Carbon Nanotubes Reinforced Al-11 wt% Si Alloy via Plasma Spray

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Abstract. In this work, multi-walled carbon nanotubes (MWCNTs) with different portions (0.5, 1, 2, 4) wt% were added to a gas atomized Al-11 wt% Si powder. The Al-11 wt% /MWCNTs nanocomposite powder was examined by FESEM, Raman spectroscopy, X-ray diffraction (XRD). Air plasma spraying (APS) was used to spray Al-11 wt% Si/MWCNTs nanocomposite powder on aluminum alloy AA6082-T6 substrates. Al-11 wt% Si/MWCNTs nanocomposite coating layer was examined using FESEM/EDS, Raman spectroscopy, XRD and HRTEM. SEM/EDS showed that Al4C3 is formed at the interface between the coating layer and the substrate in Al-11 wt% Si/4 wt% MWCNTs plasma spray coating. The adhesion test showed good adhesion in the ranges 5-15 MPa between the coating layer and the substrate. Microhardness test of the air plasma sprayed (APS) Al-11 wt% Si/MWNTs nanocomposite layer is increased with the MWCNTs wt%.

1. Introduction
Composite materials combined distinct physical and mechanical properties like thermal conductivity, electrical conductivity, strength, toughness and stiffness properties [1, 2]. Composite materials with at least one of their constituent phases being less than 100 nm are commonly termed nanocomposites. Nanocomposites will make remarkable improvements in the mechanical and physical properties of these nanocomposites [3]. Aluminum silicon alloys are widely used in internal combustion engine, owing to their good characteristics such as, high corrosion resistance and low density [4]. Wear resistance of aluminum silicon alloys strongly depends on the alloy composition [5].

Aluminum-Silicon composite powder coating material such as (Al -7Si -26 Graphite) are used to provide consistent quality clearance control in applications where rotating components may come into contact with the coating as a result of design or operational limitation in the low temperature sections of turbine engines. These powder coatings are used to minimize wear to the rotating components while maximizing gas path efficiency in seal areas [6,7].

Carbon nanotubes (CNTs) have excellent properties such as: High aspect ratio, low mechanical, electrical and thermal properties [8-10]. Carbon fibers were used to reinforce Al-Si alloys in order to combine high strength and high modulus of carbon fiber with the good ductility and high toughness of
aluminum alloys [11]. Actually, CNTs are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. High Van der Waals forces between individual tubes cause them to agglomerate into CNT ‘ropes’ or randomly ordered free-floating particles. Therefore, the major challenges is to disperse CNTs in metal matrix alloy with less damaging of CNTs [12,1].

The aim of this work is to use Al-11 wt% Si/MWNTs (MMCs) nanocomposite powder to coat aluminum alloy substrates (AA6082-T6) using plasma spraying process. The effect of MWNTs as reinforcement in Al-11 wt% Si/MWNTs nanocomposite coating will be studied together with the microstructure, microhardness and bond strength of the Al-11 wt% Si/MWNTs nanocomposite coating.

2. Materials

In this research a 3 mm of flat sheet of aluminium alloy AA6082-T6 (AALCO Metals Limited, UK) was used as a substrate to be coated with Al-11 wt% Si/MWNTs using plasma spray process. The chemical composition of the aluminium alloy substrate AA6082-T6 is shown in Table 1.

Table 1. Chemical composition of wrought aluminium alloy AA6082-T6.

| Element | Cr | Cu | Fe | Mg | Mn | Si | Ti | Zn | Al |
|---------|----|----|----|----|----|----|----|----|----|
| Nominal composition | 0.25 | 0.1 | 0.5 | 0.6-1.2 | 0.4-1 | 0.7-1.3 | 0.1 | 0.2 | Bal. |
| Measured Composition | 0.19 | 0.07 | 0.35 | 1.08 | 0.76 | 1.14 | 0.06 | 0.14 | Bal. |

The specifications of MWNTs (ARRY International Group Limited-Germany) are shown in Table 2. A gas atomized Al-11 wt% Si alloy powder (Phoenix Scientific Industry Ltd., UK (PSI)) was used with an average grain size 15-75 µm (-200 mesh/+15 µm). The chemical composition of gas atomized powder of Al-11 wt% Si illustrated in Table 3. The chemical composition analysis was carried out by X-Ray fluorescence (XRF), Spectro Xepos, Germany at the Applied Physics Department, Ministry of Science and Technology, Iraq.

Table 2. Specifications of MWNTs [ARRY® Company, Germany].

| Specifications | wt% |
|---------------|-----|
| Diameter (nm) | >80 |
| Length (µm)  | 30-50 |
| SSA (m²/g)   | 0.5-2 |
| Amorphous carbon | 220 |
| Ni/Fe        | <2 |

Air plasma spray system consist of plasma spray gun (Sulzer Metco, model F4MB-XL, Switzerland) which is mounted on flexible 6-axis robotic manipulator (ABB, model IRB -6400, Switzerland). The
process parameters are tabulated in Table 4. The tensile adhesion test had been done according to ASTM standard C633-01.

Table 3. Chemical composition of Al-11 wt% Si powder [PSI® Company Ltd., UK].

| Element       | Si  | Cu  | Fe  | Mg  | Mn  | Pb  | Sn  | Zn  | Al   |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|------|
| **Al-11Si Standard** | 11-13 | 0.3 | 0.25 | 0.1 | 0.1 | 0.02 | 0.02 | 0.2 | Bal.   |
| **Al-11Si Measured**   | 11.47 | 0.12 | 0.20 | 0.08 | 0.01 | 0.04 | -   | 0.1 | Bal   |

The Tensile adhesion tests of Al-11 wt% Si /MWNTs coating were performed using Hounsfield Test Equipment (UK, model 50H-K-S) with 50 kN capacity load cell and 0.05 mm/sec crosshead speed. The microhardness of the Al-11 wt% Si /MWNTs coating was measured using Buehler 60044, UK for well-polished cross-section samples using applying load of 50 gram at 20 second. The XRD was measured using diffractometer Shimadzu, Japan with Cu- Kα radiation at 40 kV and 30 mA, wave length (λ) 1.5418 Å, using nickel filters. The diffraction angle (2θ) is 10°-90° at scanning speed was 6° deg/min. The XRD analysis was carried out at S.C. Geological Survey and Mining, Baghdad. High Resolution Transmission Electron Microscope (HRTEM), 200kV, A FEI, Model: Tecnai G2 F30, USA, high sensitivity combining diverse applications like bright and dark field with STEM capability equipped with X-ray energy dispersive spectroscopy (EDS). Field emission scanning electron microscope (FESEM) model (Carl Zeiss Supra 40VP, Germany) and FEI Quanta 250 ESEM-US used to characterize the coating layer.

Table 4. Process sheet of plasma spray parameters.

| Spraying parameters | Pressure | Flow rate |
|---------------------|----------|-----------|
| Gun type: F4MB-XL   | Argon    | 3 bar     | SLPm      |
| Hundred             | Hydrogen | 3 bar     | SLPm      |
| Hundred             | Carrier/Argon | 3 bar | SLPm      |
| Hundred             | Current  | 500 Amp   |           |
| Hundred             | Power    | 33 kW     |           |
| Hundred             | Nozzle diameter | 6 mm |           |
| Hundred             | Powder feed rate | 40 ± 5 (g/min.) |           |
| Hundred             | Spray distance | 140 mm |           |

3. Experimental Work

To obtain a good dispersion of CNT with Al-11 wt% Si powder, two steps mixing processes were used. First, different weigh percent (0.5, 1, 2 and 4 wt %) of Carbon nanotubes were put in beaker then methanol (HPLC grade) was added (CNTs: Methanol ratio is 1:250 ml). The solution was then sonicated for 5 minutes using a sonicator, followed by magnetic stirring at 250 rpm for 5 minutes.
followed by sonication for 5 minutes. Then, a 250 g of Al-11 wt% Si powder were then added to CNT / methanol solution in paraffin oil bath at 70°C by using mechanical stirrer at 250 rpm. Argon gas was purged to the Al-11 wt% Si / MWNTs / methanol solution to make sure no oxidation takes place during methanol evaporation. After entire methanol was evaporated, the Al-11 wt% Si / MWNTs mixture was transferred to a drying oven at 70°C for 24 hours and then was saved in desiccators under vacuum.

In the second mixing step, Al-11 wt% Si / MWNTs mixture was ball milled at ambient temperature using a ball mill (Pascall Engineering, UK) with a 2.4 litter porcelain jar and 1/2 and 9/16 inches stainless steel balls. The ball to powder ratio (BPR) was taken as 10:1 and ball mill speed and milling time are 100 rpm and for 5 hours respectively. Methanol (HPLC) was added as a lubricant to prevent powder sticking on the balls and for each 30 grams of Al-11 wt% Si powder; a 400 microliter (µl) of methanol was added. The Al-11 wt% Si / MWNTs powder was then collected and dried in an oven for 48 hours and then stored in desiccators under vacuum.

Plasma spraying process was done by few passes. After the first plasma spray pass, the Al-11 wt% Si / MWNTs coating layer was cleaned with compressed air and the coating thickness was measured by digital micrometer. Four passes were made until the coating thickness measured more than 100 micrometer. The gauge radius means the distance from the powder injector to plasma nozzle centre. After thermal spraying process, the samples were cut with low speed diamond saw (Buehler, Isomat, UK), followed with cold mounted with Acrylic resin. Each sample was then ground using automatic grinding machine with silicon carbide, washed with distilled water, rinsed with Acetone and then dried. The samples were then polished with 0.1 µm diamond paste on PoliCloth, washed with distilled water, and then followed by polishing with aluminum oxide 0.05 µm, washed again with distilled water rinsed with Acetone and dried.

4. Results and Discussion

Figure 1, shows High Resolution Transmission Electron Microscopy (HRTEM) image of purified CNTs produced by CVD using Ni/Fe catalyst supplied by Arry.Co. The MWNTs image of high magnification HRTEM contains some defects that were introduced during purification process.

![Figure 1. HRTEM image shows purified CNTs produced by CVD using Ni/Fe catalyst supplied by Arry.Co.](image)

Figure 2 shows HRTEM image of MWCNT produced by CVD with Fast Fourier Transformation (FFT) to analyses the interlayer spacing and to measure the number of walls. There are about 23-22 uneven walls with uneven outer and inner diameter. These defects would affect carbon nanotubes
properties. The outer diameters were found 20-40 nm, the inner diameter were 3-5 nm, with 0.341 nm interlayer spacing which is typically similar of interlayer found in standard XRD card 0.3434 nm.

FESEM micrograph for Al-11 wt% Si/0.5MWCNTs powder after 5 hours of ball milling showed the absence of any clusters on the stubs as shown in Figures (3a,b). The dark area is the individual MWNTs that are embedded into the Al-Si particles. Many other dispersion techniques has been studied in order to get uniform spherical particles, including mechanical alloying [13], nanoparticle dispersion [14], molecular-level mixing [15] and spray drying [16]. It was found that ball milling is a good technique to obtain good dispersion of CNTs with Al-Si powder as shown by Kang et al. [17].

![Figure 2. HRTEM image of MWCNT produced by CVD using Ni/Fe catalysts (Arry Ltd.), (a) a Fast Fourier Transform (FFT), (b) Magnified filtered image shows the interlayer of MWNTs, (c) the MWNTs interlayer scale measurement.](image1)

![Figure 3. FESEM micrograph of Al-11 wt% Si/0.5 wt% MWNTs powder, solution dispersion followed by ball mill mixing for 5 hours, (a, b) LM and HM.](image2)

At higher magnification (Figure 3b) the CNTs are embedded into powder particles due to layering of particles formation during ball milling. These layers cover the new forming particle and only knotted-lumped agglom-erated CNTs settles in pores of particle surface. However, in some areas a knotted-lump of CNTs appears with larger area due to increasing the amount of CNTs. In ball milling, the
layering formation was explained by Suryanarayana [13] where the particles are repeatedly flattened, cold welded, fractured and re-welded to form large particles. The deformation of particles in ball milling led to embedding of MWNTs in Al-Si particles [17]. The small particles sizes of Al-Si have been reduced after the ball milling. This explains the small layering formation through which CNTs were embedded. Agglomerates of CNTs (knotted lumps) were found in some areas after ball mill mixing due to entanglement of carbon nanotubes with Al-Si powders.

X-ray diffraction (XRD) patterns of Al-11 wt% Si/ MWNTs powder mixture is shown in Figure 4. The peaks for aluminum and silicon are shown without appearance of CNTs peaks only very small peaks in case of 2 wt% and 4 wt% of CNTs this is due to the small amount of CNTs which is below the detection limit of the X-ray counter and also the dispersion of CNTs in Al-Si particles. The XRD patterns of Al-11 wt% Si/MWNTs coatings layer is identical to X-ray diffraction (XRD) patterns of Al-11 wt% Si/ MWNTs powder which indicate no significant phase trans-formation occur during plasma spraying. SEM/EDS examination of the coating layer cross-section was performed in order to identify the elements after plasma spraying.

Figure 4. XRD patterns of Al-11 wt% Si/MWNTs powder mixture with various amounts of MWNTs.

Figure 5 shows SEM/EDS micrograph of Al-11 wt% Si coating layer for as received powder. The optical microstructure of the coating layer is shown in Figure 5a. The selected area spectrum for the coating layer is highlighted in Figure 5b. The EDS spectrum of the coating layer shows Al, Si and Oxygen peaks , Figure 5c.

SEM/EDS micrograph of Al-11 wt% Si/0.5 wt% MWNTs coating layer is shown in Figure 6. The optical microstructure of the coating layer is shown in Figure 6a which reveals aluminum oxide, needles shape silicon embedded in aluminum matrix. The selected area spectrum for the coating layer is highlighted in Figure 6b. The EDS spectrum is shown in Figure 6c which contains carbon, aluminum, silicon. Voids were also seen clearly in the optical micrograph at high magnification, as well as un-melted particles formed during APS.

The cross section of the Al-11 wt% Si/1 wt% MWNTs nanocomposite coating layer contains aluminum oxide, needle shape silicon embedded in aluminum matrix. The EDS spectrum shows some amount of iron and this may cause some deleterious effects on the composite coating. SEM/EDS micrograph of coating layer cross-section shows more voids and there are no needles like silicon. The selected area spectrum for the coating layer shows the silicon wt% decreased.
Figure 5. SEM/EDS analysis micrograph and OM for Al-11 wt% Si coating layer cross section; (a) OM, (b) SEM area selected spectrum, (c) EDS spectrum peaks.

| Element | Weight% |
|---------|---------|
| O K     | 6.82    |
| Al K    | 84.52   |
| Si K    | 8.03    |
| C K     | 0.63    |
| Totals  | 100.00  |

Figure 6. SEM/EDS micrograph and OM for Al-11 wt% Si/0.5 wt% MWNTs coating layer cross section; (a) OM, (b) SEM area selective spectrum, (c) EDS spectrum peaks.

| Element | Weight% |
|---------|---------|
| O K     | 4.62    |
| Al K    | 89.79   |
| Si K    | 5.59    |
| Totals  | 100.00  |
SEM/EDS micrograph of Al-11 wt% Si/4 wt% MWNTs coating layer cross-section is shown in Figure 7. SEM micrograph of the coating layer Figure 7a shows a significant black clusters and a black interlayer between the coating and the substrate. The selected area spectrum for the coating layer is highlighted in Figure 7b. EDS examination shows relatively high peak of carbon in the interlayer (Spec. 2). This can be explained by three possibilities as: First the carbon nanotubes segregate form the lamellae during cooling and create mat-network on the surface. Secondly, the particles were covered with MWNTs during mixing process, so during impact the carbon nanotubes become the first impacting layer. Thirdly, the probability of graphitization of some CNTs occurs during high temperature of APS. The higher concentration of CNTs leads to clustering. This phenomenon occurs due to the surface tension forces of CNTs in the molten droplet [18]. Aluminum carbide (Al₄C₃) interface also can be formed during thermo-mechanical processing when the temperature is higher than 800°C [19-22]

![SEM/EDS micrograph of Al-11 wt% Si/4 wt% MWNTs coating layer cross-section.](image)

Figure 7. SEM/EDS analysis micrograph and OM for Al-11 wt% Si/4 wt% MWNTs coating layer, (a) SEM micrograph of selected area, (b) HM of the selected area shows the point EDS, (c) OM microstructure of the coating cross-section.

The stress vs. strain curves for the coating layer of Al-11 wt% Si and Al-11 wt% Si/MWNTs are shown in Figure 8 which gives the axial force vs. displacement curve. The maximum load at failure is 7.93 kN for Al-11 wt% Si/2 wt% MWNT, while the minimum load at failure is 2.86 kN for Al-11 wt% Si. The load range for the samples is (2.86 – 7.93 kN). The adhesion strength can be calculated according to ASTM by \( F_{\text{max}}/A \) where \( F_{\text{max}} \) is the maximum load and \( A \) is cross-section area. The adhesion strength increases with MWNTs loading. But less bonding strength obtained at increasing the proportion of MWNTs to 4% due to formation of aluminium carbide interface.

The microhardness of the substrate Al alloy AA6082-T6 has an average of 116.78 ± 2.9 HV. Figure 9 shows the microhardness curve for the coating layer with different wt% MWNTs. In general the microhardness increases with increasing MWNTs weight percent reinforcement and the maximum
hardness found at 4 wt% MWNT reinforcement. The microhardness test of 1 wt% and 2 wt% MWNTs the nanocoating composite of Al-11 wt% Si takes downward. Thus due to the increasing of the close pores inside the coating layer (as shown in Figure (15b) and effect on the hardness values. Increasing the amount of MWNTs more than 2 wt% MWNTs increases the hardness value because CNTs resist the flow of material and impede dislocation motion.

![Stress vs. strain curve](image1)

**Figure 8.** Stress vs. strain curve for the coating layer of Al-11 wt% Si and Al-11 wt% Si/MWNTs.

![Microhardness curve](image2)

**Figure 9.** Microhardness curve for the coating layer of plasma spared Al-11 wt% Si and Al-11 wt% Si/MWNTs.

5. Conclusions
The result of the current study reached to the following conclusions;
From the present work it can be concluded that:
1. The MWNTs produced by CVD (Arry Ltd.) have about 23 uneven walls with uneven outer and inner diameter.
2. The mixing process using methanol solution and mechanical stirring followed by ball milling for Al-11 wt%Si with MWNTs are a good dispersion technique, very convenient and suitable for industrial processes to achieve flowability of powder in thermal spray process.

3. Good adhesion of nanocomposite coating layer on aluminium substrate can be obtained by plasma spraying of Al-11 wt% Si/MWNTs. Where the adhesion ranges was from 5-15 MPa.

4. The microhardness is increased in general due to reinforcement effect of MWNTs.

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