Mechanics of Advanced Composite Structures 2 (2014) 107 – 111

Semnan University

Mechanics of Advanced Composite Structures

journal homepage: http://MACS.journals.semnan.ac.ir

A Case Study for Fabrication of MWCNT-TiO_2 Hybrid Reinforced Aluminium Matrix Nanocomposites

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PAPER INFO

Paper history:
Received 29 June 2014
Received in revised form 17 October 2014
Accepted 19 October 2014

Keywords:
Al matrix nanocomposite
Al–MWCNT-TiO_2
Hot extrusion

ABSTRACT

One of the most important applications of carbon nanotubes (CNTs) is as reinforcement of metal matrix composites, because of their excellent mechanical properties. In this study, Al-TiO_2-multi walled carbon nanotubes (MWCNTs) nanocomposite is fabricated using isostatic pressing followed by hot extrusion. Mechanical alloying is used to mix powders of aluminium, TiO_2 and MWCNTs. TiO_2 with the amounts of 1, 2 and 3 wt% and CNTs with 0.5, 1, 1.5 and 2 wt% are used. Mechanical properties of Al-TiO_2-CNT Nano composites were characterized with tensile and microhardness test. The morphology and microstructure of fabricated nanocomposites were characterized using field emission scanning (FESEM) and Transmission electron microscopy (TEM). The results showed that the maximum ultimate tensile strength (UTS) was observed for the Al-0.5 wt% CNT–1wt% TiO_2 nanocomposite, which exhibited about 28% increase compared to the 1wt%TiO_2- Al sample. The results showed that the addition of MWCNTs with uniform distribution improved the tensile strength and micro hardness.

1. Introduction

The need to increase the mechanical properties in aluminium alloys has motivated the study of new materials and innovative routes to prepare them. Aluminium based metal matrix composites (MMC) are demanded because of their low density and high specific stiffness. These materials can be produced by dispersing oxides, car-bides or nitrides into metallic matrix. However, a new kind of reinforcement material is raising the interest of the scientific community, the carbon nanotubes (CNTs), which include single and multi-walled carbon nanotubes (MWCNTs). One of the most important applications of CNTs is as reinforcement because of their excellent mechanical properties [1]. It is revealed that CNTs possess not only an extremely high elastic modulus but also plasticity. The excellent mechanical properties and chemical stability suggest that the CNT might be suitable as a novel fibber material for MMC. However, CNT as a reinforcement phase in metal matrix materials has recently received a modest attention in the literature [2].

Additionally, there are very few reports about CNT reinforcing aluminium composites produced by mechanical milling [6]. Thus, a new type of composite is emerging, combining two apparently immiscible phases, aluminium and CNTs, using mechanical milling and powder metallurgy (PM). This work deals with the strengthening of aluminium matrix through the addition and dispersion of MWCNT and TiO_2 using mechanical milling and consequent hot extrusion. Some proportions of MWCNT and TiO_2 are used in the preparation of aluminium composites. An analysis of microstructure, microhardness and maximum tensile strength (σ_{max}) variations is

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presented and discussed as a function of the reinforcement concentrations.

2. Experimental Procedure

2.1. Fabrication

Al (99.9% pure, −325 mesh in size), TiO_2 with average particle size of 15 nm and CNTs were used to produce the Al-TiO_2-CNT nanocomposites. Different compositions were studied, starting with pure Al and nanocomposites with additions of 0.5, 1, 1.5 and 2 wt.% of MWCNT and 1%, 2% and 3% of TiO_2 particles. Each mixture was blended in an ultrasonic bath for 5 min and mechanically milled in a high-energy ball mill for 180 minutes. In mechanical mixing process the steel balls with different dimensions and weights were used. Simultaneous use of different sizes of balls has advantages such as increasing the efficiency of the milling process and removing the dead zones. Argon was used as inert milling atmosphere. Device and milling media were made of hardened steel. The weight of the samples was set to 5 g, and the ratio of the milling media to powder weight was 20:1. All milling runs were performed with no addition of process control agent. Consolidated products were obtained by pressing during 2 min at 750 MPa in uniaxial load. Then the samples were prepared using a hot extrusion process at 500 °C. Extrusion ratio and speed were 20:1, 0.2 mm/s respectively. Fig. 1 reveals hot extrusion process schematically. Table 1 summarizes the properties of MWCNTs. Nano TiO_2 is used and the properties of nano TiO_2 are shown in Table 2.

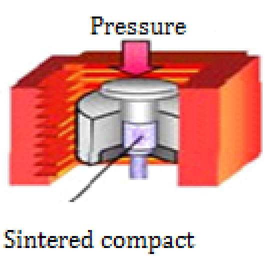


Figure 1. Schematic of hot extrusion process

Table1. Multi-Wallel Carbon Nanotubes properties.

Properties	
Purity	>95%
OD (OD = Outer Diameter)	< 10 nm
Length	5-15 μm
Amorphous carbon	< 3%
Ash (catalyst residue)	< 0.2 %
Special surface area	40-300 $m^2.g^{-1}$
Thermal conductivity	~ 2000 $w.mk^{-1}$
Colour	Black

2.2. Tensile Test

Tensile test bars were prepared according to the standard ASTM E8. The tensile test samples were heated in the oven at 500˚C for 120 minutes. Tensile testing was carried out for the heat-treated samples at room temperature using an Instron type machine (Universal testing instrument) working with a strain rate of 2.5×10^{-3}/s.

2.3. Micro Hardness

Micro hardness test samples were cut from fabricated nanocomposites and then were cold mounted. The specimen surface was polished with fine sandpaper. The hardness measurements were carried out for all specimens using a Vickers hardness tester.

2.4. Metallography

Microstructural observations were performed using high resolution field emission scanning electron microscopy (FESEM) MIRA3 TESCAN at 20 keV. Conducting samples were prepared by gold sputtering specimens. The particle size was measured using the IMAGEJ software on the FESEM images. The microstructural characterization of MWCNTs was done using transmission electron microscopy (TEM) in a CM 200.

3. Results and Discussion

Fig. 2 illustrates the optical micrograph of the cross section of cold pressing composite before sintering. It can be found that the starting Al powders with lubricous surfaces are flattened to flakes after ball milling, and the size of Al powder flakes is distributed well about 5 μm in thickness and 45 μm in length. No agglomerates of CNTs can be found in cold pressing composites.

Stress-strain curves are used to investigate the mechanical properties of Al- nanocomposites. The effect of CNT contents on the ultimate tensile strength is shown in Fig. 3. The values given are the average of three tests for samples. The maximum ultimate tensile strength is observed for the Al-0.5 wt% CNT–1wt%TiO_2 nanocomposite, which exhibits about 28% increase compared to the 1wt%TiO_2- Al nanocomposite sample. It can be described with Orowan mechanism in which the motion of the disloca-

Table2. The properties of nano-TiO_2.

Properties	
Diameter (nm)	15 ± 3
Surface Volume ratio ($m^2.g^{-1}$)	150±12
Density ($g.cm^3$)	< 0.12
Purity (%)	> 99.9

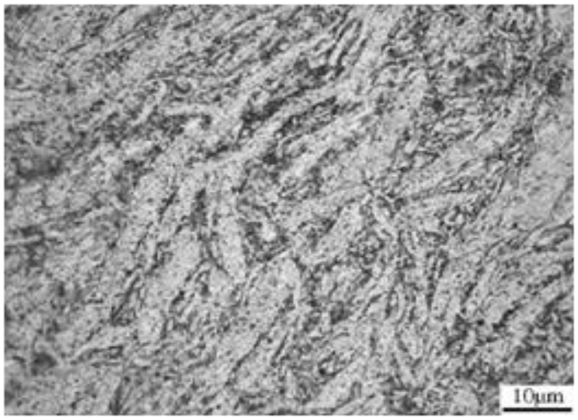


Figure 2. Optical micrograph of cross section of cold pressing composite.

tions is inhibited by nanometer sized CNTs, leading to bending of these dislocations between the CNTs.

It can be described with Orowan mechanism in which the motion of the dislocations is inhibited by nanometer sized CNTs, leading to bending of these dislocations between the CNTs. This produces a back stress, which will prevent further dislocation migration and will result in an increase in yield stress. The Orowan looping mechanism is important in aluminium alloys, which are strengthened by fine precipitates. However, this strengthening mechanism rarely has any real significance in metal matrix composites as the reinforcements are generally coarse and inter-particle spacing is large. But since CNTs effectively represent very fine particles, perpendicular to the tube axis, in the order of a few nanometers, they strengthen the aluminium matrix. Further, because oftheir high strength, the shearing of CNTs is not the determining factor for the composite strength. Particle shearing usually restricts the maximum strengthening that can be achieved by this method.

Table 3 summarizes the ultimate tensile strength (UTS) and yield strength (YS) for different samples.

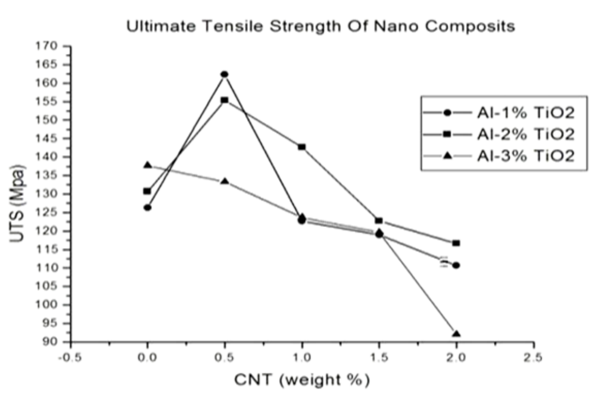


Figure 3. Ultimate tensile strength of different types of nano composites.

The results show that by increasing the percentage of TiO2 in the aluminium matrix, UTS value increases. Adding CNTs in the amount of 0.5 wt%, leads to increasing strength of nanocomposite to maximum value but with increasing the amount of CNTs to 1, 1.5 and 2 wt%, its strength reduces as shown in figure 2.

The reduction in mechanical properties of the samples with higher loadings of CNT can be attributed to the presence of CNT clusters, which represent the sources of weakness in the samples.

Comparing the tensile strength values obtained for Al-1wt% TiO_2–0.5 wt% CNT composites with previous published works, it is clear that values reported here are significantly higher than those previously published. For example, Esawi et al. [19], report a tensile strength of 62 MPa for the same CNT content. Also Kwon et al. [20] who used spark plasma sintering and subsequent extrusion to consolidate their 5 vol.% CNT–Al powders report a tensile strength of 194 MPa. In both studies, however, ball-milling is not used to disperse the CNTs. The improved properties in this work are mainly because of the better dispersion of CNTs provided by ball-milling in addition to the strain hardened powders contributing as a strengthening mechanism to the final strength of the composites.

Although the other researchers use a slightly lower mass fraction of CNTs (i.e. 2 vol. % CNT), George et al. [21] report a tensile strength of 138 MPa (still significantly lower than our reported values). In that study ball-milling is applied, but only for 5 min, so cold working of the powders may not be significant after this low milling time.

Comparison of micro hardness values shows that nanocomposites containing 0.5 wt% nanotubes have higher value of micro hardness than ones without and with 1% nanotubes. Namely the microhardness of Al-TiO_2 nanocomposite increases about 30% with respect to adding 0.5 wt% nanotubes (Figure 4). The CNT reinforcement would increase the hardness by a factor of around two. However, it cannot be denied that the work hardening by the extrusion enhances the hardness of the Al–CNT composites. The increase in microhardness of the nanocomposites compared to monolithic Al matrix can be attributed to: (a) intermetallic particles of lower size and roundness ratio in the matrix, (b) reasonably uni-

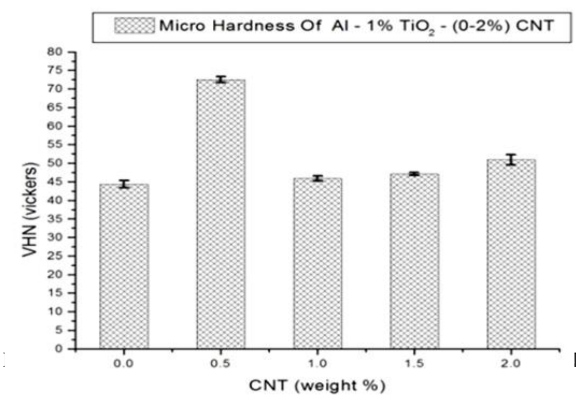
Table 3. Tensile test values for nano composites studied.

nanocomposite	Tensile test values UTS	YS
Al – 1% TiO_2	128	72
Al – 1% TiO_2 – 0.5% CNT	163	88
Al – 1% TiO_2 – 1% CNT	123	72

form distribution of harder CNT in the matrix, and (c) higher constraint to localized matrix deformation during indentation due to the presence of intermetallic particles (having lower size and roundness ratio) and nanoparticles [5, 6, 11]. This is consistent with earlier observations on Mg/Al_2O_3, AZ31/C60 and AZ31/MWCNT (MWCNT: multi-walled CNT) nancomposites [13, 14, 17].

In this study, the uniform distribution of nanotubes in the nanocomposite mechanical properties is improved. TEM reveals that CNTs disperse homogeneously in the Al-TiO2 as shown in figure 5. Fig. 6 shows an FESEM micrograph of the fracture surface of the Al–CNT composite after the tensile test. The fracture surface of the Al–CNT-TiO_2 composite has a lot of dimples associated with ductile fracture, as shown in the Fig. 6. The appearance of these dimples means that the joining between the Al particles is very strong. Detailed observation of the dimple walls reveals a lot of bridging of the aluminium matrix by the CNTs (arrow in Fig. 7b). In this case, any stress in the matrix can be transferred to the CNTs by the aluminium matrix.

Consequently, the tensile strength of the composites in this study is increased.



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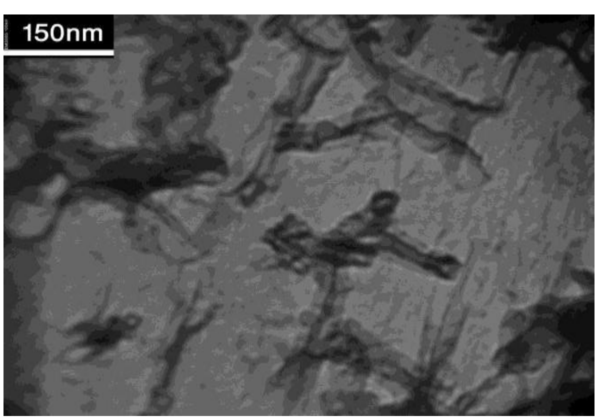

Figure 5. Homogeneous dispersion of CNTs in the Al-TiO_2 by TEM (150 nm).

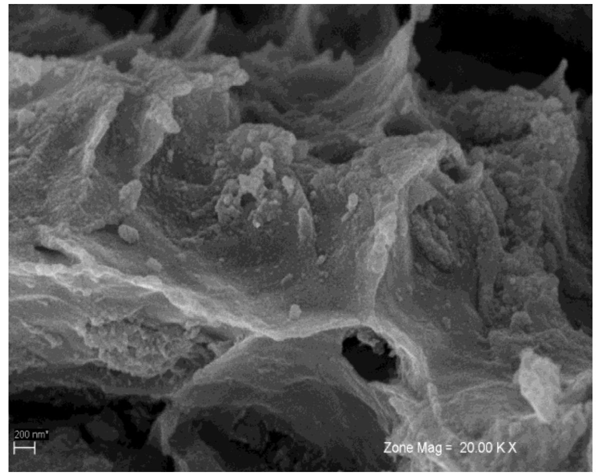

Figure 6. FESEM micrograph showing some dimples in the fracture surface of the Al–CNT-TiO_2 nanocomposite after tensile test.

The fracture surfaces of the composite are observed and the images are shown in Figs. 7(a) and 7(b). Fig. 7(a) shows some CNTs with an obviously tubular structure, which suggests that the CNTs have been embedded into the Al matrix. Meanwhile, CNTs are dispersed well in the Al matrix, and some are pulling out. Fig. 7(b) shows the typical tubular morphology of as-prepared CNTs. Some CNTs are bonding to the Al matrix in a “bridging” manner. Yang et al. [10] have also reported similar results by introducing CNTs into the Al matrix.The composites are characterized by FESEM. The uniform distribution of nanotubes in the Al matrix is clear. The reduction in mechanical properties for the samples with higher loadings of CNT is attributed to the presence of some CNT clusters. This is confirmed by FESEM microscopy. SEM micrograph of the fracture surface of a 1 wt% CNT–Al nanocomposite shows nanotube clusters (Figure 7). The bridging effect can also be responsible for improving the mechanical behaviours of the fabricated nanocomposite as shown in the Figure 3. The result of X-ray diffraction of the sintering composite is shown in Fig. 8. It is very evident that no diffraction peaks of CNTs appears, the other way round, the diffraction peaks of Al_3Ti and Al_2O_3 appear in the diffraction pattern of the composite. Al_3Ti phase formed during the fabrication of the composite may be attributed to the fact that Al powder prepared by ultrasonic gas atomization process is metastable due to supersaturated solution of the alloy elements. So, the precipitation phase Al_3Ti is prone to be formed when the composites are cooled slowly after hot pressing sintering. How ever the appearance of Al_2O_3 phase can be owing to the reaction between the atmosphere and the Al matrix during the sintering, which is also in good agreement with EDX analyses.

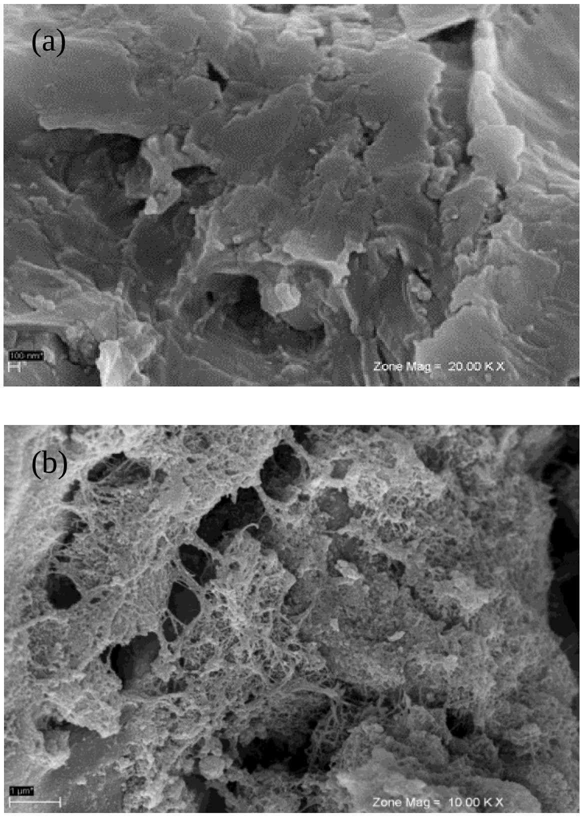

Figure 7. FESEM micrographs of (a) Al–Homogeneous dispersion of CNTs in the fractured surface of nanocomposite, (b) The bridging effect between aluminium particles.

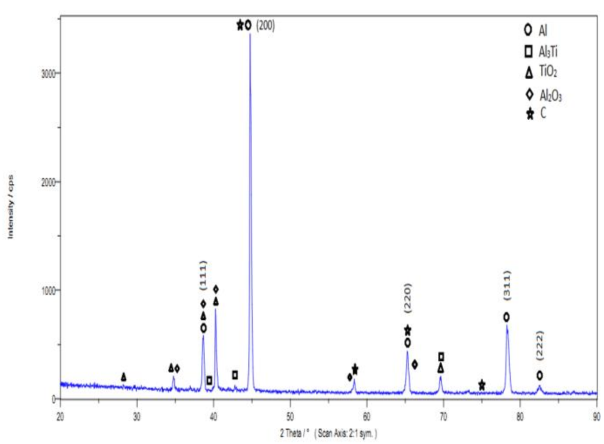

Figure 8. XRD pattern of Al-1wt%TiO2-0.5wt%CNT

4. Conclusion

The results showed that the combination of ball milling and consequent hot extrusion process was effective for fabrication of high strength Al–TiO_2-CNT nanocomposite. The results showed the maximum mechanical strengths for the composition of Al-1wt%TiO_2–0.5 wt% MWCNT. The Strength reduction in samples with more than 0.5 wt% MWCNT would be a result of CNT agglomeration. Investigation of microstructure using TEM showed that CNTs dispersed homogeneously in the Al-TiO_2 matrix. Also investigation on the fracture surface of the samples using FESEM revealed that fracture manner of the composite was involved in “bridging” and “pulling out” of CNTs on the fracture surfaces of the composite.

References

[1] Oberlin A, Endo M, Koyama T, Crystal Growth 1976; 32: 335–349.
[2] Iijima S, Brabec C, Maiti A, and Bernholc J, Chem Phys 1996; 104: 2089–2092.
[3] Falvo MR, Clary GJ, Taylor RM, II, et al, Nature 1997; 389: 582–584.
[4] Dresselhaus MS, Dresselhau, Avouris Ph, Topics in Applied Physics 80, springer (2001).
[5] George R, Kashyap KT, Rahul R, and Yamdagni S, ScriptaMaterialia 2005; 53: 1159–1163.
[6] Kuzumaki T, Hayashi T, Miyazawa K, Ichinose H, Ito K, and Ishida Y, MaterTrans 1998; 39: 574–577.
[7] Xu C, Wei B, Ma R, Liang J, Wu D, Carbon 1999; 37:855–858.
[8] Kim K, Eckert J, Menzel S, Gemming T, Hong S, Applied Physics Letters 2008; 92: 1201-1203.
[9] Kim K, Cha S, Hong S, Mater Sci Eng A 2006; 430: 27–33.
[10] Yang J, Schaller R, Mater Sci Eng A 2004; 370: 512–515.
[11] Morelli E, Yang J, Couteau E, Physica Status Solidi A 2004; 201: 53–55.
[12] Goh C, Wei J, Lee L, Gupta M, Mater Sci Eng A 2006; 423: 153–156.
[13] Goh C, Wei J, Lee L, Gupta M, Nanotechnol 2006; 17: 7–12.
[14] Shimizu Y, Miki S, Soga T, Scripta materialia 2008; 58:267–270.
[15] Hertel T, Walkup R, Avouris P, Phys Rev B 1998; 58: 13870–13873.
[16] Jiang L, Huang Y, Jiang H, Mech Phys Sol 2006; 54: 2436–2452.
[17] Kuzumaki T, Ujiie O, Annual Rev 2000; 7: 8-12.
[18] Vegard L, Philosophical Mag 2006; 32: 505–515.
[19] Esawi A, El-Borady M, Compos Sci Technol 68 (2008) 486–492.
[20] Kwon H, Estili M, Takagi K, Miyazaki T, Carbon 2009; 47: 570–577.
[21] George R, Kashyap KT, Rahul R, Yamdagni S, Scripta Mater 2005; 53: 1159–1163
[22] Woodman R, Klotz B, Dowding J, Ceramics International 2005; 31: 765–768.