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Induction Melting as a Fabrication Route for Aluminum-Carbon Nanotubes Nanocomposite

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***Abstract*—**Increasing demands of contemporary applications for high strength and lightweight materials prompted the development of metal-matrix composites (MMCs). After the discovery of carbon nanotubes (CNTs) in 1991 (revealing an excellent set of mechanical properties) became one of the most promising strengthening materials for MMC applications. Additionally, the relatively low density of the nanotubes imparted high specific strengths, making them perfect strengthening material to reinforce MMCs. In the present study, aluminum-multiwalled carbon nanotubes (Al-MWCNTs) composite was prepared in an air induction furnace. The dispersion of the nanotubes in molten aluminum was assisted by inherent string action of induction heating at 790°C. During the fabrication process, multifunctional fluxes were used to avoid oxidation of the nanotubes and molten aluminum. Subsequently, the melt was cast in to a copper mold and cold rolled to 0.5 mm thickness. During metallographic examination using a scanning electron microscope, it was observed that the nanotubes were effectively dispersed in the matrix. The mechanical properties of the composite were significantly increased as compared to pure aluminum specimen i.e. the yield strength from 65 to 115 MPa, the tensile strength from 82 to 125 MPa and hardness from 27 to 30 HV for pure aluminum and Al-CNTs composite, respectively. To recognize the associated strengthening mechanisms in the nanocomposites, three foremost strengthening models i.e. shear lag model, Orowan looping and Hall-Petch have been critically analyzed; experimental data were found to be closely satisfying the shear lag model.

***Keywords*—**Carbon nanotubes, induction melting, nanocomposite, strengthening mechanism.

I. Introduction

DUE to the depleting resources of fossil fuels, increasing fuel prices and environmental issues, the research focus has been increased on materials having high strength to mass ratios, particularly for automotive and aerospace applications. Previous work related to the incorporation of ceramic nanoparticles in MMCs [1], [2] strongly supported the beneficial effects of carbon nanotubes (CNTs), which have been known to have superior flexibility, higher aspect ratio, and enhanced mechanical properties [3]–[5]; in comparison, carbon fibers have considerably high tensile strength but display quite low fracture strains. Therefore, remarkable reduction in fracture strains of the MMC may occur due to the incorporation of larger quantities of carbon fibers in the matrix. In contrast, CNTs exhibit substantially higher flexibility besides outstanding stiffness and strength [6]. Hansang et al. [7] reported enhancement in tensile strengths of CNT reinforced MMC without compromising on ductility. Aluminum alloys have been attractive in the manufacturing industry owing to their low density, reasonably good strength and compatible processing conditions, making them materials of the choice for MM-CNTs nanocomposite fabrication.

George et al. [8] studied strengthening mechanisms in Al-CNTs composite using the shear lag, Orowan looping and thermal mismatch models. The composite was fabricated using powder metallurgy route. They observed that elastic modulus of the composite was in accordance with the shear lag model; however, all the three models were not in compliance with the experimental yield strengths data. A major factor of mismatch was clustering of CNTs in the matrix, reducing mechanical strengths of the composite significantly.

Lahiri et al. [9] reported a dual role of CNTs in strengthening of the composite fabricated by roll bonding method using nanotubes in varying contents from 2 to 10 percent. They concluded that both dispersed and clustered CNTs contributed to increase mechanical strengths by impeding dislocations movement. They proposed a model to predict strength of the composite based upon dislocation densities.

Liu et al. [10] analyzed strengthening mechanism in Al-CNTs composite fabricated by friction stirring process. The process provided better dispersion of the nanotubes within the matrix; however, the process featured severe size restriction. They correlated strengthening of the composite by a relation incorporating strengthening effects induced by load transfer and grain refinement, simultaneously. A similar type of findings was published by [11], where they studied strengthening mechanism in CNTs reinforced Al-Cu composites.

In the preceding discussion it can be inferred that dispersion of the nanotubes plays a vital role in strengthening of the Al-CNTs composite. The current paper discussed the fabrication of Al-CNTs composite using the induction melting technique, which rendered uniform dispersion of the nanotubes in the matrix, consequently augmenting the mechanical strengths. Further, the strengthening mechanisms were analyzed using the shear lag, Orowan looping and Hall-Petch models and the calculated values were compared with experimental results.

II. Experimental

The multiwalled carbon nanotubes (MWCNTs) used were synthesized using chemical vapor deposition. Detailed

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synthesis of MWCNTs has been discussed elsewhere [12]. The average diameter and length of the nanotubes were 10 nm and 1.5µm, respectively. Used electrical purity aluminum wire equivalent to grade-AA1199 (4mm diameter) was used for the matrix material. The aluminum wires were cut into 25 mm staples and treated with 10% solution of sodium carbonate to remove any kind of oil and excessive oxide layer on the surface. Subsequently, the treated aluminum was preheated for 30 minutes at 150 °C in a vacuum oven to eliminate any moisture entrapped on the surface. The flux used for the melting purpose consisted of (1) mixture of 'recycling flux', and 'remelting flux' and (2) 'cleaning flux', procured from FOSECO-UK under the trade names of COVERAL-912 and ALUFLUX-3, respectively. The purpose of using multi-flux was to reduce the melting temperature of aluminum and retention of impurities into the melt. A mixture of the flux and pre-weighed MWCNTs was prepared using mortar and pestle. For each batch of 20 g aluminum, 2 g of flux (50 wt. % COVERAL + 50 wt. %ALUFLUX) and CNTs (0, 0.1 and 0.2 vol. %) were used.

To process the Al-CNTs composite in an air induction furnace, a specific induction coil was designed to achieve appreciable thermal efficiency and stirring force during melting; the details of the coil designing are discussed elsewhere [13]. An alumina crucible (30mm diameter) was placed in the induction coil and aluminum staples were positioned vertically in it. The mixture of the flux and the nanotubes was poured in the crucible when the aluminum became semi-molten. Addition of the flux caused removal of the surface oxide and rapid melting, while the nanotubes entered into the melt as melting proceeded. The heating (at 760°C) of the molten composite continued for 10 minutes after complete melting. No manual or mechanical stirring was carried out. After the hold time the melt was poured into a rectangular copper mold (65 mm x 20 mm x 10 mm), which was preheated to 150°C. After solidification the ingots were homogenized at 540°C for one hour in argon atmosphere. Subsequently the ingots were cold rolled to attain a final thickness of 0.5 mm using a two-high roll mill. Detailed fabrication process has been discussed elsewhere [14].

To evaluate the dispersion of the nanotubes in the composite, specimens were ground and polished. Further, a deep etching was carried out in 10% sodium hydroxide solution and studied using scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). To find the crystallite size of the composite samples a Siemens D-500 X-ray diffractometer (XRD) was employed using a cobalt X-ray source. The diffractometer was operated at 40 kV and 40 mA tube potential and current, respectively, with a scan rate of 0.1° per minute and a step size of 0.02° 2θ. To calculate crystallite size, it was needed to eliminate instrumental broadening from the full width half maximum (FWHM) of the specimens under investigation. Therefore, a full annealed aluminum specimen was used to find instrumental broadening. In the present study, the first three peaks of the aluminum spectrum (i.e. 111, 200 and 220) were used for profile analyses; higher order peaks were not used due to the appearance of alpha 1 and 2 doublets. These alpha doublet peaks could cause confusions in finding respective FWHM values. The crystallite size was calculated using slope-intercept method [15]. Mechanical properties of the composites were determined using INSTRON universal testing machine and Vicker's hardness testing machine in accordance with ASTM-E8 and ASTM-E384 standards, respectively.

III. Results and Discussion

A. Optical Microscopy

Etched cross sections of rolled pure aluminum and composite are shown in Fig. 1. In the pure aluminum specimen, elongated grains with large aspect ratio were seen. The general grain structure was etched in a certain crystallographic orientation, while grain boundaries were easily distinguishable due to the mismatch of the crystalline planes of adjacent grains (Fig. 1 (a)). At higher magnification the structure appeared to be pitting or etching of numerous crystallites within a grain (Fig. 1 (b)).

In the composite specimens (Al-0.2 vol. % MWCNTs), no grain boundaries could be seen. However, at higher magnification isolated CNTs were seen in and around the etched pits (Figs. 1 (c) and (d)). Presence of CNTs in those regions was confirmed by EDS analyses (Fig. 1 (e)). These nanotubes were singly dispersed and aligned in the direction of rolling. No evidence of clustering or aggregation of the nanotubes was found.

B. XRD

Fig. 2 represents XRD scans of aluminum specimens with various concentrations of MWCNTs. The diffraction angles of the peaks were used to identify the structure and the Miller indices, which were found in accordance with PCPDF No. 851327 for pure aluminum. The XRD scans showed no evidence of significant amount of impurities, like potassium, sodium, calcium, etc., which had a chance for retention using the processing conditions having large amounts of flux. Although, on the basis of the XRD scan, it was difficult to state about non-availability of the impurities in the melt, or their quantities were below the detection limit of XRD (i.e. <2%) [16]. However, under similar conditions, the specimens having CNTs showed substantial refinement in their crystallite size. Typically, 360 nm and 320 nm crystallite sizes were observed in 0.1% and 0.2% MWCNTS-Al specimens, respectively. This systematic decrease in crystallite size could be attributed to the addition of CNTs.

C. Mechanical Testing

Stress-strain curves of the tested specimens are shown in Fig. 3. Mechanical properties for the pure aluminum used were relatively lower than from standard pure aluminum AA1199-H18, which could be attributed to the processing conditions (e.g. usage of excessive flux etc.), which resulted in entrapment of tiny flux particles and/or impurities. However, same processing conditions were used for the preparation of Al-CNT composites. Therefore, a justified comparison could be possible for the strengthening effect of the nanotubes in the aluminum matrix. A net increase in yield strength, tensile strength and hardness, for the composites having various concentrations of CNTs, was ~77%, ~52% and ~45%, respectively. The results of mechanical testing are shown in Table I.

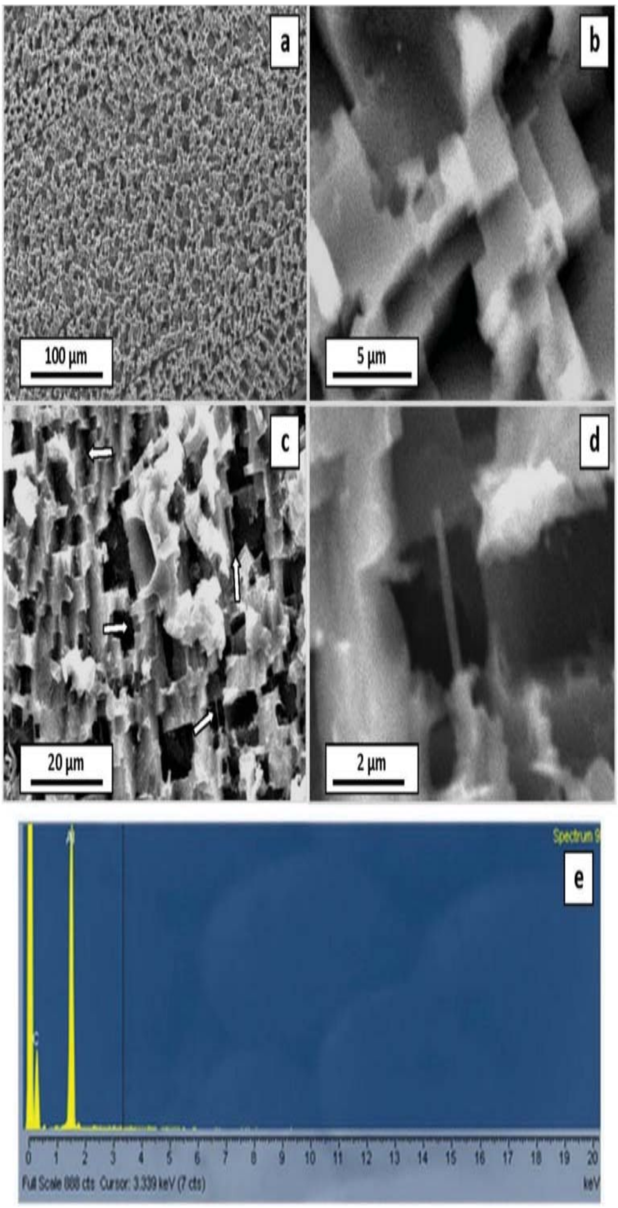

Fig. 1 SEM micrographs of various specimens in etched condition: (a) pure aluminum; (b) same as (a) but at higher magnification; (c) Al-0.2 vol. % MWCNTs composite showing dispersed nanotubes in the matrix; (d) higher magnification of (c) showing an isolated nanotube; (e) EDS spectrum of the nanotubes confirming the presence of CNTs in the matrix

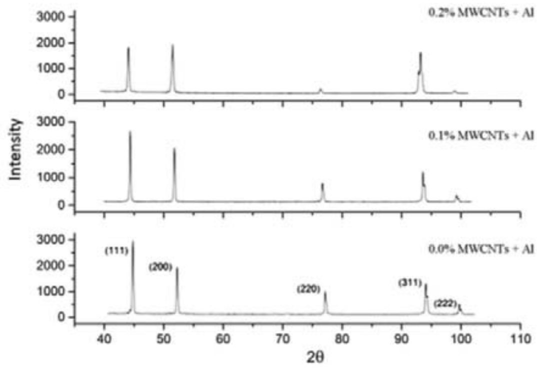

Fig. 2 XRD scans of aluminum specimens with various concentrations of MWCNTs

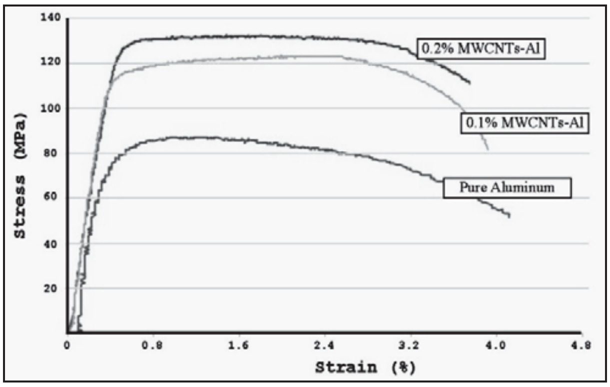

Fig. 3 Engineering tensile curves of the tested materials

D. Strengthening Mechanisms

The major aim of the CNTs' addition in aluminum matrix was to increase strength of the composite, which could be a prerequisite for any pragmatic application. During mechanical testing of the composite, it was established that an appreciable increase in mechanical strength was achievable, which was realized, in another way by the combined action of CNTs' dispersion and the wetting in/with aluminum matrix. However, the strengthening mechanisms working within the composite during loading would not be straight forward or hackneyed. Therefore, on the basis of mechanical properties, physical properties and geometry of the CNTs, three primary mechanisms associated with the composite strengthening were considered in the current study: (1) shear lag; (2) Orowan looping; and (3) Hall-Petch. The yield strengths were calculated using these models for the composites having different volume fractions (0, 0.1 and 0.2 %) of MWCNTs and compared with the experimental results to find the best fitting model for Al-CNTs composites. A superimposed plot of the various curves representing the experimental and calculated yield strengths of the composites is shown in Fig. 4.

1. Shear Lag Model [17]

In the shear lag model, the interfacial shear stress plays a vital role by transferring the load from matrix to strengthening material within the composite i.e. utilizing the stiffness of CNTs directly for the composite strengthening. A gradient of tensile strength exists over the length of strengthening fibers; maximum at the center and minimum at the ends. Therefore, longer fibers will produce more strengthening than the shorter; however, there exists a critical length which can produce maximum strengthening. It is generally quoted that high aspect ratios of the fibers are more favorable with this model, albeit the aspect ratios beyond 100 are less beneficent. Besides the critical length of the reinforcing fibers, another important factor contributing towards strengthening of the composite is presence of an interface between matrix and the reinforcements to provide a medium for transfer of load. In the absence of the interface, material will experience severe strength loss and shear lag model will not remain valid to calculate strengths.

Choi et al. [18] used the following model to calculate the yield strength (σc) of Al-CNTs composites, which was proposed by Kelly-Tyson [19] for the composites having short fiber reinforcements:

$$\sigma_c = \sigma^2 . V_2 \left(\frac{l}{lc}\right) + \sigma_1 (1 - V_2) \tag{1}$$

where, V_2 is the CNTs volume fraction, l is the average CNTs length, σ_1 is strength of the matrix, lc is the critical length of the nanotubes and could be calculated using (2):

$$lc = \frac{\sigma_2 d}{2\tau_1} \tag{2}$$

where, σ_2 the strength of the CNTs, d is the diameter and τ_1 is the shear strength of the matrix material.

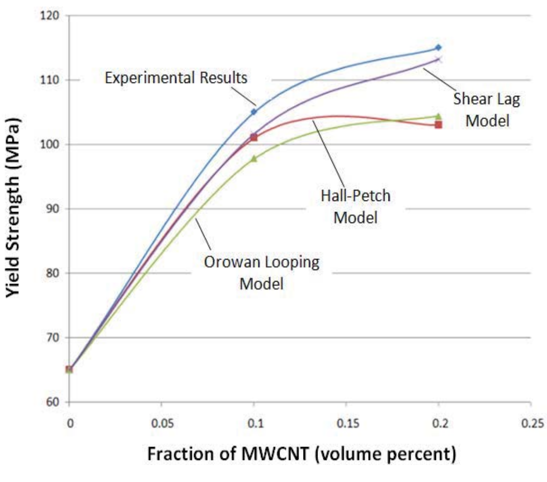

Fig. 4 Superimposed experimental and calculated yield strengths curves of the composites with various the nanotubes fractions

2. Orowan Looping Model [20]

This model entails inhibition of the dislocation movements by the pinning action of hard but fine (nanometric) particles, which leads to the bending/bowing of the dislocations between the particles (i.e. CNTs for the present case). In the presence of nanometric hard reinforcements, the dislocations are forced to bypass the obstacles instead of shearing them, which increases the capability of the material to resist deformation. It is established, however, that the micro-sized reinforcements in metal matrix composites have negligible significance for Orowan looping due to their coarse size and larger inter-particle spacing. Additionally, micro-sized reinforcements usually stay along the grain boundaries within the matrix, making the Orowan mechanism uncertain in such conditions.

The mechanism of strengthening established by Orowan looping is important for aluminum based alloys and composites. However, its significance is restricted to the size and strength of the reinforcement. CNTs proficiently representing fine nanoscale particles and possessing very high strength values, can strengthen the aluminum matrix following the Orowan looping mechanism.

Equation (3) represents the Orowan looping model for strength calculation:

$$\Delta\sigma_{or} = \frac{0.13bG}{dp\left(\sqrt[3]{0.5V_2} - 1\right)} ln\left(\frac{dp}{2b}\right) \tag{3}$$

where, b is Burger's vector; for aluminum it is 0.286 nm [20], G is matrix shear modulus; for aluminum in H18 condition it is 25 GPa [21], dp is the diameter of the nanotubes (10 nm) and V_2 is the volume fraction of CNTs in the composite.

3. Hall-Petch Effect [3], [22]

Another mechanism, which can induce strengthening into the matrix, is reduction or refinement of the grain size. The mechanism is defined by Hall-Petch relation, where reduction in grain size directly influences the strength of the material (σ^{HP});

$$\sigma^{HP} = \sigma_o + \frac{k}{\sqrt{d}} \tag{4}$$

where, σ_o is the yield strength of the matrix having infinite grain size, d is the grain size and k is Hall-Petch coefficient. Refined grain size not only induces strength but also increases ductility and fracture toughness of the matrix since the cracks produced during the deformation has size limitation owing to the smaller size of the grains. Conceptually, small grains limit the extent of strain to be developed within the grains, where stress concentration occurs by the dislocation pile-up, which subsequently produces slip in the neighboring grain. The smaller grain size causes a proportionally smaller pile-up, therefore generating smaller stress concentration to instigate the new dislocation source, hence strengthening occurs.

In Al-CNTs composites, the nanotubes can induce grain refinement in many ways:

- Presence of CNTs in the aluminum matrix increases thermal conductivity of the composite
- The nanotubes increase the work hardening rate of the composite
- The nanotubes being immiscible in aluminum behave as second phase in the composite

During re-crystallization processes, all the above mentioned features increase the nucleation rate, hence producing finer grained structures.

In the present study, the yield strengths of the composite were calculated using above models (1), (3) and (4), and plotted with experimental results (Table I and Fig. 3). It could be seen that all the studied models for theoretical yield strength were significantly closed to the experimental results. However, all the predicted yield strengths had certain deviation to the experimental results, becoming more prominent in the composites having higher CNTs contents.

TABLE I
EXPERIMENTAL AND CALCULATED MECHANICAL PROPERTIES OF VARIOUS MATERIALS

Specimens		Pure Al	Al-0.1%CNTs	Al-0.2%CNTs
Experimental Results	Hardness (Hv)	27±3	34±5	39±4
	Elongation (%)	4.14 ± 0.41	3.85 ± 0.24	3.56 ± 0.56
	UTS (MPa)	82 ± 3	112 ± 4	125 ± 4
	Yield St. (MPa)	65 ± 5	105 ± 4	115 ± 5
Predicted Yield Strengths (MPa)	Shear Lag	-	101.6	113.2
	Orowan Looping	-	97.8	104.4
	Hall - Petch	-	101.2	103.1

It is worth mentioning that the predicted strengths were lower than the experimental values in each case. The percentage digressive variation of the predicted strengths from experimental results is graphically presented in Fig. 5, where it is obvious that the shear lag model predicted more precise results than the rest of the evaluated models, which depicted the fact that it was the dominating strengthening mechanism in the composites studied in the present work. The finding also indirectly indicated good dispersion of the nanotubes in the matrix because if the CNTs remained un-dispersed or coalesced during fabrication process, the resultant experimental yield strengths should be lower than the predicted strengths [17]. The fact was also supported by the Orowan looping model, where experimental strengths were higher than the predicted ones, because the model is based upon uniformly distributed second phase particles [20]. The lower precision of Hall-Petch model for the prediction of yield strengths could be justified by the fact that the grain sizes were measured using XRD technique, which is itself not a precise method for grain size determination. Hence, experimental strengths were more deviating from predicted Hall-Petch strengths. Nevertheless, each predicted strength value remained in closed tolerance (i.e. <10 %) to the experimental results, which prompted that the strengthening of Al-CNTs composites fabricated by the induction melting technique may hold synergistic effect of various strengthening mechanisms i.e. shear lag, Orowan looping and Hall-Petch, from higher to lower order.

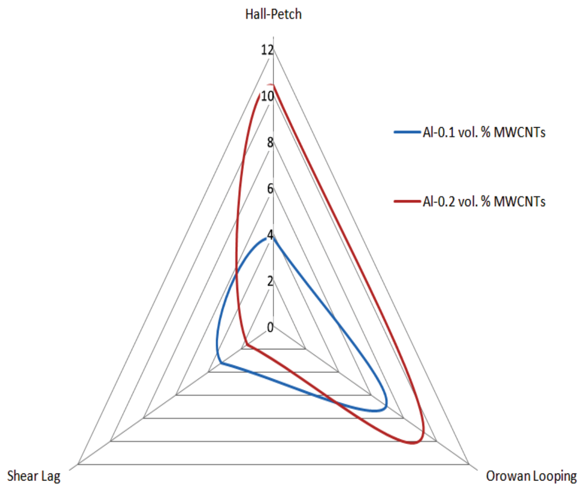

Fig. 5 The percentage variation of the predicted strengths from experimental results

IV. CONCLUSIONS

From the above results and discussion, the following conclusions were drawn:

- Al-CNTs composite was successfully fabricated using the induction melting technique.
- Microscopic studies showed dispersion of the nanotubes in the matrix, aligned in the rolling direction. The grain size of the etched composite was too small to be resolved by SEM. No evidence of CNTs clustering was found.
- Mechanical properties of the composite increased appreciably at the expense of ductility; however, the loss in ductility was not more than 15%.
- Although, it was found that out of analyzed models, shear lag was the best fitting model with experimental yield strengths, depicting the fact of appreciable dispersion of the nanotubes in the matrix. However, the experimental yield strengths of the composite remained higher than the calculated results. Therefore, the strengthening mechanism in the composite could be a synergistic effect of bypass movement of the dislocations and grain refinement, besides shear lag phenomenon.

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