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Conformal Carbon Nanotube Coatings for Ceramic Composite Structures

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ABSTRACT

Catalytic chemical vapor deposition enables the synthesis and deposition of carbon nanotubes (CNT) directly on substrates, thereby immobilizing them and potentially preventing them from bundling after synthesis. In this work, we investigate the use of this strategy to prepare ceramic hybrids with unbundled CNTs on aluminum oxide (AO) powder and fabric substrates, which are commonly used in the fabrication of ceramic laminate composites. CNT – AO powder hybrids are produced in 250 g batches with up to about 3 wt% CNT content, which is a sufficient amount for sintering into composite plates for mechanical and ballistic characterization. CNT – AO fabric hybrids are produced and it is found that the polymer coating that comes on the as-purchased fabric aids with CNT deposition. Conformal nickel and nickel oxide films deposited by an atomic layer deposition process are found to be excellent catalysts for CNT deposition. These conformal metal films are being used to create better CNT – ceramic hybrids for processing into better composite materials.

INTRODUCTION

Carbon nanotubes (CNTs) have been widely studied for the last couple of decades and it has been recognized for nearly as long that they should have a profound impact on the mechanical properties of composite materials [1]. The extreme aspect ratios, strong sp^2 carbon bonds, and high chemical stability all contribute to making CNTs ideal reinforcement fillers. However, the problems associated with dispersing these materials in the composite's matrix has hindered the realization of this impact, as the CNTs tend to aggregate into bundles making them effectively much larger particles [2]. Various strategies, such as chemical functionalization, have been attempted to aid with the dispersion of bulk CNTs in a composite matrix during processing with some success [2]. Catalytic chemical vapor deposition (CVD) differs from other CNT synthesis methods in that the CNTs can be synthesized directly on a substrate, thereby immobilizing them and potentially preventing them from bundling after synthesis [3]. In this work, we investigate the use of this strategy to prepare ceramic composite structures with unbundled CNTs. CNTs are synthesized as conformal coatings on various ceramic materials, including aluminum oxide (AO) powder and fabric mats following a conformal catalyst deposition. The CNT deposition is carried out in a large volume CVD reactor [4,5]. The conformal catalyst is deposited by atomic layer deposition (ALD) of ultra-thin nickel or nickel oxide films, or via deposition from an iron nitrate solution. The resulting hybrid materials are characterized and the processing optimized to improve the CNT coatings. The optimized CNT-ceramic hybrids are suitable for sintering into composite materials [6-10].

MATERIALS AND METHODS

CNT –AO powder hybrids are prepared by a modified catalytic CVD method [4]. The AO powder is obtained from Alteo (P172LSB) and used as received. In a typical preparation, 250 g of AO powder is evenly split between four 250-mL centrifuge tubes along with 100 mL of catalyst solution (100 g / L iron nitrate in ethanol). The tubes are shook for 5 min., allowed to sit for 10 min., and then centrifuged at 5000 rpm for 5 min. The supernatant is decanted off and the powder is air dried in a dish. The dried powder clumps are ground in a standard coffee grinder in smaller batches to produce a fine catalyst stained powder. The catalyst stained powder is loaded into the CVD reactor in a quartz pan, heated to 650 ºC under a purge of 25% hydrogen in argon (total flow rate 3000 sccm), and held at this temperature for 90 min prior to CNT growth. CNT growth is initiated by introducing 8% ethylene into the gas flow (total flow rate 6500 sccm with 15% hydrogen) for 80 min. The CNT covered powder is cooled under the reducing atmosphere and removed from the reactor. The preparation of the CNT – AO fiber mat hybrids (3M Nextel DF-11) is performed by a similar way as for the powders and has been described previously [7]. The AO fabric comes with a polymer sizing (coating) to improve mechanical processing. Experiments are performed with this sizing intact and removed by first heating the as-received fabric to 700 ºC over 2.5 h under a flow of 10 slm air in an oven (Lyndberg BF51828C-1). The mats are held at this temperature for 2 h and cooled back to room temperature over another 2 h.

Conformal layers of nickel and nickel oxide catalysts are deposited using a Kurt J Lesker plasma-enhanced ALD system with a Bis(ethylcyclopentadienyl) nickel precursor (Strem Chemicals). Nitrogen/hydrogen and oxygen plasma are used for deposition of nickel and nickel oxide, respectively. The depositions are carried out on c-plane sapphire substrates. Raman spectra are collected on a Nicolet Almega XR Dispersive Raman using 532 nm excitation and a 50x microscope objective. Thermal gravimetric analysis (TGA) is performed on a TA Instruments Q500 TGA by placing ~40 mg of the hybrid material in a deep ceramic TGA pan and heating to 900 °C at 10 °C / min under 45 sccm of air. Scanning Electron Microscope (SEM) secondary electron images showing the surface morphology of the hybrids are collected on a Hitachi S4800 Field-Emission SEM with an accelerating voltage of 5 kV.

RESULTS AND DISCUSSION

Typical characterization results following CNT deposition on the AO powder are shown in Figure 1. The SEM images show a large number of long CNTs on the surfaces of small AO particle clumps. The CNTs appearance is consistent with previous depositions in this reactor. The Raman spectrum shows the expected G, D and G' peaks, with a G/D ratio of about 1, and is consistent with multi-walled CNTs. The TGA thermogram shows a single burn event around 625 ºC with a weight change of 3.2%, after some initial moisture loss at lower temperatures. The 80 min. CNT depositions typically yield about 3% CNT, while 20 min. depositions yield about 1%. Large batches of CNT-AO powder hybrids have been produced for high-pressure sintering into composite plates for mechanical and ballistic characterization. The CNTs in these hybrid powders are unbundled and well dispersed among the AO particles. Previously, it was found that inhomogeneity of the CNTs in a sintered ceramic laminate composite led to strong and weak regions in the material. This in turn led to premature failure under dynamic (ballistic) loading conditions [6], in spite of showing increases in fracture toughness under quasi-static loading conditions [8]. It is anticipated that these new powder hybrids, once sintered, will not have these

strong and weak regions since they are more homogeneous to start with. This increased homogeneity may enable the translation of the quasi-static gains [8] into ballistic gains [6], which could be exploited for applications in armour.

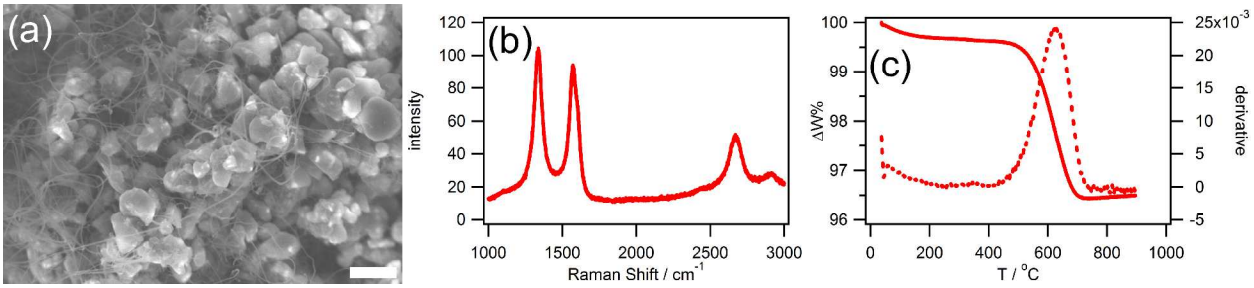

Figure 1. Characterization of CNT-AO powder hybrids by (a) SEM (500 nm scale bar), (b) Raman, and (c) TGA (weight change solid, derivative dotted).

AO (and other ceramic) fabrics are used for the production of laminate composites, which are also being investigated for applications in armour [6]. CNT – AO fabric hybrids are prepared in a manner similar to what was reported previously [7]. However, it was subsequently discovered that the polymer sizing that came on the fabrics was aiding with catalyst and hence CNT deposition. Figure 2 shows the results from CNT deposition following solution catalyst deposition with this sizing removed and intact. No significant changes in other CNT properties, including Raman spectra, are found due to the presence or absence of the sizing. It is clearly seen that more CNTs are deposited when the sizing is left intact compared with when it is burned off in the oven. In fact, more aggressive methods of removing the sizing (e.g. oxidizing acids) actually led to even less CNTs than with the simple burning off as shown in Figure 2. The actual composition of the sizing that comes on the fabric is proprietary to the manufacturer, although poly vinyl alcohol (PVA) is a key component [11]. Experiments were conducted with iron nitrate catalyst co-deposited and subsequently deposited with PVA to try to duplicate this effect in a controlled manner. These attempts were, however, unsuccessful to date. To our knowledge this effect has not been reported previously.

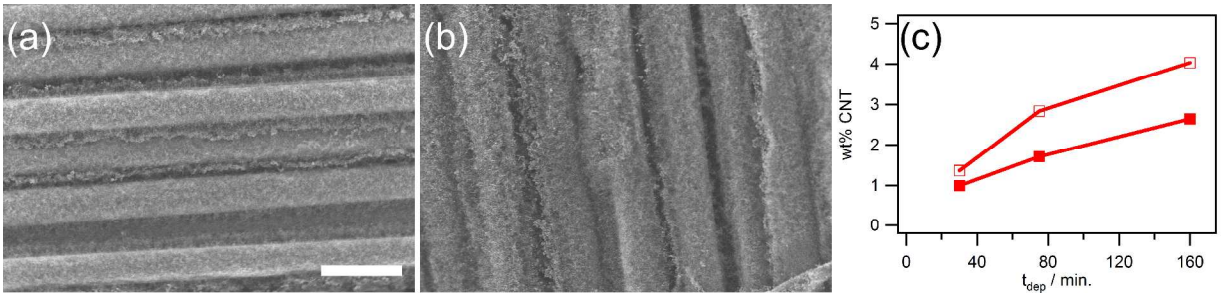

Figure 2. SEM characterization of CNT – AO hybrid fabrics after a 160 min. CNT deposition with the sizing (a) removed and (b) intact (25 μm scale bar). (c) Weight percent CNT as measured by TGA with sizing (■) removed and (□) intact.

The ceramic substrates being considered for building blocks for the nanocomposites all have three dimensional geometries that need to be coated on all faces uniformly, hence the need for conformal catalyst deposition. While the iron nitrate solution catalyst has shown some great success already [7,8], it is known that evaporated or sputter metal films (e.g. nickel or iron) will,

in general, produce denser CNT films with a higher quality of CNTs [4]. Evaporated or sputtered films are, however, deposited in a line-of-sight fashion emanating from a solid source and hence will not coat all the faces in these ceramic materials. Dense metallic films, similar to evaporated and sputtered films, can be deposited by ALD (and CVD) techniques. These techniques are not line-of-sight and therefore could potentially coat all the faces of the ceramic building blocks in a conformal fashion. A dense coating of higher quality CNTs conformally coated on all faces of the these building blocks, following from dense, conformal catalyst deposition, could potentially lead to large improvements in the mechanical performance of the nanocomposites.

In order to explore the possibility of using ALD catalyst for these applications, we have developed ALD processes for depositing nickel and nickel oxide films. Nickel was chosen over iron for these studies because of a desire to pursue its use for other applications also; however the technique can be extended to compare with ALD iron films also. These nickel and nickel oxide films have been deposited on sapphire (Al_2O_3) wafers for developmental purposes and have been processed through our CNT reactor to test for their efficacy as CNT catalysts (see Figure 3). It is found that both the ALD nickel films and the ALD nickel oxide films (~20 nm thick) act as excellent catalysts for depositing dense CNT films on these substrates. Experiments are underway to characterize these films in more detail and to exploit this new technique for coating complex ceramic structures to be incorporated into new nanocomposite materials.

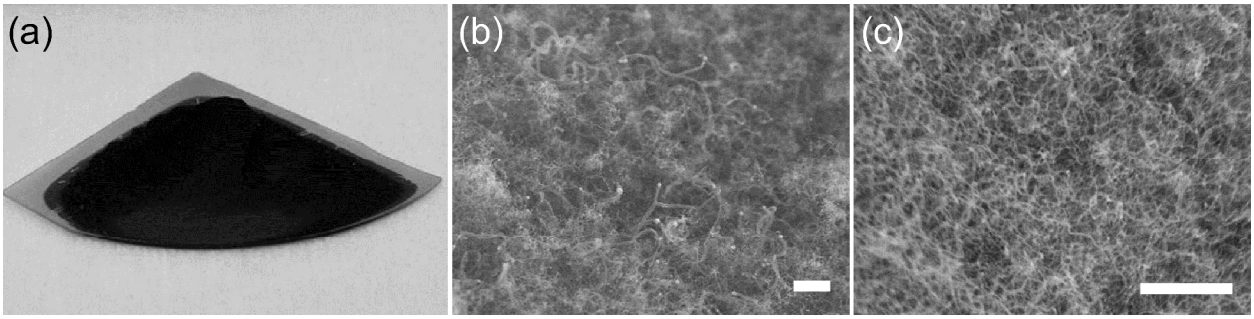

Figure 3. (a) Photograph of CNT film deposited from ALD Ni catalyst on sapphire wafer. SEM characterization of the CNT film deposited from ALD (b) Ni and (c) NiO catalysts on sapphire wafers (1 μm scale bars).

CONCLUSION

CNT – AO powder hybrids are produced in 250 g batches with up to about 3 wt% CNT content. The powder hybrids are suitable for sintering into composite plates for mechanical and ballistic characterization. CNT – AO fabric hybrids are produced for incorporation into laminate composites and it is found that the polymer sizing that comes on the fabric aids with CNT deposition. Conformal nickel and nickel oxide films are deposited on sapphire substrates using an ALD process and are found to be excellent catalysts for CNT deposition. These conformal metal films are being used to create better CNT – ceramic hybrids for processing into better composite materials.

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