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| 学 位 論 文 題 目 | |

Novel Light and Strong Aluminum-Boron Nitride Nanotube Composites
（アルミニウムと窒化ホウ素ナノチューブによる新規複合材料の開発）

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## 論 文 の 要 旨

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 (~35 GPa) and high Young’s modulus (~ 1 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 ~ 1000 °C) in air. 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). In this Thesis, the regarded composites were fabricated at nano-, micro- and macro-scales through various processing methods and their structures and mechanical properties were then reported in detail.

First, Al-BNNT composite nanohybrids with a varying Al coating thickness were

fabricated by magnetron sputtering. Al uniformly coated each BNNT. Using imaging techniques and electron diffraction analysis in a transmission electron microscope, the Al phase was found to create nanocrystalline shields around individual BNNTs. The chemical states of the hybrid nanomaterials during the initial stages of sputtering were analyzed by X-ray photoelectron spectroscopy. Direct in situ bending and tensile tests on individual BNNT–Al nanocomposites were carried out by using a dedicated transmission electron microscope-atomic force microscope holder. In parallel, high-resolution TEM images and video recordings were taken for the analysis of deformation kinetics and fracture mechanisms. The nanohybrids with a suitably thick Al coating (~ 40 nm) withstood at least nine times higher stresses compared to a pure non-armed Al metal. This pioneering work opens up a prospective pathway for making ultralight and superstrong "dream" structural materials for future automotive and aerospace applications [2].

Next, a meter long and several dozen micrometers thick Al-BNNTs composite ribbons with various fractions of multiwalled BNNTs (0.5 to 3.0 wt%) were fabricated by melt spinning using an Al-BNNTs powder mixture. BNNTs were randomly dispersed within a microcrystalline Al matrix under ribbon casting and led to more than doubling of room-temperature ultimate tensile strength of the composites compared to pure Al ribbons produced at the similar conditions. The comparative structural characteristics were analyzed using X-ray diffraction, scanning and transmission electron microscopy, and internal friction measurements as a function of temperature within a 80–800 K range. Room temperature tensile tests were carried out on ribbons. These revealed reinforcing effects on pure Al-matrices after nano/micro-BN embedment for both added phases with the notably higher numbers peculiar to the BNNT-containing samples. The intra-structural interactions between BN additions and Al-matrices are discussed based on the structural analysis and the internal friction data [3, 4].

Powder metallurgy is one of the most popular methods for Al-based MMC processing. Thus finally, for making Al-BNNTs composites with up to 5 wt% (i.e. 9.7 vol%) nanotube fractions Spark Plasma Sintering (SPS) and High Pressure Torsion (HPT) methods were utilized. 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, form 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 micrometers) 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) [5].

Over all, I have studied Al-BNNTs composites by using various fabrication processes and at the different length scales – from nano- *via* micro-, and to macro-dimensions. The strength of Al-BNNTs composites was always higher than that of pure Al samples prepared using analogous procedures. 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 growing demands of aerospace, aircraft and automotive industries.

**References**

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## 審　査　の　要　旨

〔批評〕

Ms Yamaguchi defense proceeded on a very high level. Her presentation was logical, concise and clear. Graphic illustration was also very attractive. A nice trend from nano- via micro -to macro composites of Al with various fractions of BN nanotubes was traced, and this was very highly appreciated by all the Committee Members. She could well answer questions about the difference in porosity of spark plasma sintered and high pressure twisted samples, well compared the pre-existing mechanical properties of SiC-Al composites with those of newly fabricated materials. All professors agree that she fully deserves granting a PhD degree.

〔最終試験結果〕

平成26年　2月14日、数理物質科学研究科学位論文審査委員会において審査委員の全員出席のも

と、著者に論文について説明を求め、関連事項につき質疑応答を行った。その結果、審査委員全員によって、合格と判定された。

〔結論〕

上記の論文審査ならびに最終試験の結果に基づき、著者は博士（工学）の学位を受けるに十分な資格を有するものと認める。