabilities, and straight needle-like morphologies. They have low density (1.4 g/cm^3), high ultimate tensile strength ($\sim 35 \text{ GPa}$) and high Young’s modulus ($\sim 1 \text{ TPa}$), thus the figures which are much more impressive than those typical for standard reinforcing materials, such as aluminum nitride or silicon carbide. To make decently strong composites, it is important to have intimate and robust interfaces between metals and nano-reinforcing fibers. BNNTs may be able to create such interfacial structures and maintain them up to high temperatures due to their superb thermal and oxidation stabilities (up to $\sim 1000 \text{ }^\circ\text{C}$) in air.

2. 研究の目的

In order to create this new generation of “nanotube-metal composites”, herein BNNTs were utilized as novel nanofillers for the reinforcement of light metals, such as aluminum (Al), and the regarded composites were fabricated at nano-, micro- and macro- scales through various processing methods and their structures and mechanical properties were then analyzed in detail.

3. 研究の方法

For making composites three methods were utilized, namely, magnetron sputtering, melt spinning, and a powder metallurgy using spark plasma sintering (SPS) and high pressure torsion (HPT) techniques as in detail described below.

4. 研究成果

4.1 Al-BNNTs nanocomposites

First, Al-BNNT composite nanohybrids with a varying Al coating thickness, from 5 nm to 200 nm were fabricated by magnetron sputtering. Dispersed in ethanol BNNTs were put either on a Si substrate, a copper grid, or a gold tip and Al coatings were made on them using direct dc magnetron sputtering.

Al uniformly coated each BNNT. The coatings were found to be well crystalline. Changing sputtering time controlled the Al thickness. To determine their chemical status of B, N, O and Al, X-ray photoelectron spectroscopy (XPS) analyses were carried out. According to the results, BNNT cores well withstood the magnetron sputtering without losing integrity of B-N bonds and peculiar straight morphology of perfectly structured shells. Also there was no intermediate and interfacial boride or nitride phases detected, e.g. AlB_2 or AlN , between BNNTs and Al phases. The latter is a common issue for Al-CNTs MMC for those Al_4C_3 carbides formed at the interfaces causing a negative effect onto the material mechanical properties [1]. Our studies proved that BNNTs are chemically stable in Al-BNNTs composites. It would be of a great advantage for such composite utilization in harsh environments and at high temperatures.

In-situ TEM mechanical tests on individual Al-BNNT composites shed a new light on their micro- and atomic structures, chemical status and mechanical properties. We carried out two different types of tests – bending and tension, while exploring various Al thicknesses on individual BNNT cores and studying mechanical properties and fracture behaviors of such nanocomposites thus created. The fabricated nanohybrids with a decently thick (40 nm) Al coatings on BNNTs (of 40–50 nm external diameter) demonstrated at least ~ 9 times increase in tensile stress which they could withstand without failure, compared to a pure non-armed Al metal.

Then the fractural behaviors were studied using “thin” (a BNNT with 20 nm Al layer) and “thick” Al-coated (a BNNT with 200 nm Al layer) samples. It became clear that there had been a certain difference in the fracture mechanism between thinner Al-layered and thicker

Al-layered BNNT composites. When an Al (20 nm)-BNNT nanocomposite was completely fractured in tension, the inner portion of BNNT shells slipped out of the outer BN layers which had remained rigidly fixed to the Al shield. On the other hand, an Al-BNNT nano hybrid with a 200 nm Al layer, that could not be broken under tension due to force limitations, was managed to be cracked under bending along the Al grain boundary. The thinner sample fractured abruptly in a brittle manner, while the thicker sample fracture (started within the Al grains) was terminated at the BNNT core that possessed the huge strength peculiar to of BNNT multilayers up to ~35 GPa [3]; thus such nanocomposites may withstand very large forces and stresses.

4.2. Al-BNNTs microcomposites

Next, a meter long and several dozen micrometers thickness Al-BNNTs composite ribbons with various fraction of multiwalled BNNTs (0.5 to 3.0 wt. %) were fabricated by melt spinning using an Al-BNNTs powder mixture [4,5]. BNNTs were dispersed into ethanol and mixed with an Al powder. After evaporation of ethanol, the powder was compacted by pressing the pellets. Each pellet was ~0.5 g in weight; 4-5 pellets were used for each melt-spinning run. The pellets were heated by the induction currents up to 1000 °C before quenching onto the revolving copper drum.

Tensile tests were carried out at room temperature by using a tensile test machine (AG-plus 10kN, SHIMADZU, Japan) at a deformation rate of $1.67 \times 10^{-4} \text{ s}^{-1}$. The samples were cut to ~8 cm length to clamp them on both sides. The maximum measured strengths of Al-BNNT 3wt.% ribbon was 145 MPa which is about 2.5 times larger than that of similarly casted pure Al ribbon (60 MPa).

Scanning and transmission electron microscopy observations (SEM, TEM) confirmed the decent integration of the two phases into a dense and compact composite, Figure 1. BNNTs were seen randomly oriented within the Al matrix, creating a sort of cross-linked network inside the metallic Al matrix, in a way analogous to a steel bars-reinforced concrete. Protruding BN nanotubes from the edge of the Al sample are particularly well seen in Fig. 1b; this sample was prepared using a focused ion beam (FIB) technology.

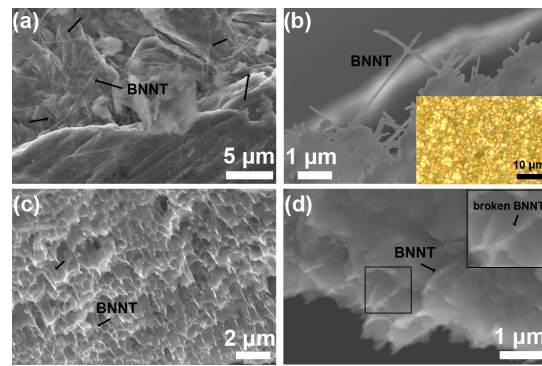


Figure 1. (a) Dispersion of BN nanotubes in the Al powder prior to melt-spinning; b) TEM image of BN nanotubes network within Al matrix after melt-spinning, the inset shows an optical micrograph of the grain structure; (c,d) SEM images of the fracture surfaces of Al-BNNT 3 wt.% sample after the tensile tests at room temperature; the inset in (d) shows broken individual tube found close to the fracture surface.

Importantly enough, the tubes were found to locate themselves within the grains and at the grain boundaries, and at least partially they participate in carrying the tensile load, as evidenced by their broken pieces present at the composite fracture surfaces.

4.3. Al-BNNTs macrocomposites

Finally, powder metallurgy as one of the most popular methods for Al-based MMC processing was tried. In this study, two different processes were implemented - spark plasma sintering (SPS) at 600 °C and high-pressure torsion (HPT) at room temperature. Al-BNNTs mixture powders were prepared in ethanol using an Al powder (30 μm fraction) and dispersed BNNTs.

Al matrix-BNNTs composite compacts (about 5 mm in thickness and 10 mm in diameter) were formed by SPS under high vacuum (50 MPa) at 600 °C. Samples were polished by a sand paper, diamond paste and SiO₂ paste and then etched by Keller's reagent to observe Al grain structures. The Al grain size was about 10-30 μm for all samples.

HRTEM images of SPS Al-BNNTs 1 wt.% samples taken showed the tubes are embedded into Al matrix or located themselves close to the grain boundaries.

Microhardness of SPS samples was measured by using a DuraScan70, Emcotest machine at 0.2 HV regime at room temperature. It is noted that there has been no drastic difference between pure Al and Al-BNNT samples. Notable porosity of BNNT-loaded SPS samples could be the reason for this.

BNNTs are also well known for their high thermal conductivity of $\sim 350 \text{ W m}^{-1}\text{K}^{-1}$ [6] in addition to their excellent mechanical properties, so Al-BNNT composites could also have a great potential to become unique thermoconductive materials. Some Al-CNT MMC materials showed better thermal properties than those of pure Al [7-9]. The key would be a good dispersion of BNNTs in Al matrix, so we shall try to analyze the relationship between the Al-BNNT structure and thermal properties in the nearest future.

Al matrix-BNNTs composites pellets ($\sim 0.5 \text{ mm}$ in thickness and 10 mm in diameter) were formed by HPT method using powder solidification and intense shearing deformations at high pressure (2.5 GPa) at room temperature [10].

Microhardness tests were carried out by using a DuraScan70, Emcotest machine at 0.2 HV regime at room temperature. The hardness of Al-BNNT 5wt.% was $\sim 180 \text{ MPa}$, i.e. nearly a doubled figure compared to similarly fabricated pure Al.

Room temperature tensile strength was measured by using a tensile test machine (AUTOGRAPH AGS-10KNJ, SHIMADZU) at a deformation rate of $2.0 \times 10^{-3} \text{ s}^{-1}$. The displacements were controlled by a video extensometer with a $3\text{-}\mu\text{m}$ resolution. The samples were cut to “dog bone” shapes by electrical discharge machining (EDM). The maximum measured strengths of Al-BNNT 3 wt.% sample is 350 MPa which is more than ~ 1.75 times larger than that of the pure Al sample made using the same technique (200 MPa).

All samples were observed by TEM after fracture. Due to severe deformations achieved by HPT, Al grain sizes became smaller (about 20 nm) compared to that in original tablets. BNNTs were found to be randomly oriented along Al grain boundaries and/or within Al grains.

Over all, we have studied Al-BNNTs composites by using various fabrication processes and at different length scales – from nano- via micro-, and to macro-dimensions. The strength of Al-BNNTs composites was generally higher than that of pure Al samples prepared using analogous procedures as summarized in Figure 2. These results demonstrate that BNNTs can be a promising candidate for the

reinforcement of light metal matrices which may be used in harsh environments and conditions and for the wide needs of aerospace, aircraft and automotive industries.

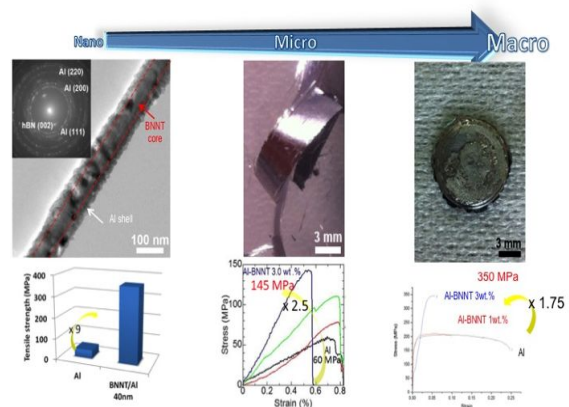


Figure 2. Al-BNNTs composites using a variety of fabrication methods and their tensile strength increases.

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[産業財産権]

出願状況(計 0 件)

名称 :

発明者 :

権利者 :

種類 :

番号 :

出願年月日 :

国内外の別 :

取得状況(計 1 件)

名称 : 窒化ホウ素ナノチューブの製造方法
発明者 : 板東義雄, Zhi C.Y., Golberg D.
権利者 : 独立行政法人物質・材料研究機構
種類 :

番号 : 4817103

取得年月日 : 平成 23 年 9 月 9 日

国内外の別 : 国内

[その他]

ホームページ等

http://www.nims.go.jp/units/u_nanotubes/index_e.html

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