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Reactive wetting and filling of boron nitride nanotubes by molten aluminum during equilibrium solidification

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ABSTRACT

Interactions between long boron nitride nanotube (BNNT) fibrils and molten aluminum (Al) pool are probed in this study to assess the feasibility of fabricating composite materials by solidification route. BNNTs were found to survive high temperature and reactive conditions present in molten aluminum. Very limited interfacial reaction was observed, resulting in the formation of AlN, AlB_2 and AlB_{10} in trace amounts. AlN was the principal reaction product, resulting in improved interfacial wetting. Calculations based on surface energies revealed improved work of interfacial adhesion due to AlN formation. BNNTs were found to be well integrated in the aluminum matrix, signifying AlN induced excellent wetting. We also report capillarity-induced high temperature filling of BNNT by molten Al. The filling was promoted by AlN formation. In addition, formation of B-rich AlB_{10} phase inside the nanotube was observed. Nanotube filling by metal and subsequent reaction to form nano-ceramic phases is expected to alter mechanical properties of the cast Aluminum-BNNT composites. This study establishes the suitability of solidification route for developing high strength Al-BNNT composites in future.

1. Introduction

Aluminum (Al) and its alloys are undisputedly the most widely used material system for automotive and aerospace applications due to their light weight and superior specific mechanical properties. Al alloys with reasonable strength have been engineered; however, their load bearing capability still falls short for applicability in critical structural components. As a result, steel and costlier Ti alloys have to be employed, resulting in increased weight, more fuel consumption and higher cost of operation. To mitigate this, considerable research efforts have been undertaken lately to develop high strength and light weight Al composites [1,2]. Carbon Nanotube (CNT) reinforced Al composites have been actively researched in past two decades due to strengthening effect of nanotubes [3–14]. Despite their excellent mechanical properties, integration of CNTs in Al matrix is a major challenge due to their poor dispersion [3,4]. Moreover, CNTs are reported to undergo oxidation at temperatures exceeding 400 °C [15,16]. Therefore, most of the high temperature processing techniques, like casting, hot rolling and forging cannot be easily employed without damaging CNTs. Boron Nitride Nanotube (BNNT), a structural analogue of CNT with alternate B and N atoms has as attractive mechanical properties as CNT [17–19]. They are reported to exhibit highly impressive elastic modulus of ~1 TPa and a tensile strength of ~61 GPa [20–22]. In addition, BNNT is resistant to oxidation at temperatures as high as 1000 °C [15,16,23]. Since the melting point of Al is ~660 °C, this opens up the possibility of manufacturing BNNT reinforced Al composites by casting. Conventionally, casting has been at the center stage of the metallurgical processes due to its capability of fabricating complex shapes easily and economically. High temperature oxidation resistance of BNNT gives it an edge over CNT as a reinforcement candidate for Al composites synthesized by casting route.

BNNT based Al composites have been fabricated by powder metallurgical techniques such as pressureless sintering [24], spark plasma sintering [25–27], high pressure torsion technique [27,28] and cold rolling [25,26], as well as physical vapor deposition processes, such as magnetron sputtering [29] and ion implantation [30]. It is noteworthy that molten route fabrication of Al-BNNT composites has not received much attention by researchers. Yamaguchi et al. reported Al-BNNT ribbons by melt spinning in an Ar atmosphere [31]. The composite ribbons with varying BNNT fractions (0.5–3.0 wt%) were fabricated by pelletizing Al-BNNT

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mixture, followed by melting of the pellets and subsequent spinning of the ribbons. Cohesive Al-BNNT interface was obtained, devoid of any interfacial products. Melt spinning involves rapid solidification. Contrary to this, conventional casting of metal matrix is typically a slow, equilibrium solidification process. Casting of Al-BNNT composite is hitherto not reported in the literature.

Load bearing capability of a composite depends on the quality of matrix-filler interface and the length of the nanotubes. Good interfacial bonding results in superior load transfer from matrix to reinforcement phase. Lahiri et al. examined solid state reactions taking place at Al/BNNT interface, and observed very slow formation of AlN and AlB_2 [32]. Casting process would involve contact between BNNT and molten Al. The wetting of BNNT by molten Al would therefore determine the quality of metal-nanotube adherence and the subsequent strengthening mechanisms. Due to prolonged contact between molten Al and BNNT during casting, wetting phenomena is likely to be complex due to simultaneous formation of reaction products. In addition to contact interface, length of nanotubes is also an important parameter for effective strengthening. Nanotube length should be greater than a critical length for which maximum stress at the center of the fiber is equal to its fracture strength. Rapid strides have been made in recent years towards high-yield fabrication of long BNNT fibrils [33–35]. This opens up the window to develop metal matrix composites with superior strength. Processing of such long (~100–200 μm) BNNT based composites by molten route can also lead to capillarity induced filling of nanotubes by molten metal, resulting in interesting core-shell nanostructures. So far, there is no detailed study on the interactions between molten Al and BNNT.

In this study, BNNTs are mixed in molten Al to prepare a metal matrix composite by equilibrium solidification route for the first time. Interfacial phenomena and reactions between nanotubes and molten Al are investigated by X-Ray diffraction, scanning electron microscopy and high resolution-transmission electron microscopy. Energetics of the wetting of BNNT by molten Al is discussed. The phenomena of nanotube filling with metals during molten route processing is also investigated. We believe this fundamental study would pave way for the future studies on the development of high strength Al-BNNT composites by solidification route.

2. Experimental

Extremely long (~100–200 μm) and fine (~10 nm diameter) nanotubes were used in this study. They were obtained in the form of fibril balls from BNNT, LLC (Newport News VA, United States). Nanotube fibers (10 mg) were peeled from the ball and were uniformly mixed with Al pellets (20 g) in a crucible. The mixture of Al pellets and BNNTs was heated to 700 °C in a muffle furnace in air. The molten Al-BNNT mixture was gently stirred to ensure homogeneous composition. The mixture was soaked in the furnace at 700 °C for 1 h, and was then slowly allowed to cool inside the closed furnace until it reached ambient temperature (around 10 h).

X-ray diffraction (XRD) of the solidified sample was carried out using Siemens D-5000 X-ray diffractometer (Munich, Germany), based on CuK_α radiation at an operating voltage and current of 40 kV and 35 mA, respectively. SEM imaging was performed on cast samples using JEOL JSM-6330F field emission SEM (Tokyo, Japan), at an operating voltage of 20 kV and a working distance of 15 mm. TEM samples were prepared using JEOL-JIB 4500 focused ion beam (FIB) milling system using Ga^+ ions. TEM samples were ~100 nm in thickness. TEM imaging was performed using Tecnai FEI F30 HRTEM at an operating voltage of 300 kV. Lattice spacing calculations were performed by fast and inverse fast Fourier transform (FFT & IFFT) analysis using Digital Micrograph software (Gatan, Inc.).

3. Results and discussion

3.1. Interactions at BNNT-molten aluminum interface

BNNTs were found to survive high temperature conditions involved in the melting of Al. A network of long nanotube clusters in the solidified Al matrix is shown in Fig. 1(a). A low magnification TEM image (Fig. 1(b)) shows the presence of fine nanotubes in cast Al-BNNT composite. XRD characterization of the composite pellet was performed to identify the phases. Peaks corresponding to h-BN were detected, as shown in Fig. 2. Despite high chemical inertness of BNNT, some interfacial reaction products were noticed, as evidenced by XRD pattern. Peaks corresponding to AlN, AlB_2 and AlB_{10} are shown in Fig. 2.

The reactions and phenomena at the interface were examined by HR-TEM investigations. Fig. 3(a) shows the formation of AlN due to the reaction between Al and h-BN. Regions corresponding to Al matrix, AlN and Al/AlN interface are clearly shown. Unlike earlier report on solid-state reactions between Al and BNNT where AlN was discontinuously formed [32], here we see a continuous and homogeneous formation of the product along the nanotube boundary. This is clearly shown in Fig. 3(b), where AlN is seen to be formed along the entire length of BNNT as a film. AlB_2 was not detected by TEM. Lahiri and co-workers thermodynamically calculated the formation of reaction products and showed that the volume of AlN formed is 1.55 times more than that of AlB_2 [32]. It was shown that formation of AlN is more feasible compared to AlB_2

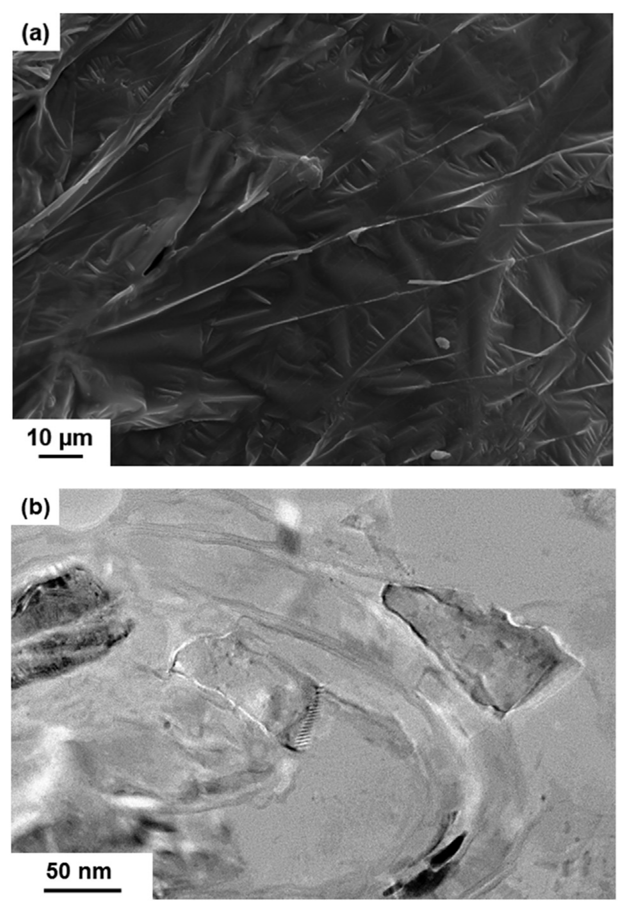

Fig. 1. (a) SEM image showing a network of long nanotube clusters well meshed in Al matrix post solidification. **(b)** Low magnification TEM image showing long and intact BNNTs in cast Al-BNNT composite.