Carbon Nanotube Reinforced Aluminum Nanocomposite via Plasma and High Velocity Oxy-Fuel Spray Forming

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Free standing structures of hypereutectic aluminum-23 wt% silicon nanocomposite with multiwalled carbon nanotubes (MWCNT) reinforcement have been successfully fabricated by two different thermal spraying technique viz Plasma Spray Forming (PSF) and High Velocity Oxy-Fuel (HVOF) Spray Forming. Comparative microstructural and mechanical property evaluation of the two thermally spray formed nanocomposites has been carried out. Presence of nanosized grains in the Al–Si alloy matrix and physically intact and undamaged carbon nanotubes were observed in both the nanocomposites. Excellent interfacial bonding between Al alloy matrix and MWCNT was observed. The elastic modulus and hardness of HVOF sprayed nanocomposite is found to be higher than PSF sprayed composites.

Keywords:

1. INTRODUCTION

Major interest and investment in the field of composite materials started in mid-1950s, primarily to meet the demand for lower weight and higher strength for aerospace structures, electronics, sports equipment, and other applications.¹ Since then a considerable progress in the field of composite material has been achieved, driven by the incessant requirement for advanced materials of improved performance, where wide varieties of particulates and fibers have been used as reinforcement. Recently, a considerable amount of research in novel nanocomposite synthesis has been directed towards using multiwalled carbon nanotubes as reinforcing material, as this allotrope of carbon possesses extremely high elastic modulus (300–950 GPa) and superior tensile strength (11–63 GPa).²¹²⁴ However, employment of CNT reinforcements in synthesizing nanocomposites has been largely restricted to polymer-based composites.²¹²⁴ Research on CNT reinforced metal matrix bulk nanocomposites is still in its infancy stage due to multifarious complicity. First of all, incorporating nanosized second phase particles such as CNTs in metal matrix composite is challenging due to processing difficulties.²¹²⁴ Secondly, it is extremely difficult to achieve homogenous distribution and effective retention of CNTs in the matrix after the consolidation process. Moreover, it is very important to achieve effective interfacial bonding between matrix and reinforcement for successful load transfer in metal matrix nanocomposites. Hence, the biggest challenge is to develop a suitable synthesis technique, by which retention and uniform distribution of carbon nanotube possessing good interfacial bonding with matrix can be achieved.

Synthesis of Cu-based composite with MWCNT reinforcement by hot pressing and sintering has been demonstrated by Dong et al., where the composites exhibited improved fracture toughness, wear resistance, and hardness.¹⁶ It has also been showed that nickel coating on MWCNT surface enhances the adhesion of nanotube with Mg-matrix. Feasibility of electroless plating in synthesizing Ni and Co based composites with MWCNT has been shown by Chen et al.¹⁹²¹ Kuzumaki et al. demonstrated improvement in hardness and effective elastic modulus with chemical stability of MWCNT in Ti matrix at 1200 K during sintering.²² Though these processing techniques have shown promise of using carbon nanotubes as reinforcement for metal matrix, most of these techniques are limited in making small sized laboratory scale coupons. There are...
not many success stories of near net shape bulk nanocomposite structure fabrication due to the problems discussed earlier in this section. The feasibility of fabricating multiwalled carbon nanotube reinforced hypereutectic Al–Si bulk nanocomposite structure by Plasma Spray Forming (PSF) was shown in our earlier study. In the present research work, MWCNT reinforced hypereutectic Al–Si nanocomposites have been fabricated by plasma spray forming and high velocity oxyfuel (HVOF) spray processes. Although both of these processes fail under thermal spray technique, the spray deposits obtained from the two processes experience considerable dissimilarities in microstructure and mechanical properties, attributed to the inherent variation in deposition method. A detailed microstructural and mechanical property characterization of the nanocomposite structures fabricated by these two thermal spray techniques has been carried out in this endeavor.

Other than reinforcing low-density alloys with high mechanical strength second phase particles (e.g. MWCNT), strength can also be improved by accomplishing nanosized grain structure in the matrix leading to Hall–Petch strengthening. The extremely high cooling rate ($10^5$–$10^8$ K/s) in thermal spray technique in synergy with a suitable powder precursor makes it feasible to achieve nanostructured matrix in the composite. It is indeed a unique concept to synthesize bulk nanocomposites with nanocrystalline matrix reinforced with MWCNT, which has been attempted in this present study.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Hypereutectic aluminum-silicon alloy was selected as the matrix component of the composite due to its wide acceptance in aerospace and automobile industries attributed to their high strength to weight ratio, high specific stiffness, and superior wear and corrosion resistance. Gas atomized, spherical hypereutectic Al-23 wt% Si (Al-23Si-2Ni-1Cu in wt%, theoretical density of 2.61 g/cc), prealloyed powders of 15–45 μm size were thermally sprayed along with 10 wt% multiwalled carbon nanotube (MWCNT, 95% purity) as reinforcing constituent. Henceforth the hypereutectic Al–Si alloy will be mentioned as Al–Si in this paper. The density of the MWCNTs was 1.3–1.5 g/cc, a dimension of 40–70 nm diameter, and 0.5–2.0 micron length. Al–Si powders and multiwalled carbon nanotubes were blended and mixed in a ball mill for 48 hours to promote homogeneous mixing. The comparatively larger micron-size Al–Si powders act as carrier for the multiwalled carbon nanotubes and thus will facilitate in unrestricted flow of the nano-sized carbon tubes during the thermal spray forming. The details on the starting materials for thermal spraying have been provided in our earlier work.

2.2. Plasma and High Velocity Oxy-Fuel Spray Forming

Hypereutectic Al–Si nanocomposite structures with carbon nanotube reinforcement were fabricated by two types of thermal spray process, viz Plasma Spray Forming (PSF) and High Velocity Oxy-Fuel Spraying (HVOF). The principle behind the thermal spray techniques is to spray metallic/nonmetallic powders or mixture of them in molten or superheated state at a high speed on a substrate where deposit build-up takes place with rapid solidification of individual molten droplets or splats. In plasma spray process, the heat source is a plasma flame produced by passing inert gas (often argon) in between two electrodes whereas in high velocity oxyfuel process combustion of fuel gas produces the required heat energy. The velocity of the particles exiting from the flame is usually 350–1000 m/s in case of PSF and 700–1400 m/s for HVOF process. The extremely high cooling rates in plasma spraying and high velocity oxyfuel spraying makes it feasible to achieve excellent grain refinement and possibly nanostructured materials due to high nucleation rate and restricted grain growth during resolidification of splats. Near net shape fabrication via these two thermal spraying by removing the spray deposit from rotating mandrel-substrate has been demonstrated in our earlier works. The blended mixture of Al-23 wt% Si powder and multiwalled CNT, prepared as described in the earlier section, was sprayed by adopting both PSF and HVOF spray forming on well-polished 6061 aluminum rotating mandrels of different dimensions. The processing features of these two thermal spray processes are delineated in Table I.

<table>
<thead>
<tr>
<th>Table I.</th>
<th>Salient processing features in plasma and high velocity oxyfuel spray forming.</th>
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<tbody>
<tr>
<td><strong>Features</strong></td>
<td><strong>Plasma spray forming (PSF)</strong></td>
</tr>
<tr>
<td>Heat source</td>
<td>Plasma arc with gun voltage and current 35 V and 800 A, respectively</td>
</tr>
<tr>
<td>Spray gun</td>
<td>SG-100® plasma gun, Praxair Surface Technologies, Indianapolis, IN</td>
</tr>
<tr>
<td>Particle velocity</td>
<td>350–1000 m/s</td>
</tr>
<tr>
<td>Temperature</td>
<td>10,000–15,000 K</td>
</tr>
<tr>
<td>Gases used</td>
<td>Primary gas: Ar</td>
</tr>
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<td></td>
<td>Secondary gas: He</td>
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match in thermal expansion coefficient of 6061 Al (mandrel) and the spray formed composite material. The smooth machined surface of the mandrels also assisted in spray deposit removal. Plasma (Fig. 1(a)) and HVOF sprayed (Fig. 1(b)) hollow and tapered cone-shaped Al–CNT nanocomposite structures are shown in Figure 1.

2.3. Characterization

Qualitative and morphological analysis of porosity and primary silicon in the nanocomposite matrix was performed on optical micrographs by using a quantitative image analyzer (Image Pro Plus, version 5.1, Media Cybernetics, MD, USA). The distribution and retention of MWCNT in the Al–Si matrix in both deposits was investigated by employing a JEOL, JSM-633OF Field Emission Scanning Electron Microscope. The morphological change of MWCNTs was also studied by performing transmission electron microscopy using a Philips PW 6061 TEM system (model CM 200, Eindhoven, Netherlands). First stage thinning of 3 mm diameter samples were done by a dimple grinder from Gatan, Inc. (Model 656 Mk3, California, USA) followed by final thinning using a twin jet polisher from E.A. Fischione Instruments, Inc. (Model 110, Pennsylvania, USA) along with an automatic power controller (Model 120). Micro-Raman spectroscopy of the spray formed composites was carried out to validate the retention of carbon nanotube structure and to perform qualitative residual stress analysis. Ti-sapphire crystal target with a laser wavelength of 785 nm was used for this purpose. The laser was produced using a laser source from Spectra Physics (Model 3900S, California, USA) and the detector was from Kaiser Optical Systems, Inc. (Michigan, USA). The residual stress in the nanocomposites was estimated by X-Ray Diffraction analysis. A Siemens 500D X-ray diffractometer with CuKα radiation was operated at 40 kV and 20 mA for this purpose. The elastic modulus and hardness values of the spray formed composites were evaluated by nanoindentation technique. Indentation experiments were conducted using a nanoindenter® XP (MTS System Corporation, Oak Ridge, TN). A three-sided Berkovich shaped diamond indenter was used for indentation. The load and displacement data obtained from the tests were analyzed using the methods reported by Oliver and Pharr.40, 41 The initial calibration of the instrument was done using a standard fused silica sample provided by MTS. The microhardness measurement of the spray formed Al-MWCNT nanocomposite was done using a Vickers microhardness (Shanghai Training Optical Instrument Co., Ltd., model HXD-1000 TMC, Shanghai, China). The microhardness indentations were made by a Vickers indenter operating at a load of 100 g and a dwell time of 15 s.

3. RESULTS AND DISCUSSION

3.1. Microstructural Analysis

Figure 1 shows the cylindrical shaped spray formed structures, which exhibit rough outer surface. A fraction of MWCNTs and Al–Si powder formed large partially melted agglomerates attributed to the very high specific surface area (∼200 m²/g) of MWCNTs.42 These large agglomerates caused inconsistent and pulsed powder flow during the spray forming, which resulted in rough outer surface area of the spray formed composites. The indication of presence of carbon in both the sprayed structures is evident from the black spots on the grayish surface. These black spots are less visible in case of HVOF spray formed nanocomposite (Fig. 1(b)). This is attributed to the higher spray velocity in HVOF process (700–1400 m/s) than that in PSF (350–1000 m/s), which causes explosion of agglomerates.36, 37

Metallographically polished cross-sectional views of the nanocomposites are shown in Figure 2. Due to the inherent differences in PSF and HVOF spray processes, powder particles encounter a variation in degree of heating, the flight time and subsequently varying degree of consolidation and porosity (Table I). Higher degree of melting and subsequent resolidification of powder agglomerates can be observed in PSF nanocomposites (Fig. 2(a)) as the agglomerates experienced higher amount of heat and longer flight time due to relatively lower velocity (Table I). In contrast, the HVOF nanocomposite clearly exhibited the dense and layered splat structure. Partial melting of the splats is attributed to the comparatively low temperature, as HVOF spraying is a combustion based process (Table I). The dense and compact HVOF sprayed structure is resulted due...
to higher velocity that causes both, mechanical bonding between the splats and metallurgical bonding due to partial melting. The two sprayed deposits exhibits different porosity level attributed to the disparity in process parameters. Porosity level is higher in PSF sprayed deposit (6.7 ± 0.4%), than that in HVOF one (3 ± 0.3%) (Table II).

Pores in PSF nanocomposites are larger (2–4 μm) and caused by inconsistent flow of agglomerated powder particles. The dense microstructure in HVOF is attributed to the higher velocity impact of the molten/semimolten powder mixture. The effect of variation in degree of melting, porosity, and impact on mechanical properties i.e., hardness, elastic modulus, and residual stress is discussed later in this paper. The density of the deposits was also measured by water immersion and found to be higher in HVOF sprayed deposit (2.54 gm/cc) than PSF (2.45 gm/cc) (Table II). Theoretical density of Al-23 wt% Si, without any porosity was estimated as 2.60 gm/cc and considering 10 wt% incorporation of MWCNT, the theoretical density changes to 2.36–2.42 gm/cc (assuming MWCNT density to be 1.3–1.5 g/cc). However, both the sprayed deposit shows higher value of measured density than the theoretical value due to some loss of MWCNTs during spraying. Lightweight nanotubes are difficult to flow through the core of the plasma/HVOF flame and often result in partial loss as overspray.

Bright field TEM images of both nanocomposites are shown in Figure 3. Both PSF (Fig. 3(a)) and HVOF (Fig. 3(b)) sprayed composites exhibit presence of nano-sized α-Al grains with uniformly distributed ultrafine primary silicon particles (10–90 nm) in the Al-Si alloy matrix. SAD patterns insinuate presence of aluminium and silicon in the nanocomposites. The less intense, but well-defined ring pattern indicates presence of ultrafine crystalline structure.

The evolution of nanostructure in the matrix took place by virtue of two simultaneous processes, i.e., (i) formation and fragmentation of dendritic structure under the heavy impact of sprayed molten agglomerates and (ii) restriction of grain growth during solidification, attributed to extremely high cooling rate (PSF: 10^6–10^8 K/s and HVOF: 10^3–10^5 K/s).28 The dendritic-Al during directional solidification became repeatedly get deformed and fragmented due to the heavy impact of the successive molten particles, which resulted in huge number of nucleation sites for new grains to form. The high solidification rate restricted the grain growth and thus a nanocrystalline Al-Si alloy matrix was achieved. Hereof, it should be mentioned that the as-received gas-atomized micron-size (15–45 μm) Al-Si alloy powders contain Al-Si (α-aluminum) grains in the size of ~3 μm with distinct grain boundary. Detailed discussion on the microstructural features of the as-received Al-Si powder has been provided in an earlier paper by our research group.43 It is important to note that nanocrystalline microstructure has been achieved via thermally spraying using micron-size powders as precursor.

The average grain size was also estimated from the X-ray diffraction spectra of the two nanocomposites using Scherer’s formula and was observed as 87 nm and 64 nm for PSF and HVOF, respectively. PSF composite exhibits higher grain size than that of the HVOF sprayed one, although the cooling rate is higher in PSF. This is

<table>
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<th>Features</th>
<th>Plasma spray forming (PSF)</th>
<th>High velocity oxyfuel spray forming (HVOF)</th>
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<tbody>
<tr>
<td>Degree of melting and resolidification</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>Porosity content, %</td>
<td>6.7 ± 0.4</td>
<td>3.2 ± 0.3</td>
</tr>
<tr>
<td>Measured density, gm/cc</td>
<td>2.45</td>
<td>2.54</td>
</tr>
<tr>
<td>(water immersion test)</td>
<td></td>
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<tr>
<td>Primary Si volume</td>
<td>14.1 ± 1.9</td>
<td>14.9 ± 1.0</td>
</tr>
<tr>
<td>fraction, %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary Si size</td>
<td>40–90 nm</td>
<td>10–30 nm</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>55.5 ± 9.6</td>
<td>82.8 ± 9.3</td>
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<td>Hardness from</td>
<td>1.99 ± 0.14</td>
<td>1.97 ± 0.16</td>
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<tr>
<td>nanoindentation (GPa)</td>
<td>1.65 ± 0.11</td>
<td>1.93 ± 0.14</td>
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<td>Vickers microhardness (GPa)</td>
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Fig. 3. Presence of nanosized grains in the Al-Si alloy matrix in both PSF (a) and HVOF (b) sprayed nanocomposites.

attributed to the comparatively heavier impact of splats and subsequently higher degree fragmentation of dendritic arms during solidification of splats in HVOF sprayed nanocomposite. It is expected that presence of nanosized grains in the deposits will result in higher mechanical strength of the deposits according to the Hall-Petch relationship.26

The nanosized primary silicon particles, resulted by diffusing out of silicon from the hypereutectic Al-Si alloy are present both in PSF (40–90 nm) and HVOF (10–30 nm) sprayed nanocomposites. The primary silicon particles in as-received Al-Si powders were in the size range of 40–100 nm.44 Hence, it can be noticed that higher degree of Si particle refinement is achieved in the thermally sprayed deposits. These nanosized Si particles can act as potential barrier for dislocation movement and thus can improve the mechanical strength and hardness of the sprayed structures.44 Presence of high elastic modulus primary silicon particles (110 GPa) as second phase will also provide “composite strengthening” according to Rule of Mixture theory.45 The high immobile dislocation density due to the mismatch of thermal expansion coefficient at the vicinity of Al-Si grains and primary Si particles will also contribute in improving the tensile strength of the spray formed structures.46 Although the hypereutectic Al-Si alloy powder contains Ni (2 wt%) and Cu (1 wt%), SAD patterns (Fig. 3) and XRD spectra does not reveal intermetallic formation, which can be attributed to lack of sufficient time for diffusion and precipitation of intermetallics.

3.2. Carbon Nanotube in Nanocomposites

Multiwalled carbon nanotubes in the blended powder agglomerates experienced an aggressive environment of very high temperature and mechanical impact (due to high velocity) during both thermal spray processes. Hence, it is essential to scrutinize the retention of original, physically and chemically undamaged carbon nanotubes in the spray formed composites towards improving the mechanical properties. Although melting point of carbon nanotube is around 3500 °C, researchers have expressed different opinions on the stability of carbon nanotube structure at high temperature.47 According to some researchers, the MWCNTs are stable even after a temperature of 2800 °C.48,49 On the contrary, Ajayan et al. reported structure change in MWCNTs beyond 700 °C.50 Herein, it should be mentioned that presence of unimpaired MWCNTs at very high temperature during plasma spraying has been confirmed in our earlier published work.25 Thermodynamic feasibility of CNT retention in the composites was also confirmed in the same study.25

In our present study, scanning and transmission electron microscopy and Raman spectroscopy has been carried out to validate the intactness and distribution of MWCNT in the both PSF and HVOF nanocomposites. The SEM micrographs of the fracture surfaces distinctly show presence of MWCNTs in both the cases (Fig. 4). A very good distribution of MWCNTs embedded in the solidified matrix can be noticed in both cases. These distributed MWCNTs would precisely act as short fiber reinforcement in the Al–Si matrix and contribute in improving tensile strength of nanocomposites.51 However, as the length of the MWCNT (0.5–2.0 μm) is smaller than the required critical fiber length (5–8 μm) for the effective load transfer from Al–Si matrix, the maximum stress on MWCNT may never reach its ultimate tensile strength.53 Failure of the nanocomposites can occur via two mechanisms. If either the Al-Si matrix or the interface of matrix and MWCNT were stronger than reinforcement (MWCNT), the failure of nanocomposites would occur through stochastic MWCNT breakage at weaker sites along the length.54,55 However, as the fiber reinforcement (MWCNT) is stronger than both
the matrix and the interface, the failure of nanocomposites will occur through pulling out of MWCNTs. Although the failure mechanism is not very clear at this point, pulling out of some MWCNTs from well-solidified Al–Si matrix in both the nanocomposites can be observed (Fig. 4). The pulling out of MWCNTs occurred as the fiber/matrix interface failed before the MWCNT reached its failure strength. The energy dissipation during pull out of MWCNTs embedded in the matrix will possibly lead to improved fracture toughness of the nanocomposites.51

It was expected that damage to MWCNTs would be higher in case of PSF as compared to HVOF due to higher temperature of the plasma and relatively higher residence time in the flame. However, MWCNTs in PSF deposit are longer and more intact (Fig. 4(a)), whereas the CNTs in HVOF deposit are short and broken, attributed to the higher impact of the powder-CNT agglomerates. MWCNT surface in the both nanocomposites is smoother than as-received MWCNTs (Fig. 4(c)), which is attributed to formation of a thin layer (in the nanometer range) of resolidified Al–Si or formation of some reaction product. The smoother CNT surface is more pronounced in PSF nanocomposite than HVOF due to higher degree of melting. The possible formation of reaction product layer and the influence on interfacial phenomena has been discussed later in this paper.

TEM image of PSF nanocomposite in Figure 5(a) shows a MWCNT bending under a primary Si particle. The primary Si was formed by the phenomena of Si dissolution from hypereutectic Al-23 wt% Si matrix during the solidification in plasma spraying. The bending of MWCNT shows the unaltered flexibility of MWCNTs after experiencing the harsh environment of plasma spraying, thus implying possible improvement in flexural strength of the nanocomposites. According to Ijima and Nardelli, CNT bending occurs by periodic disruption or kink formation at the inner side of the bent CNTs, which is under compression.53,54 They have also reported that number of kinks increases with increase in shell numbers of MWCNTs.

An interesting phenomenon, formation of multiple Y-junction CNT is observed in the nanocomposites (Figs. 5(b) and (c)). Y-junction MWCNTs are aligned along the surface of primary silicon particles in PSF composites (Fig. 5(b)), whereas in HVOF nanocomposite (Fig. 5(c)) it is being observed in the Al–Si matrix. Formation of Y-junction in single-walled CNTs during electric arc discharge experiment, by catalytic chemical vapor deposition growth, CNT growth using templates or during fullerene decomposition has been reported recently by a number of researchers.55–59 There are various models to explain the Y-junction phenomenon, which are based on the insertion of non-hexagonal (n-H) rings in the hexagonal network in the region where the three branches of the Y are joined together.55–59 All these models consider sp2 hybridization during networking of carbon atoms, however, differ in kind, number, and positioning of n-H (pentagonal or heptagonal) rings. In our case, the formation of Y-junction is attributed to the welding between closely spaced MWCNTs. A similar phenomenon has been observed by Ajayan et al. when electron beam radiation on carbon nanotube results in sputtering of carbon atoms, leading to dimensional change and surface reconstruction by virtue of diffusion, which further causes welding and annealing of crossing carbon nanotubes.60 However, it is not clear about the numbers of CNT walls taking part in forming the junction or the effect on the electrical and mechanical properties of MWCNTs. It can be assumed that formation of web-type arrangement in Y-junction MWCNTs will provide an overall toughening effect to the composite structure.

Raman spectra (Fig. 6) of the nanocomposites corroborates well with that of as-received MWCNT, which insinuates the intactness of MWCNT structure in the deposits. Presence of MWCNTs in both the composites is confirmed by the G-lines, which signify the presence of graphene structure.62
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Fig. 5. Bright field TEM images shows (a) bending of MWCNT against a Si particle in PSF nanocomposite, (b) formation of Y-junction MWCNTs network surrounding Si particle in PSF nanocomposite, and (c) multiple Y-junction formations in HVOF nanocomposites.

Fig. 6. Raman spectra of the Plasma and HVOF nanocomposites, indicating presence of CNT structure.

3.3. Interface Between Carbon Nanotube/Al–Si Matrix

The interface and wettability between multiwalled carbon nanotube and Al–Si matrix is a critical factor in affecting the mechanical properties of the nanocomposite. Improved wettability signifies improved interfacial bonding between the matrix and the reinforcement and thus effective load transfer to the reinforcement. A bundle (diameter ~200 nm) of MWCNTs, completely covered with resolidified Al–Si alloy can be seen in the cross-sectional image of PSF nanocomposite (Fig. 7(a)). The sheathed MWCNTs form a bridge over a micron size pore and provides potentially improved strength to hold the matrix against possible failure. A high magnification cross-sectional view of HVOF sprayed composite (Fig. 7(b)) shows layers of successive splats with well-defined splat boundaries with trapped CNTs. Aligned CNTs are observed between splats with an adherent interface without any porosity. Such strong interface is indicative of good wettability and bonding even though the degree of melting is less in case of HVOF nanocomposites. To the authors’ best knowledge, there is no literature available on the wetting phenomena and interfacial properties in Al-CNT system. Researchers have studied interface in Al-graphite system, where the wettability behavior improves only after the gradual formation of an interfacial product layer (aluminum carbide) on graphite surface. Formation of a layer of reaction product of ~5 nm thickness on MWCNT surface can be seen in both the nanocomposites (Fig. 8). The MWCNT in HVOF composite (Fig. 8(a)) is a closed end one and shows a certain amount of deformation at the end, which may be attributed to high velocity impact of powder-MWCNT agglomerates. The product layer is continuous in case of PSF (Fig. 8(a)) and localized in case of HVOF (Fig. 8(b)). The continuous layer in PSF nanocomposite is attributed to the higher degree of melting and hence better flowability of Al–Si alloy over the MWCNT surface.
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Fig. 7. High magnification cross sectional SEM images: (a) PSF nanocomposite shows CNTs covered with layer of resolidified Al–Si alloy and (b) aligned CNTs between the layered splats in HVOF nanocomposite.

This product layer insinuates better wettability of Al–Si alloy on MWCNT surface and thus may help in improving the adhesion between the reinforcement and matrix. As silicon carbide formation is thermodynamically more favorable than aluminum carbide in hypereutectic Al–Si alloy, the carbide layer might be of silicon rather than aluminum. An extensive study based on thermodynamics, kinetics, and crystallography of interfacial reaction product formation in Al–Si alloy with MWCNT reinforcement has been carried out by our research group. The study reveals that an ultrathin (0.5 nm) silicon carbide layer is formed on the MWCNT surfaces instead of aluminum carbide suggesting excellent wettability of molten Al–Si alloy on MWCNT. However in-depth discussion on the interfacial reaction product layer formation is being presented elsewhere and beyond the scope of this paper.

3.4. Evaluation of Mechanical Properties

3.4.1. Residual Stress Analysis

The nanocomposites experience quenching residual stresses due to the high solidification rate (10^6–10^8 Ks^{-1}) during PSF and 10^3–10^5 Ks^{-1} in HVOF) during the spray forming processes. Besides, the heavy impact of molten/semimolten Al–Si powder–MWCNT agglomerates imparts certain amount of stress in the deposits. Qualitative residual stress evaluation in the nanocomposites has been attempted from their respective Raman spectrum (Fig. 6). The peak positions in the spectra do not show significant variation between PSF and HVOF nanocomposites, which indicates a little difference in state of residual stresses. The D line for both the composites (1224 cm^{-1} for PSF and 1231 cm^{-1} for HVOF) are at higher wave number in comparison with the D-line for CNT used (1219 cm^{-1}) during spraying. This signifies presence of quenching stresses of compressive nature in both deposits. The residual stress has also been computed from the XRD spectra of the sprayed structures using the elastic modulus values obtained from nanoindentation experiment. The calculated residual stress is 134 MPa and 273 MPa for...
PSF and HVOF sprayed nanocomposite, respectively. Both the nanocomposites exhibit residual stress of compressive nature, which has also been concluded earlier from the Raman spectra. As the coefficient of thermal expansion of aluminum (23.6 × 10⁻⁶/K) is higher than that of primary Si (2.8 × 10⁻⁶/K–7.3 × 10⁻⁶/K) and MWCNT reinforcement (−7 × 10⁻⁶/K), the Al–Si matrix should experience tensile residual stress and primary Si particles and MWCNT reinforcement should be in compression.66–68 However, the solidification shrinkage of Al–Si matrix leads to overall compressive residual stress in both the Al–Si matrix and MWCNT reinforcement. HVOF sprayed nanocomposite exhibited higher residual stress due to dominant effect of heavier impact of sprayed powder mixture on the substrate.

3.4.2. Elastic Modulus and Hardness Measurement

Elastic modulus and hardness of the nanocomposites have been measured by performing nanoindentation experiment under constant displacement mode. The load-displacement curves indicate plastic deformation in both the cases (Fig. 9). The elastic modulus and hardness data are reported in Table II. The elastic modulus (82.8 ± 9.3 GPa) is higher in HVOF sample, which is attributed to lower porosity content (Table II). The higher residual stress in HVOF nanocomposite would cause higher dislocation density and thus contributes to higher elastic modulus value. As the primary Si content does not differ much in the two nanocomposites (Table II), the change in porosity level is the primary factor for variation in elastic modulus value. The hardness values estimated from nanoindentation result are comparable at 1.99 ± 0.14 GPA and 1.97 ± 0.16 GPA, Vickers microhardness testing was performed as the effect of micron size large pores is often excluded hardness data obtained from nanoindentation. The Vickers microhardness values of both the PSF (1.65 ± 0.11 GPA) and HVOF (1.93 ± 0.74 GPA) sprayed composite is in accordance with porosity, degree of melting, and resulting microstructure in both cases. Hardness values are also comparable to the nanoindentation data.

4. CONCLUSION

(1) Successful fabrication of bulk near net shape structure Al-CNT nanocomposite was achieved by two different thermal spray process viz plasma spray forming and high velocity oxy-fuel spray forming. (2) The HVOF sprayed composite experience dense and more compact microstructure. Both the spray deposits contain nanosized grains in the Al–Si alloy matrix. (3) Physically intact and undamaged multiwalled carbon nanotubes were successfully retained in both PSF and HVOF spray formed composite structure. (4) Formation of reaction product layer on MWCNT surface enhanced the wettability of molten Al–Si alloy on MWCNT during thermal spraying. (5) HVOF sprayed nanocomposite exhibited higher residual stress, higher elastic modulus, and higher hardness compared to the PSF sprayed nanocomposite.

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References and Notes
