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Processing and Characterisation of MWCNT reinforced Aluminum Matrix Composites

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Abstract

Metal matrix composites comprising aluminum matrix and multi-wall carbon nanotubes (MWCNTs) as reinforcements are fabricated using cold uniaxial compaction followed by sintering and cold extrusion as secondary processes. The MWCNTs are pretreated with sodium dodecyl sulfate (SDS) for improved adhesion with aluminum powder. The effect of sintering temperature on the microstructure is explored using differential scanning calorimetric (DSC) spectrum. The tensile yield and ultimate strength of Al/MWCNTs increased to 90% with 2 wt% addition of MWCNTs. Various theories for the strengthening and stiffening of Al/MWCNTs composites are explored.

Keywords: Aluminum matrix composites, multi wall carbon nanotubes, sintering, extrusion, mechanical properties

1. Introduction

Carbon nanotubes (CNTs) discovered by Iijima are one of the most exciting nanostructural materials of 20th century due to their superior mechanical, thermal and electrical properties[1-3]. Theoretical and experimental investigations studies on CNTs have reported their Young's modulus and tensile strength to be of the order of 3 TPa and 2 GPa, respectively [4-9]. Their excellent mechanical properties combined with low density of 2.0 g/cm^3 makes them as a viable reinforcing phase in a variety of polymer, ceramic and metallic matrices to design high performance composite materials. Aluminum alloys are widely used in aerospace, automotive industries as they possess low density, capable of being strengthened by precipitation hardening, have good corrosion resistance, high thermal and electrical conductivity[10]. CNTs could be an ideal choice, because of their nanosize, to design aluminum matrix composites (AMCs) to improve Al alloys wear and creep resistance. This has led to keen

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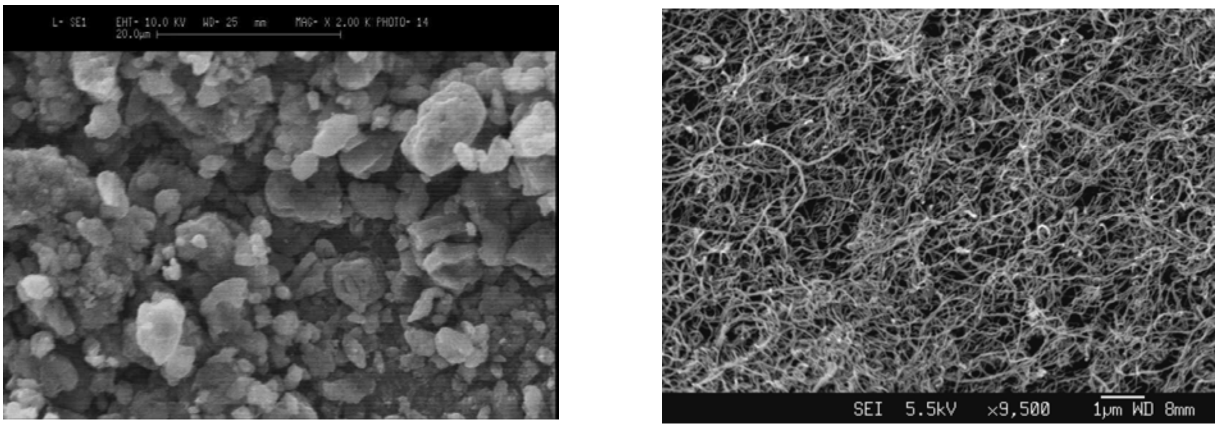
interest in the fabrication of high performance composites using various feasible manufacturing routes to tailor their properties. Recent research on producing these metal matrix composites reinforced with CNTs has been based on near net shape routes, such as cold compaction, melt deposition, cold isostatic pressing, hot compaction etc. for the primary processing followed by secondary process like hot extrusion to further enhance the properties of the metal matrix composites [11-14]. The recent studies have given a new dimension of producing these composites for many applications including aerospace and automotive industries. Hence, the aim of this paper is to compare the enhancement in mechanical properties of aluminum matrix composites reinforced with different weight percentages (0.5, 1.0 and 2.0) of multi wall carbon nano tube to the monolithic 99.96% pure aluminum fabricated by cold compaction as a primary processing followed by sintering and cold extrusion as a secondary processing route. To the best of authors' knowledge the current experimental data on Al/MWCNTs is very much limited and that too cold extrusion processing is not explored. The secondary process involved here are found to be very economical, when compared to the initial expenditure involved in some of the net shape forming routes like spark plasma sintering, hot isostatic pressing. Various theories for the strengthening and stiffening of Al-MWCNTs composites are also explored. In a recent paper, Loo et al.[15] have fabricated multi-wall carbon nano tubes (MWCNT) reinforced silica composites using sol-gel route and they have outlined the importance of surface treatment of CNTs for their effective dispersion. To date the MWCNTs are much cheaper than SWCNTs and hence we will be using MWCNTs in the current experimental studies for cost-effectiveness. The mechanical properties of obtained Al-MWCNTs are comparable to that obtained using other processing routes.

2. Materials and Methods

The aluminum (Al) powder used is pure Al (99.6 wt% Al) produced by argon gas atomization supplied by Alfa Aesar, Germany. The Al powder has nearly spherical shape particles with many satellite sub-particles with APS particle size of 20-30 µm. The SEM micrograph of the aluminum powder is shown in figure 1(a). The MWCNTs were produced by the catalytic pyrolysis of methane and supplied by Shenzen Nano Tech Port Co. Ltd, China. The MWCNTs have a nominal diameter of 10 nm, length of 5-15 µm and surface area of 40 – 300 m^2/gm. The scanning electron micrograph of Al powder particles and the micrographs of MWCNTs obtained through field emission scanning electron microscopy (FESEM) are shown in figure 1(b). The FESEM image shows that the CNTs tend to clump together due to vander walls forces of attraction between them.



(a) (b)

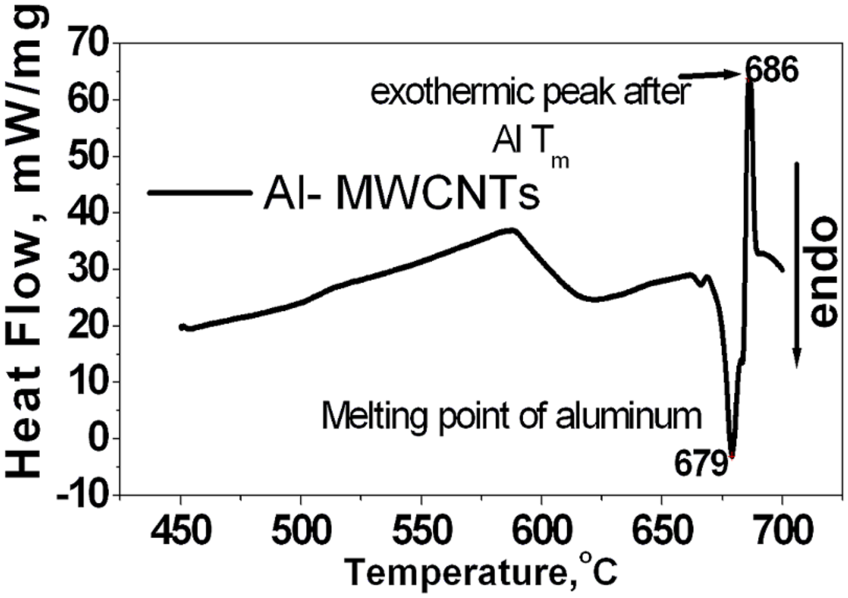
Figure 1 (a) Scanning Electron Micrograph of aluminum powder, (b) Field emission micrographs of MWCNTs.

2.1 Surface Treatment of MWCNTs

Raman spectroscopy with He:Ne laser of 633 nm wavelength was used to characterize the MWCNTs obtained from the manufacturer [16, 17]. The spectrum of MWCNTs showed a disorder (D-band) at 1348 cm^{-1} and tangential G-Band at 1590 cm^{-1} respectively. This G band Raman shift confirmed the presence of amorphous carbon (less than 3% by wt) as stated by the manufacturer. The MWCNTs are first cleaned by distilled (DI) water and then surface treated before mixing with aluminum powder. Initially MWCNTs are sonicated for 4 hrs in 63% by vol. nitric acid and filtered. The filtered acidic MWCNTs are neutralized with sodium hydroxide solution, and then dried by baking them in an oven at 110ºC for 2 hours. Finally for better adhesion between the MWCNTs and Al powder, they were treated with sodium dodecyl sulfate (SDS) surfactant, which decreases the vander Walls forces of attraction between the MWCNTs [18, 19]. Two gram of SDS was dissolved in 200 ml of water. The nanotubes were added to the SDS solution and sonicated for 4 hours. These treated nanotubes were filtered and baked at 110ºC for 2 hours for drying. When ionic SDS is used as the surfactant, the negative charges in SDS micelles that absorb on MWCNTs are said to prevent re-aggregation of MWCNTs.

2.2 Composite Preparation

Initially, required amount of Al powder and surface treated MWCNTs were transferred to a horizontal blending machine which had air tight metallic containers. The powders were mechanically mixed for about two hours in the blender set at 200 rpm. Measures were taken to prevent the loss of powder mixture during blending. After blending immediately the monolithic Al and MWCNT reinforced Al specimens were produced using cold uniaxial pressing in a 25 Ton hydraulic press, which can provide the manufacturer suggested 2 $Tons/cm^2$ compaction pressure. The cold pressed cylindrical specimen are 18 mm in diameter and 30 mm in length. These green compacts are then free-sintered at a heating rate of 10˚C per minute up to 580˚C (based on 660˚C melting temperature of Al powder) in a furnace maintained for 90 min and then cooled to room temperature at a rate of 3˚C per minute in the furnace itself. Finally, the sintered specimens are extruded in a hot-tool steel die of 45^0 die angle at room temperature to 12 mm diameter and length of 45 mm using the same 25 Ton hydraulic press. The extrusion load was calculated to be 22.8 tons with an equivalent plastic strain of 0.81.The reduction in area was 55.55% and extrusion ratio was 2.25. The initial sintering temperature was set to 580˚C as adopted by George et al [12] in their Al-MWCNT composites fabrication by hot extrusion. At this temperature Al starts to react with the MWCNTs which leads to the formation of Al_4C_3 (Aluminum carbide) phase between the Al-MWCNT interface, which was verified in a differential scanning calorimeter (DSC) spectrum shown in figure 2a: there was an exothermic peak observed after aluminum melting point. The presence of interfacial compound aluminum carbide deteriorates composite properties. Hence, the sintering temperature was reduced to 520˚C and observed the absence of Al_4C_3 peak in the composites. The curves shown in Figure 2b, observations were made on the effect of MWCNTs over the transition temperature (T_{trans}) of AMCs compared to pristine Al which shows that the strength of the Al-MWCNT composite is retained for longer periods. The optimal sintering temperature needs to be further investigated. The X-ray diffraction (XRD) spectrum of Al and Al-MWCNT composites shown in figure 2c confirmed the absence of aluminum oxide as well as aluminum carbide as no reference aluminum oxide and aluminum carbide peaks were observed. Jiang et al. [20] has also highlighted the careful selection of sintering temperature in designing CNT reinforced alumina composites


Heat Flow, mW/mg
Temperature,°C
Al- MWCNTs
exothermic peak after
Al T_m
686
Melting point of aluminum
679
endo
70
60
50
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30
20
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500
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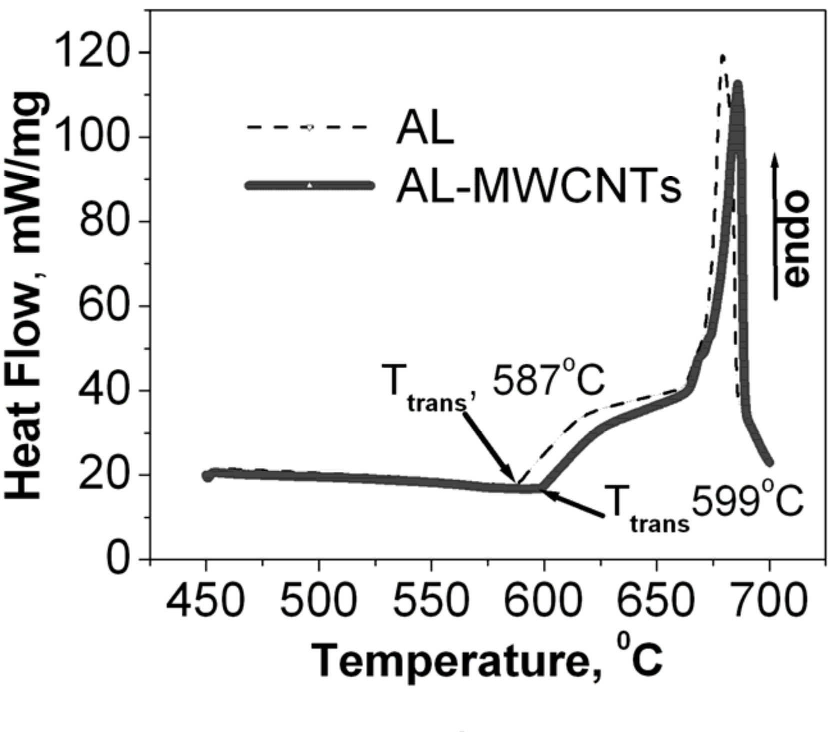
700

(a)


Heat Flow, mW/mg
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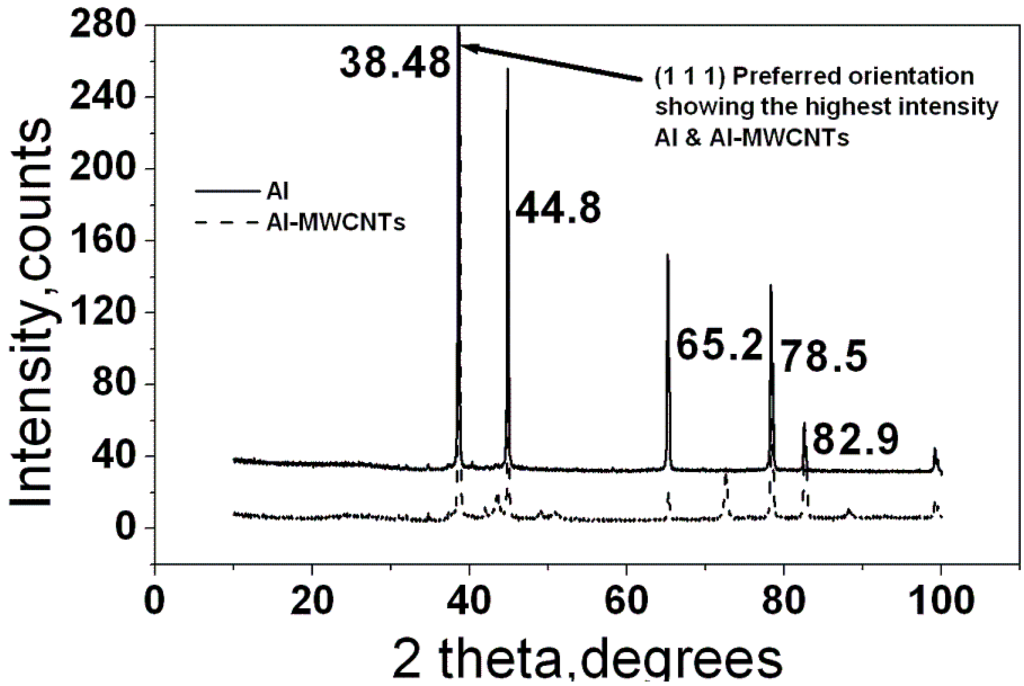
(b)



(c)

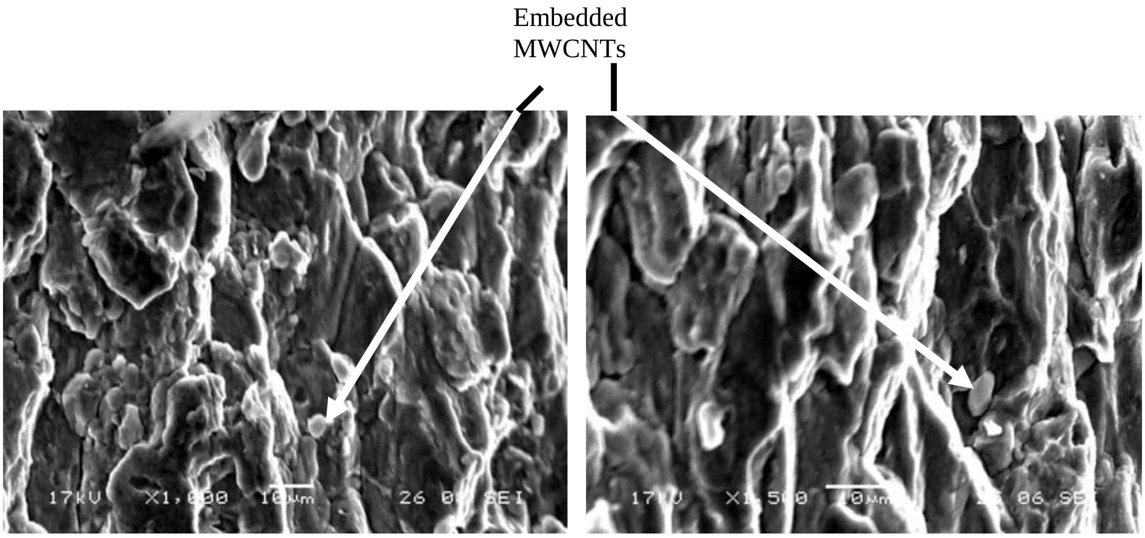
Figure 2. (a) Differential Scanning Calorimetric (DSC) spectrums for AL-MWCNTs sintered at 580˚C, (b) DSC Spectrum for Al and Al-MWCNT composite sintered at 520˚C and (c) X-ray diffraction (XRD) spectrum of Al and Al-2 wt% MWCNT composite.

3 Results

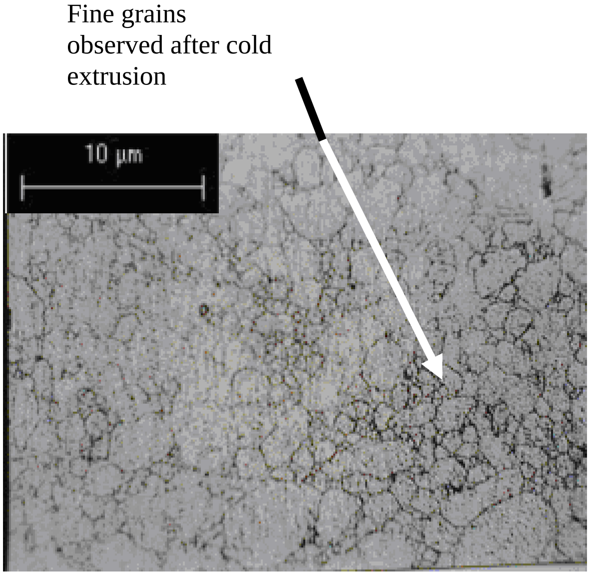
3.1 Density and Micro structural Analysis

The densities of the extruded Al and Al-MWCNT composites were measured by the Archimedes principle with deionised water as the immersion medium and were listed in Table 1. The extruded samples density was increasing with increasing MWCNTs weight percentage. This unexpected result is against the rule of mixtures given that the density of MWCNTs is less than that of Al. Similar trend is also reported in the literature [11-14] for CNT reinforced MMCs. The role of porous MWCNTs in controlling the densification is beyond the scope of the paper. The density gradient along the length of the specimen was less than 2%. The extruded Al-MWCNT composites have a smooth surface finish as shown in figure 3a. The microstructure of the specimen along the extruded direction showed that large percentage of grains are oriented along the extrusion direction as shown in figures 3b and 3c and a homogeneous bridging of MWCNTs in the matrix was evident. The microstructure indicated some preferential alignment of MWCNTs perpendicular to the extruded direction. Further, the grain structure has certain anisotropy as a result of the lateral deformation constraint provided by the extrusion die. The grain size (shown in figures 3d) after extrusion decreased due to high strain rate applied in the cold extrusion process.

(a)



(b) (c)



(d)

Figure 3. (a) A photograph of extruded cylindrical AMC specimen, (b, c) SEM micrographs of Al/MWCNT composites showing the grain orientations and presence of MWCNTs in the extruded direction, (d) Grain size reduction observed through optical micrographs of cross-sectioned extruded aluminum sample.

3.2 Mechanical characterization

The mechanical micro and macro properties of composites were obtained by micro hardness testing and uniaxial tensile tests. The micro hardness test was carried out in a CSM™ micro hardness tester using a Berkovich indenter under load control. The indentation load was set to 3N and the load-penetrations responses are recorded. The measured average micro Vickers hardness values in HV (taken from 4 different sampling points) for extruded Al and Al-MWCNT composites are listed in Table 1. The results show that the hardness values of Al-MWCNTs increases as MWCNTs weight percentage increases. Quantitatively, the increase in hardness is not so significant: about 8% increase in hardness was observed when MWCNTs wt% was 2.

Table 1 Properties of extruded aluminum and Al-MWCNT composites.

Description	Density, g/cc	Yield Stress @ 0.2% off-set strain, MPa	Ultimate Tensile Strength, MPa	Average Vickers micro hardness, (Hv)
Aluminum	2.468±0.01	90.98	98.32	68.70±0.64
Al + 0.5 wt% MWCNTs	2.512±0.02	114.11	121.62	70.23±0.33
Al + 1.0 wt% MWCNTs	2.584±0.02	138.69	151.29	71.37±0.45
Al + 2.0 wt% MWCNTs	2.649±0.015	176.37	184.37	74.16±0.91

Uniaxial tensile tests were conducted on cylindrical specimens of 7 mm diameter and gauge length of 10 mm using a Universal Testing Machine under displacement control at 0.2 mm/min. An extensometer is used to measure the strain accurately and Instron load cell reading provided the load values. The measured uniaxial stress and strain response of pristine aluminum and Al-MWCNT composites are shown in figure 4. The measured 0.2% off-set yield stress and ultimate tensile strength of the composites and pristine Al samples are listed in Table 1. With increasing MWCNT wt% in Al matrix the composite samples consistently showed increasing stiffness and strength, this indicates effective dispersion of CNTs and good interfacial bonding between the matrix and MWCNTs. The reason for the increase in strength of the composite was attributed to the severe deformation (including their distortion or breakage) of MWCNTs during the cold extrusion process. This is evident from the Raman spectra shown in Figures 5a and 5b for MWCNTs alone and the composite fabricated: the intensity of D-band peak becomes prominent for the composite. The deformation might break-up the MWCNTs. All this should lead to increased resistance to dislocation motion.

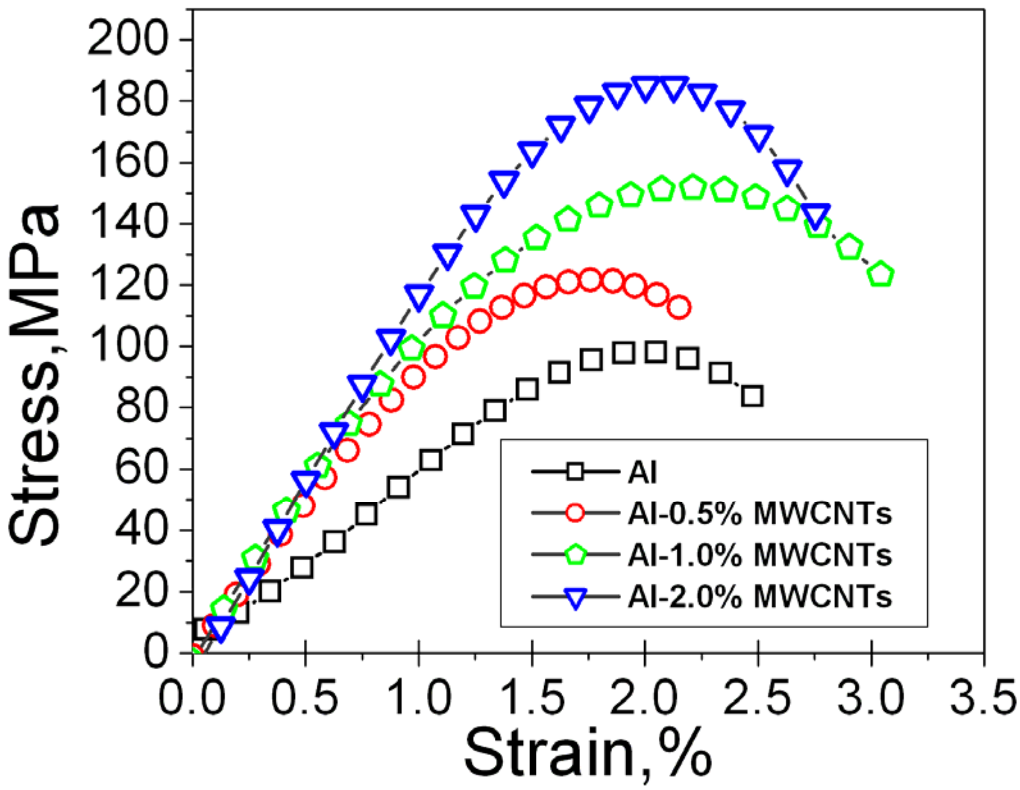


Figure 4. Uniaxial tensile stress – strain response of pristine Al and Al-MWCNT composites.

The yield strength and ultimate strength increased on an average approximately 90% with an addition of 2 wt% of MWCNTs. Within experimental scatter the tensile strain to fracture for the extruded samples is in between 8 to 12%. It is to be noted that there was no further heat-treatment carried on the extruded samples. The fractured surfaces of 1 wt% Al-MWCNT composite sample is shown in figure 6a and we notice that even after fracture the MWCNTs were holding on to the matrix. The matrix failure is also shown in figure 6b.

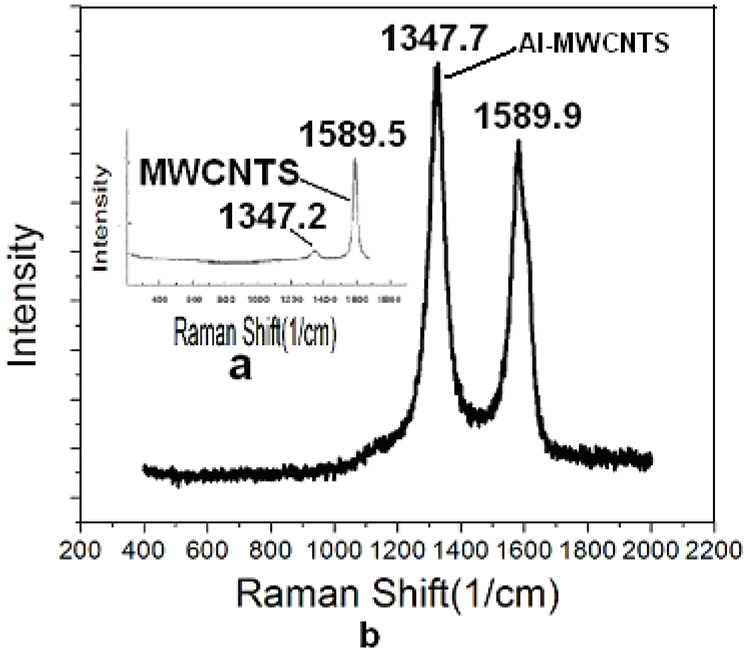
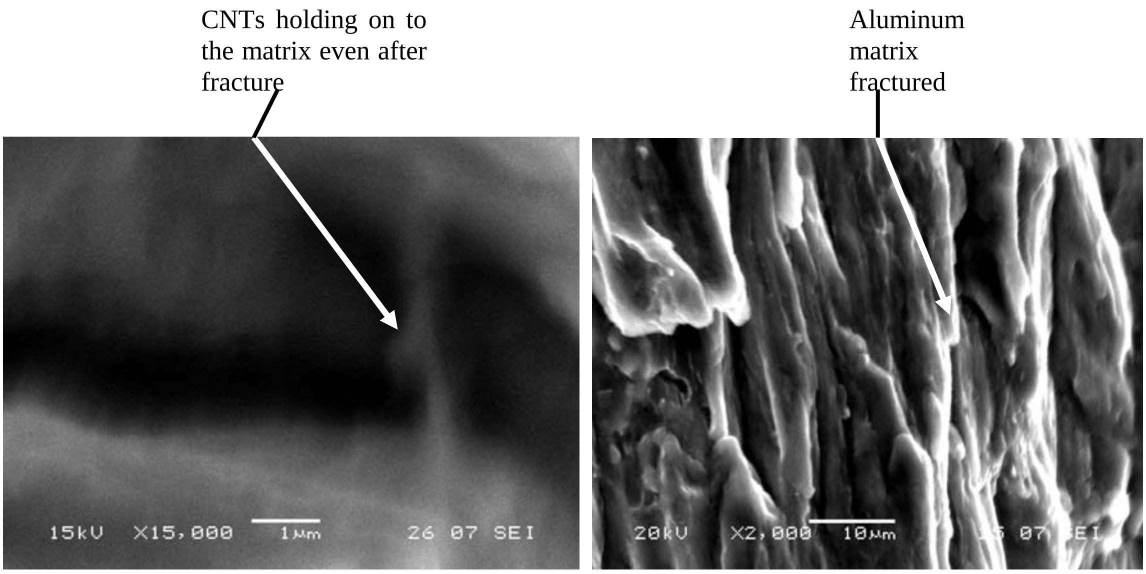


Figure 5. Raman spectra of (a) MWCNTs after surface treatment and (b) extruded Al-MWCNT composite.



(a) (b)

Figure 6. (a) Fractured surface of Al/1wt % MWCNT and (b) fracture surface fractograph.

3.3 Discussion

The mechanical characterizations of Al/MWCNT composites reveal that the adopted powder compaction route is a viable method for their manufacture. There is a consistent increase in the modulus and tensile strength of the fabricated composites with increasing wt% of MWCNTs. SDS seems to be an effective surfactant in dispersing the MWCNTs in Al matrix. In the following we briefly discuss various mechanisms that have contributed to the improved mechanical behavior of Al/MWCNT composites.

George et al. [12] have elucidated three different mechanisms for the strengthening of composite materials. They include thermal mismatch, Orowan looping and shear lag theory. Shear lag model [21] has been used to describe the stiffening effect of MWCNTs in Al/MWCNT composites. According to this theory, the Young's modulus (E_c) of the composite is given by

$$E_c = V_f E_f \left(1 - \tanh(ns)\right)/(ns) + (1 - V_f) E_m \quad -- \quad (1)$$

where $n = (2E_m / E_f (1 + \upsilon_m))\sqrt{\ln(1/V_f)}$, E_f =Young's modulus of MWCNTs, E_m = aluminum Young's modulus, s = aspect ratio of MWCNTs (~100), V_f = reinforcement volume fraction and υ_m = aluminum matrix Poisson's ratio. The modulus measured from the initial slope of the stress – strain curve is compared with the shear lag model of equation (1) in Table 2. Consistently the conservative upper-bound shear lag model over-estimates the Young's modulus value by about 12%.

Table 2 Young's modulus of the specimens

Description	Experimental Young’s Modulus (GPa)	Shear lag Young’s modulus, GPa
Al + 0.5 wt% MWCNTs	61.92	71.97
Al + 1.0 wt% MWCNTs	66.15	74.17
Al + 2.0 wt% MWCNTs	74.62	81.95

The possible reasons for the strengthening of Al-MWCNTs composites could be as follows:

1. As noted before, CNTs are nanometer dimensions: in metal matrix composites, the strengthening of metals by a given volume fraction of hard particles is greater for small particles than for large as it increases their rate of work-hardening.

2. During the sintering process, due to the large mismatch in the coefficient of thermal expansion between the aluminum matrix and MWCNTs results in prismatic punching of dislocations at their interface leading to the work-hardening of the aluminum matrix.

   When a stress is applied to a material the interplanar spacing (d) changes. Using Bragg’s law one can determine the interplanar spacing using x-ray diffraction technique. By measuring the interplanar spacing of pristine Al, Al-MWCNT composites for different incident angles of x-ray, the process induced residual stresses can be estimated [22]. In our current experimentation due to instrument limitations we could only measure the interplanar (d) for normal incidence. The measured interplanar spacing for pristine Al was 2.3393 ^{0}A and it was 2.3252, 2.3235 and 2.3194 ^{0}A for 0.5 wt%, 1.0 wt% and 2.0 wt% Al-MWCNTs composites respectively. The interplanar spacing gave a relative increase in residual stresses from the extruded aluminum sample to the 2 wt% Al-MWCNT sample and showed the prominent role of MWCNTs playing a major role in the strengthening of the composite by inducing lattice strains.

3. Orowan looping[23] is another strengthening mechanism in nanosized metal matrix composites. Here the motion of the dislocations is inhibited by nanometer sized carbon nanotubes, leading to their bending between the CNTs. This produces a back stress, which will prevent further dislocation movement leading to an increase in yield strength. The extrusion operation after the free sintering makes it difficult to make a direct comparison of composite strength with Orowan looping theory.

4. Conclusion

Aluminum matrix composites reinforced with 0.5, 1.0 and 2.0 wt% of multi-wall CNTs were successfully manufactured using cold compaction followed by sintering and cold extrusion techniques to near net shape. Careful controlling of sintering temperature has prevented the formation of intermetallic compounds such as aluminum carbide. The micro-hardness and uniaxial tensile tests have revealed enhanced mechanical properties of Al-MWCNT composites indicating that the proposed manufacturing route is a viable cost-effective one. There was no observed percolation of MWCNTs up to the 2 wt% volume fraction. It would be further interesting to study the wear and creep properties of these composites and also explore strengthening mechanisms.

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