Synthesis and characterization of plasma spray formed carbon nanotube reinforced aluminum composite

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Received 10 February 2004; received in revised form 6 April 2004

Abstract

A trend has been perceived in the field of composite materials to employ carbon nanotubes as reinforcement in synthesizing composites of unique properties. In this endeavor, free standing structures of Al-based nanostructured composite with carbon nanotubes as second phase particles has been synthesized by plasma spray forming technique. Optical microscopy, scanning electron microscopy, X-ray diffraction, transmission electron microscopy has been carried out to analyze the composite structure and to verify the retention of carbon nanotubes. Besides, density and microhardness measurements have been performed to understand the effect of carbon nanotube reinforcement on the mechanical properties of the composite. The characterization affirms the presence of unmelted and chemically unreacted carbon nanotubes in the composite. Moreover, the composite experienced an increase in relative microhardness due to the presence of carbon nanotube.

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Keywords: Al-based nanocomposite; Carbon nanotubes reinforcement; Plasma spray forming

1. Introduction

Carbon nanotubes (CNTs) have evolved tremendous amazement and experience several discriminating applications by virtue of its remarkable mechanical, electrical and thermal properties [1–5]. Depending on their length and diameter, chirality and orientations, carbon nanotubes exhibit almost five times elastic modulus (∼1 TPa) and closely 100 times tensile strength (∼150 GPa) than those of high strength steels [6–9]. The unimaginable high strength of CNTs makes them potential reinforcement for the composite materials. Besides, the nanosized carbon tubes also provide superior dispersion strengthening to the composite structures.

A larger portion of the research on CNT based composites has been focused on polymer-matrix composites (PMCs) in order to improve their electrical conductivity along with the enhancement in mechanical strength [10–12]. Carbon nanotubes reinforced PMCs are largely prepared by repeated stirring, solution-evaporation with high-energy sonication, surfactant-assisted processing and interfacial covalent functionalization [10–17]. However, the research on CNT reinforced metal matrix and ceramic matrix composites has been rather limited. CNTs reinforced ceramic matrix composites (CMCs) have been synthesized by sonication and dry pressing, hot pressing and high temperature extrusion and in situ production to achieve homogenized dispersion of carbon nanotubes [18–22].

A very limited research has been done in the field of CNT reinforced metal matrix composites (MMCs) because of the complexity associated with the interfacial reaction between CNTs and metal matrices, and lack of a suitable synthesis technique. Increase in fracture toughness, wear resistance and hardness for CNT reinforced Cu composite has been reported by Dong et al. after synthesizing the composite by hot pressing and sintering [23,24]. Chen et al. observed the feasibility of electroless plating in synthesizing Ni and Co based composites with CNT [25,26]. Furthermore, Kozamaki et al. confirmed increase in hardness and effective elastic modulus with chemical stability of CNT in Ti matrix after sintering at 1200 K [27].
Several efforts have been endeavored in order to employ graphite (allotrope of carbon) as reinforcement for Al-based composites [28,29]. However, formation of brittle and hygroscopic carbides (e.g. Al₄C₃) during the processing deteriorates the mechanical properties of these composites [27]. Despite, carbon nanotubes are suitable constituent as reinforcement in Al-based composite due to their chemical stability in aluminum [27,30]. CNT reinforced Al-based composites are being synthesized by hot pressing technique, where the strength and overall hardness of the composites were improved [30–32]. The wettability and the interfacial bonding phenomenon between nanotubes and Al matrix play a significant role in this context [33]. In addition, the bonding strength between the different concentric carbon nanotubes is poor, as a very weak van der Waals forces exist to link the individual graphene sheets. Thus, the effectiveness of multi-walled tubes for using it as reinforcement in composite is also a critical issue [34].

In this attempt, a novel processing approach has been undertaken to synthesize a CNT–Al nanostructured composite by plasma spray forming technique. Hereof, it must be mentioned that the exercise of plasma spray process to synthesize CNT reinforced Al-based composite has never been reported in the literature [30]. Microstructural evaluation of the composite has also been carried out in order to characterize the composite and to validate the retention of carbon nanotubes in plasma sprayed deposit.

2. Experimental details

2.1. Materials

Al–Si alloys are widely used in aerospace and automobile industries due to their high strength to weight ratio, high specific stiffness and superior wear and corrosion resistance [34,35]. Gas atomized, spherical hypereutectic Al–23wt.% Si (density of 2.61 g/cm³), prealloyed powder (Fig. 1a), was used as the matrix constituent. An optimum size range (15–45 μm) and spherical morphology has been selected to achieve the best flowability of powders during plasma spraying. Coarser powder particles often remain unmelted or partially melted which subsequently results in porosity and weak bonding in the spray deposited structure. Likewise, the irregular shaped, fine particles tend to restrict the consistent powder flow by clogging the plasma gun. 10 wt.% carbon nanotube of 95% purity (Fig. 1b) was used as the reinforcements for synthesizing the composite structure. The bulk density of the CNTs was 1.3–1.5 g/cm³ with a dimension of 40–70 nm diameter, and 0.5–2.0 μm length.

2.2. Powder treatment

Proper blending of the powders and CNT in specific proportion is required to ensure homogenous distribution of reinforcement in the matrix during synthesizing a composite. Al–Si powders and carbon nanotubes were blended and mixed in a ball mill for 48 h to promote homogeneous mixing. It is envisaged that blending will assist in unrestricted flow of the nanosized carbon tubes during the plasma spray forming. It is a difficult task to spray individual nanoparticles/nanotube because of their low mass and the resultant inability to be carried in a moving gas stream and to be deposited on a substrate [36]. The comparatively larger micron-size Al–Si powders will act as carrier of the nanosized carbon tubes during the spraying. A similar philosophy was successfully adopted for plasma spray forming nanostructured Al₂O₃ components [37]. Fig. 2 illustrates homogeneously blended Al–Si powders and carbon nanotubes (Fig. 2a). It can be clearly noticed that CNTs are also residing on the surface of Al–Si powders (Fig. 2b and d). Bigger agglomerates or knotted lumps were also found to be formed during blending due to entanglement of carbon nanotubes with Al–Si powders (Fig 2a and d).

Fig. 1. SEM images of the spherical Al–23wt.% Si powders: (a) as the matrix and the nanotubes; (b) as the reinforcement in the composite.
2.3. Plasma spray forming

Plasma spray is a thermal spray method that has been used extensively for depositing metallic and ceramic coatings to serve different purposes [37,38]. Plasma spray forming (PSF) is the modified technique for the near net shape architecture of wide range of alloys, intermetallics, ceramics, composites and functional gradient materials [39,40]. The molten particles are directed toward a rotating mandrel where they deposit and rapidly cool forming the desired shape. The plasma gun and the mandrel are computer controlled allowing fabrication of complex shapes. The process results in the fabrication of parts sprayed to the near net shape.

Fig. 2. SEM micrograph of homogeneously blended Al–Si powders and carbon nanotubes (a), showing CNTs residing on the surface of Al–Si powder (b and d) and bundles of entangled CNTs (c).

Fig. 3. Schematic of plasma spray forming of blended powders.
The blended powder was plasma sprayed using an SG 100 gun (Praxair Surface Technologies, Indianapolis, IN) on a cryogenically cooled, rotating, smooth, tapered 6061 Al mandrel. Argon and helium gases were used as primary and secondary gases, respectively. The processing details of the plasma spray forming have been elucidated in our earlier work [37]. The degree of melting of powder particles and agglomerates during the spraying is a complicated phenomenon concerning the size and the trajectories. A schematic of the trajectory of the blended powder particles is shown in Fig. 3. A larger fraction of fine particles including carbon nanotubes does not flow through the hot core of the plasma due to their smaller size. Thus in the process of deposition, there is a great potentiality that an appreciable amount of carbon nanotubes gets entrapped within the deposition, although a part of the loosely bound carbon nanotubes with the agglomerates flies away with the high velocity carrier gas or experiences phase transformation due to high temperature of the plasma. Optimization of gun voltage and current (35 V, 800 A) were achieved in order to promote higher densification of the composite structure during the solidification process of the molten powders. The deposited conoid structures as in Fig. 4 (62 mm diameter, 100 mm length and 0.3 mm wall thickness) were removed from the mandrel by applying the concept of mismatch in thermal expansion coefficient of 6061 Al (mandrel) and the spray formed composite material. Heavy quenching of the mandrel with the spray deposited composite structure was done in liquid CO2 environment to separate the conoids from the mandrel. The polished surface (roughness index of 0.5 μm) of the mandrel also aided in separation of the spray formed structure.

2.4. Microstructural characterization

A comprehensive evaluation of the plasma spray formed Al–CNT composite structure was carried out using optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Phase analysis of the composite was executed by using a Siemens 500D X-ray diffractometer with Cu Kα radiation operating at 40 kV and 20 mA. A JEOL, JSM-6330F Field Emission Scanning Electron Microscope was engaged to perform the microstructural evaluation and to verify the distribution and retention of carbon nanotubes in the spray formed composite structure. Besides, Raman spectroscopy of the composite was carried out to validate the presence of carbon nanotubes in the composite. Ti-sapphire crystal target with a laser wavelength of 785 nm was used for this purpose. Elemental analysis of the composite was also determined by performing energy dispersive spectroscopy (EDS). TEM investigations were carried out using an FEI Technai F30 high-resolution transmission electron microscope operated at 300 kV in order to understand the detailed morphology and formation of nanostructure. A FEI (Hillsboro, OR) 200 TEM-FIB (focused ion beam) equipped with a 25–50 kV gallium liquid metal ion source (LMIS) was employed for preparing TEM samples from the composite structure. The microhardness measurement of the spray formed Al-CNT composite was done using a LECO DM 400 Microhardness Tester. The microhardness indentations were made by a Vickers diamond indenter operating at a load of 300 g and dwell time of 15 s.

3. Results and discussions

3.1. Microstructural evaluation

Fig. 4 shows plasma spray formed hollow cone-shaped Al–CNT composite structures (62 mm diameter, 100 mm length and 0.3 mm wall thickness). The rough outer surface of spray formed conoids is due to the inconsistent and pulsed powder flow during the spray forming, which was caused by large bundles of powder as seen in Fig. 2. The black spots on the grayish surface signify the presence of
carbon in the composite structure. The existence of carbon as grayish-black phase is further distinct in the optical micrograph (Fig. 5) of the polished and etched deposit structure. The grayish-black carbon phase is evenly distributed throughout the Al–Si matrix with a wide range of size distribution. The pores are not visible apparently, however some of the black spots may denote some degree of porosity in the composite structure.

The SEM micrographs of as-sprayed outer (Fig. 6) and inner wall (Fig. 7) of the conoids depict the morphological details of the composite structure. The outer surface distinctly exhibited splat formation for both the individual Al–Si powders and the powder–carbon nanotube agglomerates (Fig. 6). The agglomerates of Al–Si powders and carbon nanotubes (melting point 3773 K) did not melt fully during the spray process due to their larger volume, inconsistent and pulsed flow through the plasma, and presence of high melting point carbon nanotubes. Partially melted and unmelted agglomerates collided on the substrate at high velocity and thus constructed fragmented splat structure (Fig. 6). Hence, the
probability of carbon nanotubes retention in the spray deposited composite was increased. However, CNTs cannot be observed on the outer surface. No pores or cracks are visible on the outer surface. The inner wall delineated smoother surface due to the replication of well-polished surface of the mandrel (Fig. 7). A few pores (5–20 μm) were also observed at the inner wall, which is attributed to the large unmelted and partially melted agglomerates caused by inconsistent flow during the plasma spraying. It can be noticed that maximum amount of pores are formed at the agglomerate splats, which is ascribed to the partial melting of the agglomerates. An effort will be initiated in our future work to employ spray-dried agglomerates of the Al–Si powders and carbon nanotubes in order to overcome the difficulty of clogging.

3.2. Phase analysis and thermodynamic consideration

Retention of the carbon nanotubes in the plasma spray formed structure is the critical issue in this present study. The XRD spectrum (Fig. 8) of the spray formed composite showed the presence of graphite (carbon allotrope), aluminum, silicon and Al–Si phase and traces of metastable monoclinic alumina (θ). Raman spectroscopy performed on the composite distinctly exhibits the peaks for multi-walled carbon nanotubes along with the Si peak from prealloyed
aluminum powder (Fig. 9). The D-line in the spectrum represents the structure defect or amorphous carbon whereas the presence of G-line authenticates the presence of graphene structure [40].

The temperature associated with the plasma spray forming (10,000–15,000 K) is considerably higher than the melting point (3773 K) and boiling point (5100 K) of graphite. Thus, there was a possibility of melting or sublimation of carbon nanotubes during the plasma spray forming. However, controlled plasma parameters and partial melting of larger agglomerates of Al–Si powders and carbon nanotubes due to their larger volume and inconsistent flow through the plasma insinuates the retention of CNTs in the composite. The transformation of carbon nanotubes into other carbon allotrope such as graphite and/or diamond is also likely at higher temperature and at high pressure achieved due to the heavy impact of the agglomerates at extremely high velocity experienced during plasma spray forming [41–43]. There is also a possibility of oxidation of carbon nanotubes to carbon monoxide (ΔG = −145 kJ at 298 K) and carbon dioxide (ΔG = −395 kJ at 298 K) gases at high temperature of plasma spray forming. However it is clear from the Elling-
ham Diagram, that the formation of aluminum oxide \((\Delta G = -1590 \text{kJ at } 298 \text{K})\) and silicon oxide \((\Delta G = -860 \text{kJ at } 298 \text{K})\) is thermodynamically more feasible than oxidation of carbon \([44]\). The XRD pattern confirms the presence of graphite phase in the composite structure.

The formation of aluminum carbides \((\text{Al}_4\text{C}_3)\) is also crucial in this regard as the carbides depreciate the mechanical properties of the composite \([27,30]\). Formation and epitaxial growth of carbides along the reactive prism planes in graphitic structure (zigzag planes i.e. \(\{100\}\)) or armchair planes i.e. \(\{110\}\) deteriorates the mechanical properties of composites \([27]\). The preferred carbide formation and growth on the prism planes rather than on the graphitic basal planes is attributed to the higher availability of surface free energy at the prism planes. On the other hand, carbon nanotubes are thermodynamically stable in Al matrix at high temperature due to their cylindrical graphitic structure, which ensures the absence of the prism planes and consists of only a rolled up graphene basal plane \([27,30]\). Due to this reason, \(\text{Al}_4\text{C}_3\) phase formation was suppressed during plasma spray forming. The XRD spectrum does not exhibit any carbide peak, which validates the chemical stability of carbon nanotubes in Al matrix. Kuzumaki et al. also confirmed thermal and chemical stability of CNT in Al matrix \([30]\).

Formation of aluminum oxide (metastable monoclinic \(\theta\) alumina) was also noticed in the XRD spectrum, which is attributed to the high temperature processing of the prealloyed Al–Si powder in air. As the entire deposition was a very rapid process, formation of metastable aluminum oxide was exhibited instead of stable rhombohedral \(\alpha\)-alumina \([45]\). However, the contribution of the metastable aluminum oxide in the XRD spectrum was not that strong, which can be attributed to trace oxide formation.

EDS analysis was also performed to carry out the elemental analysis of the composite. The SEM image (Fig. 10a) exhibits grayish matrix of Al–Si alloy with black spots. EDS performed on one of the black spots (Fig. 10b), presented carbon, aluminum and oxygen as \(\sim 50, 28\) and \(9\) wt %, respectively. Although the deposition process was carried out with helium and argon as carrier gases, the presence of oxygen signifies the oxidation of aluminum during the air plasma spray forming at high temperature. There may be some oxidation of carbon nanotubes at the high temperature of deposition, although the aluminum oxide formation is more feasible thermodynamically.

### 3.3. Carbon nanotubes distribution and retention

Fig. 11 shows a lower magnification SEM image of fractured cross-section of the Al–CNT composite structure, which shows the retained carbon nanotubes (shown by rectangular area) in the spray formed structure. The nanotubes are present at the edges of fractured splat indicating the entrapment between successive splats. CNTs in the blended powder got entrapped between Al–Si splats due to different trajectories of powder particles. The presence of dangling CNTs is shown distinctly by the arrow marks in the high magnification SEM image (Fig. 12). The smooth surface of retained carbon nanotubes does not indicate any physical damage or reactivity during spray forming. As discussed in the earlier paragraphs in this section, a fraction of the CNTs did not get melted during the spray deposition. It also did not react actively with ambient oxygen, as the
feasibility of aluminum oxide and silicon oxide formation is much higher. Besides, the CNTs did not form carbides by reacting with aluminum due to the absence of prism planes.

The TEM micrograph from the preliminary investigation of the composite structure is presented in Fig. 13. Carbon nanotubes are not seen in this structure. However, it shows of grayish, ultrafine grains (∼30–150 nm). This is attributed to the extremely high cooling rate (10⁶ to 10⁸ K/s) during the solidification of the molten powders and agglomerates in plasma spray deposition [38]. Besides, the cryogenic cooling of the mandrel while plasma spray forming aided in achieving ultra fine grain size in the spray deposit. Selected area diffraction pattern (SAD) shows diffraction rings, which are broad and diffused indicating nanocrystalline structure. Exhaustive TEM study is underway to further conceive the interfacial phenomena between the Al–Si matrix and the carbon nanotubes, their retention and distribution inside the matrix.

### 3.4. Density measurement and microhardness testing

The density of the spray formed Al–CNT composite structure, was measured by Archimedes principle as 2.59 g/cm³, which is higher than the theoretical density (2.37–2.43 g/cm³) of the Al–Si alloy composite with 10 wt.% CNT reinforcement (Table 1). However, the pores in the composite (Fig. 7) provide an opposite tendency to higher relative density. The increase in density may be attributed to the formation of various carbon allotropes of varying densities during plasma spray deposition. In this context, carbon nanotubes have a bulk density of 1.3–1.5 g/cm³, whereas graphite and diamond has a density of 1.9–2.3 and 3.5–3.53 g/cm³, respectively [46,47]. The formation of higher density aluminum oxide (3.9 g/cm³) also justifies the increase in the density. Besides, there was a possibility of flyaway of nanosized carbon tubes due to the high velocity parent gas, which may have caused the higher relative density of the composite.

A comparative study of microhardness values of the composite and the 6061 Al has been carried out in Table 1. The hardness of the spray formed composite (146 ± 10 VHN) is higher than that of 6061 Al (85 ± 10 VHN) due to the dispersion strengthening by retained carbon nanotubes and nanocrystalline structure. Besides, the extremely hard CNTs (62–150 GPa) contributed in enhancing the overall hardness of the composite structure [48]. However, the hardness is not high enough to indicate the transformation of graphite to diamond. Lower hardness may also be attributed to the comparatively low bonding strength between the concentric walls of the multi-walled carbon nanotube [33].

<table>
<thead>
<tr>
<th>Different materials</th>
<th>Theoretical density (g/cm³)</th>
<th>Measured density (g/cm³)</th>
<th>Microhardness (VHN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6061 Al (mandrel)</td>
<td>2.69</td>
<td>N/A</td>
<td>85 ± 10</td>
</tr>
<tr>
<td>Al–CNT composite</td>
<td>2.37–2.43</td>
<td>2.58</td>
<td>146 ± 10</td>
</tr>
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Table 1: Comparative study of Al–10wt.% CNT composite and 6061 Al with respect to density and microhardness.
4. Conclusions

1.CNT reinforced aluminum matrix composite was synthesized near the net shape of hollow conoid (100 mm taper-length, 62 mm diameter, 2 mm thickness) through plasma spray forming process.

2. Carbon nanotubes were successfully retained in the spray formed composite structure. The CNTs were observed largely between the consecutive Al–Si splats with dangling structure.

3. The CNTs were chemically stable during the spray forming. They did not react to form oxides or aluminum carbides even at very high processing temperature.

4. The measured density of the composite was higher than the theoretical one due to the possible transformation of CNT in the Al-based composite.

5. The hardness property gets also enhanced with the addition of CNT in the Al-based composite.

Acknowledgements

The authors express their sincere gratitude to Dr. Y. Liu of Mechanical and Materials Engineering and Dr. M. Bouchaib of Center for the Study of Matter at Extreme Condition at Florida International University, Miami for assistance with XRD analysis, SEM and Raman spectroscopy. Authors will also like to acknowledge the financial support obtained from Missile Defense Agency (Contract # DASG60-02-P-041).

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