Investigation of New Method to Achieve Well Dispersed Multiwall Carbon Nanotubes Reinforced Al Matrix Composites

A.H.Javadi , Sh.Mirdamadi , M.A.Faghisani , S.Shakhesi

Abstract—Nanostructured materials have attracted many researchers due to their outstanding mechanical and physical properties. For example, carbon nanotubes (CNTs) or carbon nanofibres (CNFs) are considered to be attractive reinforcement materials for light weight and high strength metal matrix composites. These composites are being projected for use in structural applications for their high specific strength as well as functional materials for their exciting thermal and electrical characteristics. The critical issues of CNT-reinforced MMCs include processing techniques, nanotube dispersion, interface, strengthening mechanisms and mechanical properties. One of the major obstacles to the effective use of carbon nanotubes as reinforcements in metal matrix composites is their agglomeration and poor distribution/dispersion within the metallic matrix. In order to tap into the advantages of the properties of CNTs (or CNFs) in composites, the high dispersion of CNTs (or CNFs) and strong interfacial bonding are the key issues which are still challenging. Processing techniques used for synthesis of the composites have been studied with an objective to achieve homogeneous distribution of carbon nanotubes in the matrix. Modified mechanical alloying (ball milling) techniques have emerged as promising routes for the fabrication of carbon nanotube (CNT) reinforced metal matrix composites. In order to obtain a homogeneous product, good control of the milling process, in particular control of the ball movement, is essential. The control of the ball motion during the milling leads to a reduction in grinding energy and a more homogeneous product. Also, the critical inner diameter of the milling container at a particular rotational speed can be calculated. In the present work, we use conventional and modified mechanical alloying to generate a homogenous distribution of 2 wt. % CNT within Al powders. 99% purity Aluminium powder (Acros, 200mesh) was used along with two different types of multiwall carbon nanotube (MWCNTs) having different aspect ratios to produce Al-CNT composites. The composite powders were processed into bulk material by compaction, and sintering using a cylindrical compaction and tube furnace. Field Emission Scanning electron microscopy (FESEM), X-Ray diffraction (XRD), Raman spectroscopy and Vickers macro hardness tester were used to evaluate CNT dispersion, powder morphology, CNT damage, phase analysis, mechanical properties and crystal size determination. Despite the success of ball milling in dispersing CNTs in Al powder, it is often accompanied with considerable strain hardening of the Al powder, which may have implications on the final properties of the composite. The results show that particle size and morphology vary with milling time. Also, by using the mixing process and sonication before mechanical alloying and modified ball mill, dispersion of the CNTs in Al matrix improves.

Keywords—multiwall carbon nanotube, Aluminum matrix composite, dispersion, mechanical alloying, sintering

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I. INTRODUCTION

IN recent years, there has been a steadily increasing interest in the development of composites. The motive is to transfer mechanical and physical properties of reinforcement to bulk engineering materials. [1,2]. Metal Matrix composites (MMCs) have proven to be important advanced materials that may serve as alternatives to many conventional materials, particularly when lightweight materials with high specific strength and stiffness, desirable coefficient of thermal expansion and good damping properties are needed [3, 4].

Rod shaped reinforcements such as CNTs are considered to strengthen the matrix more effectively than spherical reinforcements due to the resultant shorter inter-reinforcement spacing [1]. Besides, CNTs exhibit extraordinary mechanical properties [1, 5]. Not surprisingly, CNTs have emerged as new reinforcements for a number of material systems including polymeric, metallic and ceramic matrices [6]. In general, powder metallurgy and casting techniques are utilized for the fabrication of these composites [7]. Several fabrication routes namely ball milling, extrusion, hot pressing, equal channel angular pressing, spark plasma sintering, electro-deposition, electro-less deposition and thermal spraying have been used to synthesize metal matrix composites with CNTs [4].

It has been confirmed that the mechanical properties of metal matrix composites were improved, when an appropriate amount of nanotubes were added [2]. However, CNT–metal matrix composites are currently falling behind in bulk fabrication due to the difficulty of dispersing the CNTs, as compared to polymer and ceramic-CNT composites [7]. Due to the small size of the CNTs as compared to the matrix powders, agglomeration of the CNTs has been reported as a common problem which hinders the attainment of the desired properties. The presence of clusters in the processed composites, especially when CNT contents larger than about 1 wt. % are used, has often led to reduction in the strength and stiffness in addition to the reduced ductility [7]. The high dispersion of CNTs and strong interfacial bonding are the key issues which are still challenging. Lin Wang and et.al [8] reported that by employing smaller diameter MWCNTs and Al powders, it was possible to prevent agglomeration of mixture powders during the MA. Esawi and et.al [9] explained planetary ball milling has been proven to be a promising technique for dispersing CNTs in the aluminum matrix. Despite the success of ball milling in dispersing CNTs in Al powder, it is often accompanied with considerable strain hardening of the Al powder, which may have implications on the final properties of the composite. In another work, Esawi and et.al [6] use mechanical alloying (MA) up to 48 h to generate a homogenous distribution of 2 wt% CNT within Al

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powders. The result showed that individual CNTs were embedded in the aluminum matrix after 48 h of milling [6]. The main problem of this process is time prolongation. Also, Plasma spray drying is an effective way of dispersing CNTs in Al matrix to obtain thick coating [10].

Efforts have thus focused on finding effective dispersion techniques that can disperse the CNTs homogeneously within the matrix powders. The two techniques that have been investigated are sonication, in which the CNTs are dispersed with the matrix powders in ethanol, before being compacted and sintered, and high energy ball milling in which the matrix powders and the CNTs are subjected together to the impact and friction effects of the milling media. Combining sonication and ball milling has also been investigated [11].

It is clear that successful dispersion of CNTs in metallic matrices is needed before we can realize any sort of significant benefits in terms of property gains in the composite. This paper investigates mechanical alloying (MA) as a means for dispersing CNTs in Al. MA (through the energetic ball milling of powders), involves continuous impact, welding, fracturing and re-welding of powders such that dispersions would be effectively and homogeneously distributed within the ductile particle matrix. It has previously been successfully used to produce homogeneous and well dispersed distribution of reinforcements in a powder matrix [12,13].

II. EXPERIMENTAL PROCEDURE

Materials

The starting materials in this study consisted of Al powder and multiwall carbon nanotube with specification as follow:

Al powder (Acros, purity 99%, 200 mesh, Code: 200935000), multi-wall carbon nanotubes fabricated by CVD method from Neutrino company with purity >95% (1- OD diameter 60-80 nm, ID diameter 10-20nm, length 1–2 μm, special surface area 40-300m²/g) and (2- OD diameter 20-30 nm, ID diameter ~5nm, length 10- 30 μm, special surface area >200m²/g).

Mixing And Mechanical Alloying

Carbon nanotube–aluminium powder mixtures were prepared by a mechanical mixing process. The MWCNTs were dispersed in 150 ml ethanol by an intensive sonication for 5 min at 140 W using Labsonic ultrasonic homogenizer. In the next step, Al powder was added to the solution and mixed with nanotubes suspended in ethanol by the same time ultrasonicating. The solution was heated to a temperature of 50 ∘C and ultrasonicated until most of the ethanol was evaporated. The mechanical mixing process produced relatively homogeneous mixtures of MWCNT and Al powder.

After the mixing process, the mixture of 2 wt% MWCNT and 98 wt% Al powder were placed in 300 ml mixing jar containing 25 stainless steel milling balls of 10 mm diameter (giving an initial ball-to-powder weight ratio (BPR) = 10:1). The jar was filled with argon and was then agitated using conventional and modified horizontal ball mill at 250 rpm for varying milling times up to 24 h. Samples were extracted from the batch after various times and used for field emission

scanning electron microscopy (FESEM) analysis. Methanol was added as a process control agent (PCA) in order to minimize cold welding of the Al particles.

Consider a MA process using a conventional horizontal ball mill, illustrated in Fig. 1. In this system, the balls or rods and powders are placed in a container which rotates about its horizontal axis at a speed of co. The balls and powders will move along the inner surface of the container if the container rotates sufficiently quickly. If it is assumed that the balls and powders have the same speed as that of the container, the normal accelerate of the ball, as shown in Fig.1 can be written as Eq.(1). This equation use to design the dimension of container [14]:

$$a_i = \frac{D-d}{2}\omega^2 \qquad (1)$$

Where D is the inner diameter of the container and d is the diameter of the ball. According to Newton's law, the ball should satisfy the Eq. (2) during movement [13]:

$$\sum_{j=1}^{N} f_{ij} = m_i\, a_i \qquad (2)$$

Where f_{ij} is the force acting on the ith ball, m_i is the mass of the ith ball and a_i is the acceleration in the normal direction of the ith ball. Three forces, namely gravity P, friction force F between the inner wall and the ball, and normal force N are exerted on a ball during milling as shown in Fig.1 [14].
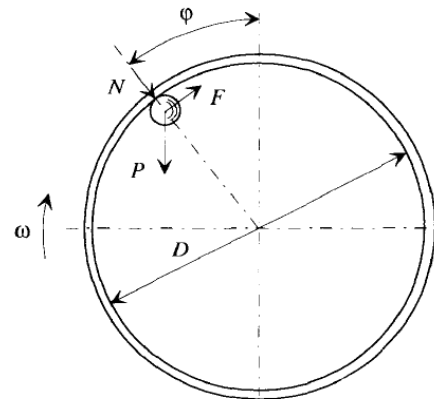

Fig. 1 Force balance of a ball during rotation in a horizontal ball mill [14]

In modified milling, the ball movements during the milling process are confined to the vertical plane by the mill chamber walls and by the applied external magnetic field. The strength and direction of the magnetic field are adjusted externally by repositioning the magnets. The trajectories of the balls are controllable and reproducible for each mode of operation in this design. The general patterns of the ball movement are a function of the magnet positions and the rotational speed of the mill (Fig.2). Introducing a magnetic field into the conventional ball mill reduces the grinding time and saves energy (Fig. 3). Also, Figure 4 shows the effect of mill rotation speed on the size reduction in conventional and modified milling [15].
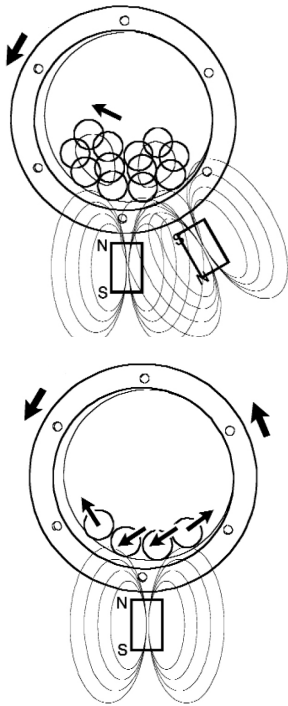
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Finally, the ball-milled powder mixtures were compacted in a 13 mm diameter compaction die at 475 MPa (Fig.5) and then were sintered at 600°C in quartz tube furnace as setup illustrated in Fig. 6.

Fig. 2 modified milling design by applying a magnet [15]
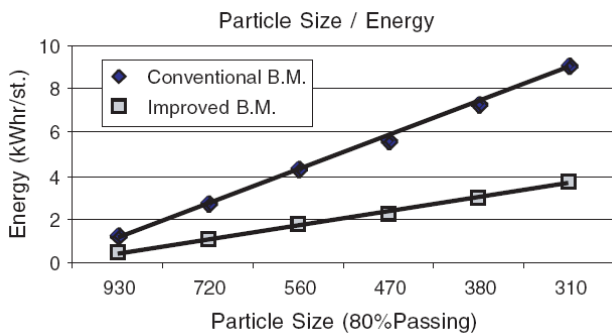
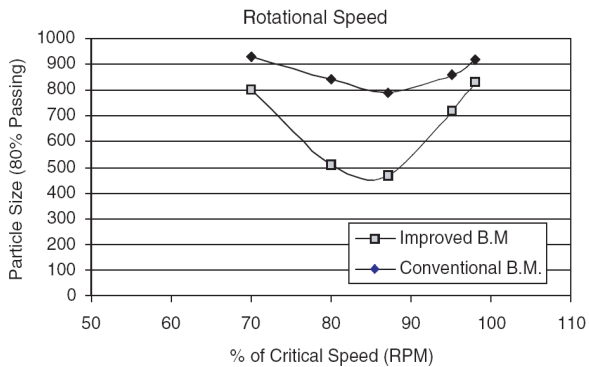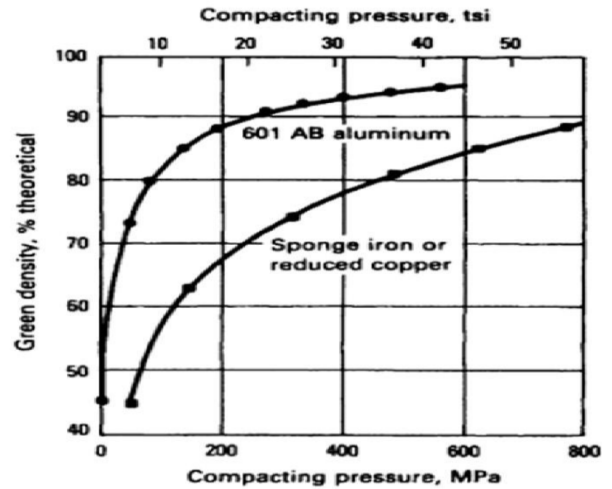Fig. 3 Energy consumed in the particle size reduction in conventional and modified ball milling[15]

Fig. 4 Effect of the rotational speed on the grinding ability of the modified and conventional ball milling [15]

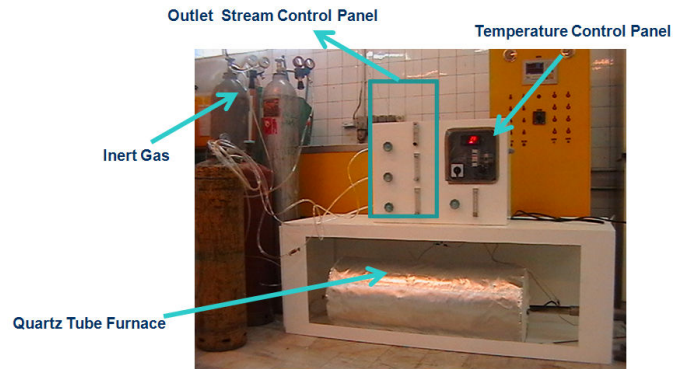Fig. 5 Relationship between green density and compaction pressure of Al alloy [16]

Fig. 6 Experimental setup for sintering process

Analysis Instruments

The starting materials were characterized by field emission scanning electron microscopy (FE-SEM) (using a Hitachi model SE 4160) to examine the dispersion of the CNTs within the Al matrix and to characterize the composite and raw materials morphology and size.

The microstructures of the samples after every step were observed with an optical microscope (leica Co. DM 4000 M), scanning electron microscope (Camscan model MV2300), using energy-dispersive spectrometry (EDS model Oxford). Raman spectroscopy (Almega Thermo Nicolet Dispersive Raman Spectrometer with the spectral range 100-4200 cm^{-1}) was used to evaluate the disorder of the CNTs. The macro-hardness of Al powders and sintered compact were measured by a Vickers hardness tester (Wolpert, 1kg -30kg)

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III. RESULT AND DISCUSSION

Figures 7 to 9 show the FE-SEM and TEM images of Al powder morphology and the size of MWCNTs employed in this study.
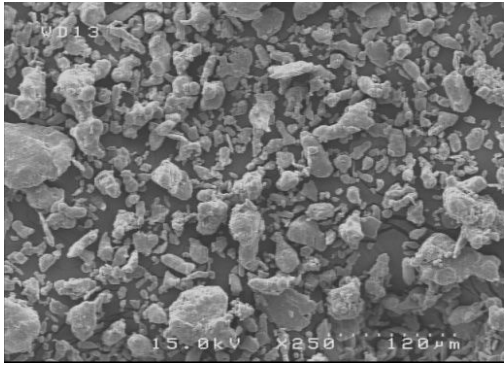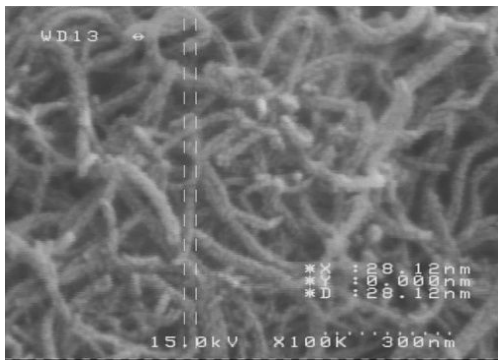

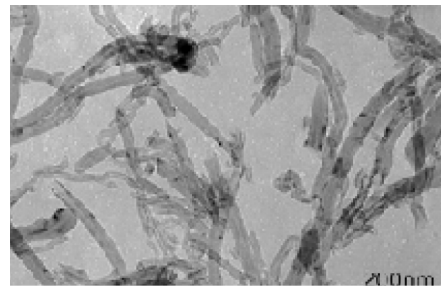Fig.7 the FESEM image of Al powder morphology

(a)

(b)

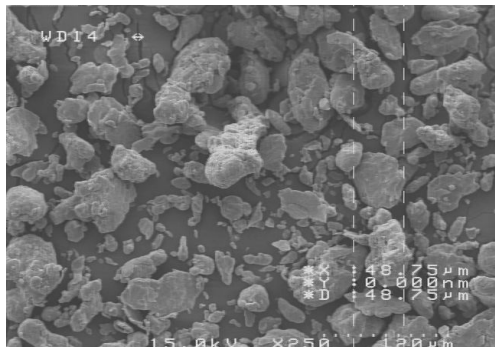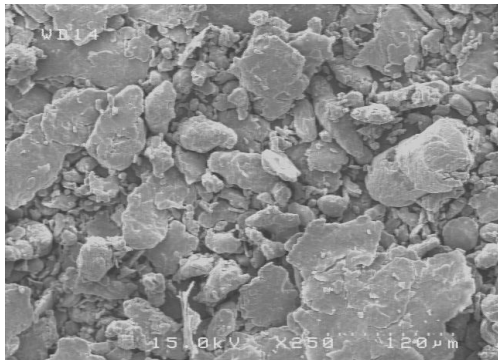Fig.8 the FE-SEM image of MWCNT a) OD diameter 60-80 nm b) OD diameter 20-30 nm

(a)

(b)

Fig.9 the TEM image of MWCNT a) mean OD diameter 60-80 nm b) mean OD diameter 20-30 nm

Two competing processes are involved in a typical MA: one is cold working of the powders that would lead to a decrease in ductility and eventual fracturing of the particles; and the other is cold-welding of particles that tends to increase the particle size [17]. In general, once powders are ball milled, cold welding becomes the predominant process resulting in the agglomeration of the particles with increasing ball-milling time (Fig.10). It is seen that the particles were initially flattened to flake-like ones at the early stage of the MA while their size increased slightly (12 h) like the case of the pure Al powders. However, such flake-like and cold welded shapes were maintained with further ball milling up to 24 h.

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(a)

(b)

Fig. 10 The morphology of Al particles after a) 1h conventional ball mill b) 24h conventional ball mill

The fraction of the CNTs in the CNT–Al mixture in this study is the same 2 wt.% as in the previous work by Esawi, Morsi and Lin Wang [6,8,12].   observations on the ball-milling behaviour of the pure Al powders and the CNT–Al mixture powders by Lin Wang & et.al [8] indicate that the size of MWCNTs played a certain role of the grinding aids, which prevented agglomeration of particles. Smaller diameter means increased total number of CNTs in the CNT–Al mixture powders used in the current study. If it is assumed that smaller-diameter CNTs have smaller number of carbon walls, it is also possible that the would have substantially larger total surface area. Larger number of CNTs and their larger total surface area imply the reduced contact area between the Al particles during the ball milling, which would then prohibit the agglomeration of the Al particles due to cold-welding [8].

Now, in this study, using the modified ball milling and sonication before mechanical alloying show the acceptable result in well dispersion of CNT in Al matrix.

Initial experiments using conventional mechanical alloying of the CNT and Al powders without mixing process resulted in CNT clustering/ agglomeration due to the large difference between the aluminum particles and the nanotubes. By using the mixing process before mechanical alloying and modified ball mill, dispersion of the CNTs in Al matrix improves. Figure 10 shows the agglomeration of MWCNTs in composite fabricated by conventional horizontal ball mill. It can be seen from Fig. 11 that 1- The dispersion of long CNTs in matrix is better than short CNTs as explained above. 2- The aluminum particles were flattened and long CNTs were grinded under the impact of the balls after 24h milling.
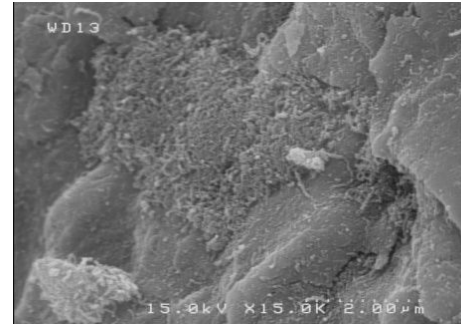
(a)
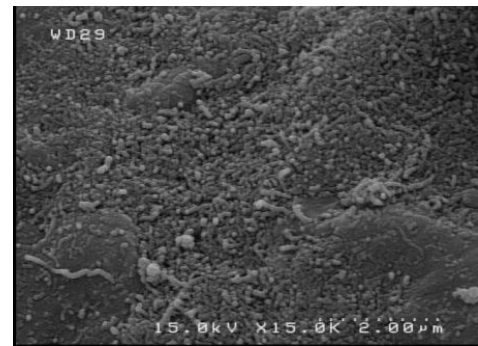
(b)

Fig. 11 Clustering of MWCNT after 24h milling in conventional milling process a) long MWCNT b) short MWCNT

The FE-SEM images of Al particle in Fig. 12 shows nanotubes attached to the surface of a Al particle after the mixing process.

Fig. 12 The FE-SEM image of Al-MWCNT after the mixing process

Most of the CNTs were not straight and very flexural. However, CNTs were dispersed homogeneously and rarely tangled together after sonication (Figs. 13, 14). Moreover, CNTs were merely a little damaged in length and outer walls,

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and no other forms of carbon and metal catalysts were identified during the FE-SEM. EDX profiles of composite (Fig. 14) confirm Homogeneous distribution of CNT in Al matrix after sonication.

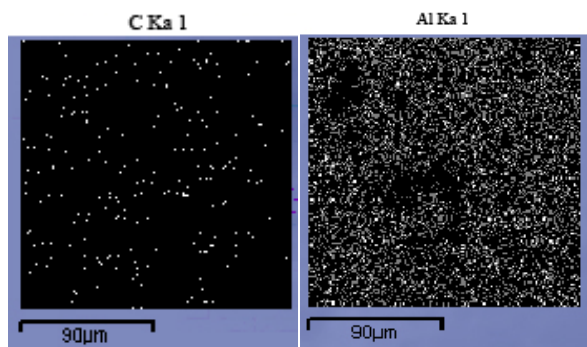Fig. 13 FE-SEM image of Al-CNT composite after sonication

Fig. 14 EDX profile of composite after sonication with the same magnification a) carbon distribution b) aluminum distribution

Figure 15 shows XRD profiles of the ball-milled composite for 24h after sintering. The results indicate forming of aluminium carbide after sintering in 600°C in tube furnace illustrated in Fig. 6. Structural stability of CNTs is essential for achieving strengthening. Al_4C_3 is formed in CNT reinforced composites as the reaction 3 [18].

$$4Al+ 3C = Al_4C_3 \quad \Delta G_f = -258.32 + 0.0968T \quad (3)$$
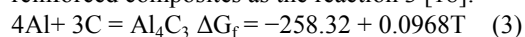
The free energy of formation of Al_4C_3 is -35.7 kJmol^{-1} at 2300 K that proves thermodynamic feasibility at the temperature experienced by in flight particles. The amount of Al_4C_3 formed was calculated by the ratio of the area under Al_4C_3 peaks to the area under all the peaks.
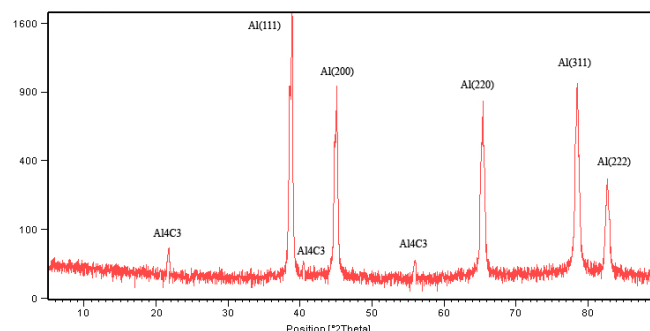

Fig. 15 XRD pattern of the milled sample for 24h after sintering

The relative density of the sintered compact was 96.1%. In general, Al powders have low sinterability because the strong oxide scale on the surfaces of Al particles prevents direct contact between the particles. The high density obtained in the present study was attributed to the reduced atmosphere due to the use of a carbon mold.

Figure 16 shows the raman peaks of sintered Al-CNT composite. The raman peaks of sintered Al-CNT composite at 1587 and around 1355 cm^{-1} correspond to a typical G-line (graphite) and D-line (defect), respectively (Fig.16). There was no change in either the magnitude or shape of the peak from original CNT. The value of ID/IG was nearly 0.8 before and after pressing and sintering process. This implies that no structural change in the CNTs appeared for any of the processes and specimens. The general reason for a structural change in a CNT is a reaction with oxygen at high temperature.
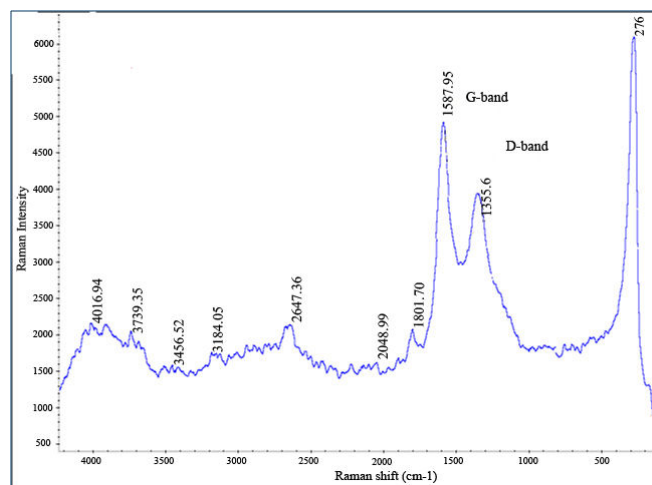

Fig. 16 Raman spectra of the sintered Al–CNT composite

The FE-SEM of compacted composite materials has been shown in Fig.17. As you can see, the image does not show any damage or change in microstructure of MWCNTs after compaction in 475 MPa.

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Fig. 17 FE-SEM image of Al-CNT composite after compaction

The macro-hardness of the sintered Al–MWCNT composite was about 48 HV, whereas that of pure Al was 22 HV. The CNT reinforcement would increase the hardness by a factor of around two.

IV. CONCLUSION

One of the common problems in the development of CNT/metal matrix composites is controlling the agglomeration of the nanotubes. In this study, it has been shown that by employing the modified ball mill and sonication before mechanical alloying, it was possible to prevent agglomeration of mixture powders during the MA, which would have adverse effects on the properties of final composite products due to the increased porosity. The milling conditions were selected to promote shorter milling times and hence reduce the associated strain-hardening effect while being effective in dispersing the CNTs. The high density obtained in this study was attributed to the reduced atmosphere due to the use of a carbon mold. The result of raman spectroscopy implies that no structural change in the CNTs after sintering process.

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