



Effect of ball-milling time on mechanical properties of carbon nanotubes reinforced aluminum matrix composites

Z.Y. Liu, S.J. Xu, B.L. Xiao*, P. Xue, W.G. Wang, Z.Y. Ma

Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China

ARTICLE INFO

Article history:

Received 14 March 2012
Received in revised form 23 July 2012
Accepted 28 July 2012
Available online 21 August 2012

Keywords:

A. Metal–matrix composites (MMCs)
B. Mechanical properties
E. Powder processing

ABSTRACT

Carbon nanotubes reinforced pure Al (CNT/Al) composites were produced by ball-milling and powder metallurgy. Microstructure and its evolution of the mixture powders and the fabricated composites were examined and the mechanical properties of the composites were tested. It was indicated that the CNTs were gradually dispersed into the Al matrix as ball-milling time increased and achieved a uniform dispersion after 6 h ball-milling. Further increasing the ball-milling time to 8–12 h resulted in serious damage to the CNTs. The tensile tests showed that as the ball-milling time increased, the tensile and yield strengths of the composites increased, while the elongation increased first and then decreased. The strengthening of CNTs increased significantly as the ball-milling time increased to 6 h, and then decreased when further increasing the ball-milling time. The yield strength of the composite with 6 h ball-milling increased by 42.3% compared with the matrix.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Since the landmark paper by Iijima [1], carbon nanotubes (CNTs) have attracted great attention for structural and functional applications. Excellent mechanical, thermal properties along with high aspect ratio, large surface area and light weight, make CNTs become ideal reinforcement for composites [1–6]. Although main research efforts over the past decade have been focused on CNTs reinforced polymer and ceramic matrix composites [4–6], recently, researchers have gradually pay much attention to CNTs reinforced metal matrix composites. Among these metals, aluminum has been considered preferentially as an ideal metal matrix for lightweight high-strength composites which are widely applied in the automotive and aerospace industries [7].

However, the reinforcing effect of CNTs in Al has not been realized so well due to the difficulties in homogeneously dispersing the CNTs into Al matrix and the formation of brittle phase Al_4C_3 resulting from the interface reaction between Al and CNTs. Many processing methods, such as acidification, organic polymer treatment [8,9], have been applied to disperse the CNTs into the Al matrix. However, mechanical properties of the CNT/Al composites achieved limited improvement by the above methods, because most of the CNTs were distributed along the original powder boundaries, and the volume fraction of CNTs, which could be dispersed into the Al matrix, is very limited.

High energy ball-milling is a type of grinding method used to grind materials into extremely fine powder for use in paints, pyrotechnics and ceramics. During the mill, a high pressure is generated locally due to the collision between the tiny and rigid balls. It has been successfully applied to disperse or shorten CNTs [10]. Recently, high energy ball-milling has been widely used to disperse the CNTs into the Al matrix [11–14]. As a simple mechanical dispersion method, high energy ball-milling of CNTs with inorganic material will be more effectively break up the entangled CNTs [15] and thus it could result in uniform dispersion of the CNTs in the Al matrix, though this process would produce morphological and structural damage to the CNTs. Esawi et al. [12,13] investigated the effect of morphology and content of CNTs on the mechanical properties of CNT/Al composites fabricated by high energy ball-milling. They found that large-diameter CNTs were dispersed more easily into the Al matrix than the small-diameter ones which have a stronger tendency to agglomerate. The mechanical properties of the composites increased significantly as the CNT content increased to 2 wt.%, and then decreased when further increasing the CNT content. Choi et al. [14] reported that after 6 h ball-milling, the CNTs were dispersed into the Al powders and the fabricated CNT/Al composites exhibited a strong bonding between CNTs and Al matrix.

Till now, some previous studies are available of the effect of ball-milling time on the morphological evolution of the CNT/Al composites powders [16–18]. However, the related mechanical properties of the composites have not been discussed. Therefore, it is of primary importance to study the CNT dispersion under different ball-milling times and to produce the CNT/Al composites

* Corresponding author. Tel./fax: +86 24 83978630.
E-mail address: blxiao@imr.ac.cn (B.L. Xiao).

with good mechanical properties by optimizing the ball-milling time. Ci et al. [19] investigated the formation of aluminum carbide in deposited CNT–Al composite. It was found that severe reaction

between CNT and Al as the annealing temperature increased higher than melt point. However, CNTs might be structure damaged during ball milling for the ball milled CNT/Al composites. The reac-

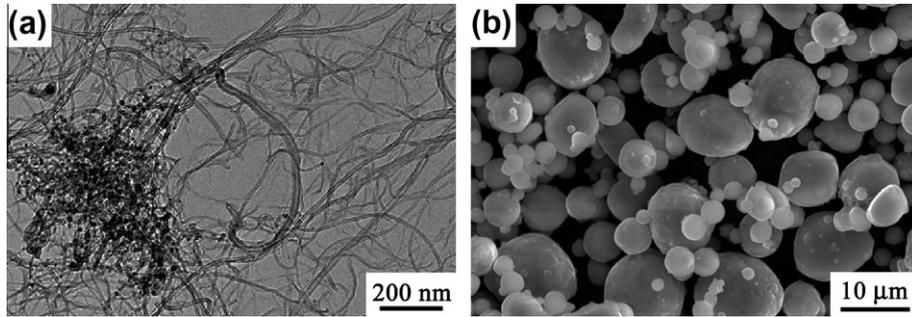


Fig. 1. Morphology of as-received (a) CNTs and (b) pure Al powders.

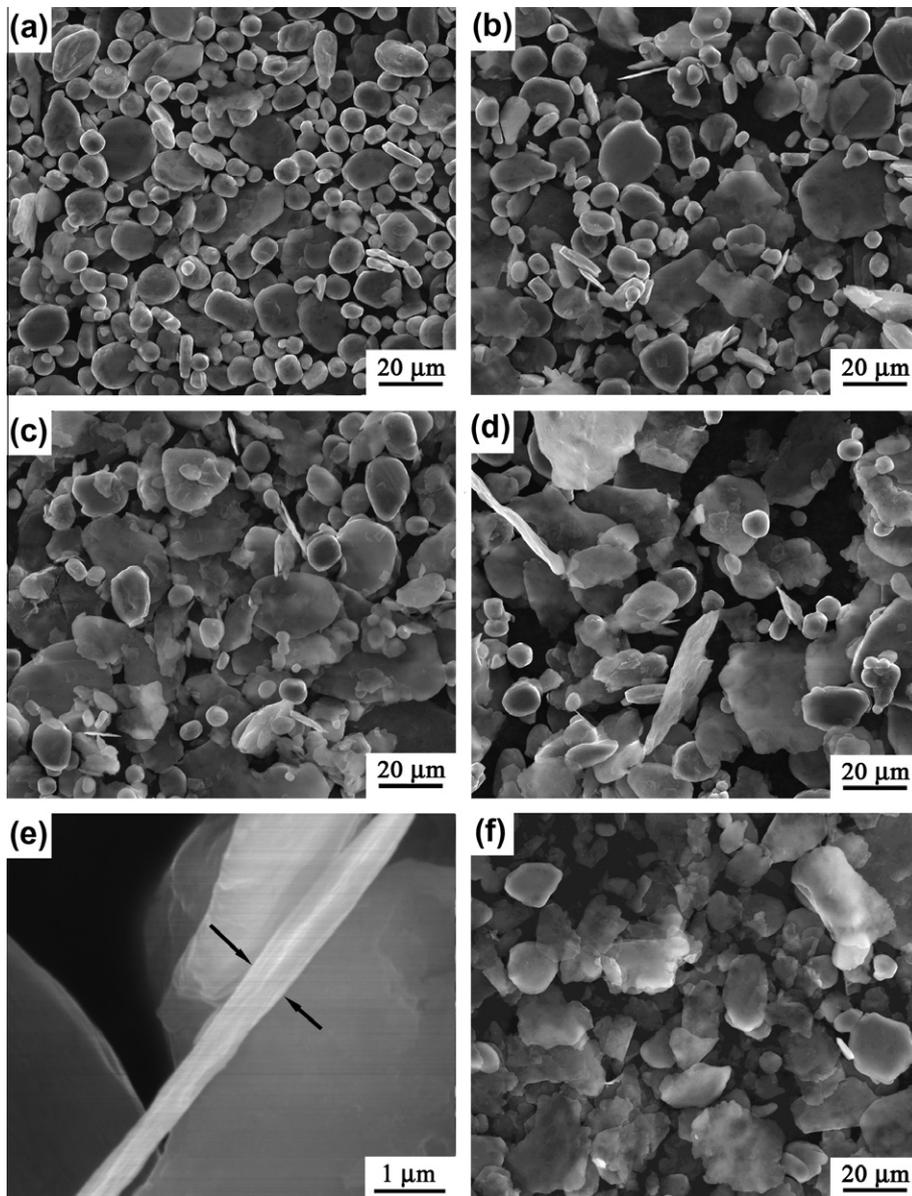


Fig. 2. SEM images of mixture powders with different ball-milling times: (a) 2 h, (b) 4 h, (c) 6 h, (d), (e) 8 h, and (f) 12 h.

tion between CNT and Al could be happened at lower temperature during powder metallurgy processing, and thus the relationship of ball mill time and CNT damage should also be focused.

In this study, multi-wall CNTs (MWNTs) reinforced pure Al composites were fabricated by high energy ball-milling and powder metallurgy (PM) technique. The aim is to investigate the effect of ball-milling time on the dispersion, morphologies and damage of the CNTs, and understand the strengthening effect of the CNTs by deducting the strain hardening of the Al matrix caused by high energy ball-milling.

2. Experimental

Pure Al powder (99.5% purity, about 13 μm in diameter) and MWNTs (about 10–20 nm in diameter and 5 μm in length), supplied by Tsinghua University, were used in the present study. The morphologies of the raw materials are shown in Fig. 1.

To obtain a homogeneous distribution of CNT and lower damage of CNTs, 99.5 g Al and 0.5 g CNT powders were ball-milled with stainless steel balls in a stainless steel jar using a Planet-Ball-Grinding machine at 300 rpm. The ball-to-powder ratio of weight was 8:1 and the milling time was set to be 2, 4, 6, 8 and 12 h, respectively. 1.8 wt.% stearic acid was added into the powders as a process control agent (PCA) to prevent excessive cold welding of the powders. The as-milled powers were cold-compacted in a cylinder die, degassed and hot-pressed at 560 $^{\circ}\text{C}$ into cylindrical billets with a diameter of 40 mm and a height of 30 mm. The as-pressed billets were hot forged at 450 $^{\circ}\text{C}$ into disk plates with a thickness of about 7.5 mm.

The milled mixture powders were examined using field emission scanning electron microscopy (FE-SEM, SUPRA 35). For analyzing the dispersion and damage of the CNTs, the composites were sectioned perpendicular to the forging direction and then observed by optical microscopy (OM, Axiovert 200 MAT) and transmission electron microscopy (TEM, FEI Tecnai G2 20). Further, the composites were subjected to Raman spectroscopic examination (JY Labram HR 800, excitation about 1 μm) to qualitatively analyze the damage of the CNTs.

Dog-bone tensile samples with a gauge length of 2.5 mm, a gauge width of 1.4 mm and a gauge thickness of 0.8 mm were ma-

chined perpendicular to the forging direction and then polished. Tensile tests were conducted on an Instron 5848 tester at an initial strain rate of 1×10^{-3} . At least three tensile samples were tested for one material. After tensile tests, the fracture surfaces of the samples were examined using FE-SEM.

3. Results and discussion

Fig. 2 shows the morphologies of milled mixture powders under different ball-milling times. It can be seen that more mixture powders became flattened as the ball-milling time increased from 2 to 8 h, which was caused by the shearing effect of the balls. The largest surface areas were achieved in the 8 h ball-milled mixture powders, and the thickness of some flattened powders was reduced to as small as 0.5 μm (Fig. 2e). However, when further increasing the ball-milling time to 12 h, some mixture powders were fractured and exhibited an irregular shape, as shown in Fig. 2f. This was because cold working of powders, caused by long time shearing action, led to a decrease in ductility and eventual fracturing of powders. Wang et al. [16] and Esawi et al. [17] also discovered that the mixture CNT–Al powders presented such a flake-like shape in the early stage of ball-milling of the 2 wt.% CNT–Al powders without PCA addition. However, the mixture powders underwent a shape change from flake-like structure to more or less granular structure as ball-milling time increased, because a dynamic equilibrium between fracturing and agglomeration was attained at last.

Detailed SEM observations of the mixture powder surfaces were carried out to investigate the dispersion uniformity of the CNTs in the Al powders, as shown in Fig. 3. It is clear that the CNTs were gradually dispersed into the Al powders as the ball-milling time increased to 6–8 h. When the ball-milling time was relatively short (2 h), the entangled CNT clusters were adhered to the surfaces of the Al powders (Fig. 3a). When increasing the ball-milling time to 4 h, the number of entangled CNT clusters decreased (Fig. 3b). After long time (6–8 h) ball-milling, nearly no CNT clusters could be found on the surfaces of the Al powders and many CNTs with tips outside the Al powders could also be observed, as shown in Fig. 3c and d, indicating that most of the CNTs were dispersed into the Al powders. A schematic of CNT distribution during ball mill is shown in Fig. 4. At the beginning, aluminum powders had sphere

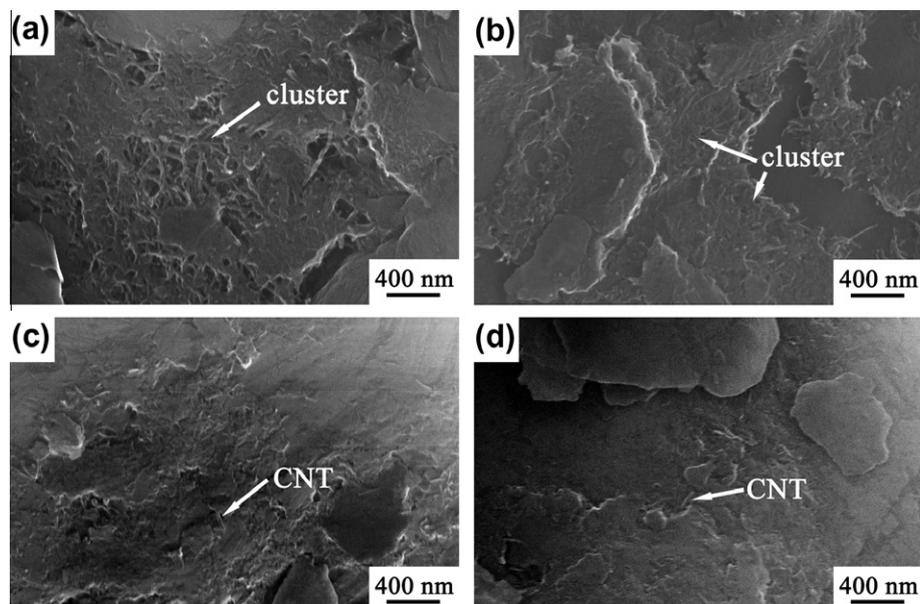


Fig. 3. Surface morphology of mixture powders ball-milled for (a) 2 h, (b) 4 h, (c) 6 h, and (d) 8 h.

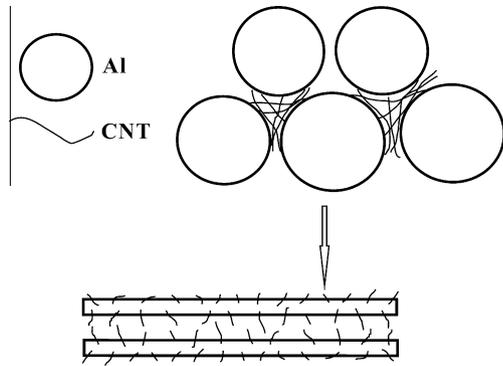


Fig. 4. Schematic of CNT distribution during ball mill.

morphology and CNT clusters tended to disperse at the wells among several aluminum particles. As the ball milling time increasing, two things happened. On one hand, the aluminum powders changed to flaky morphology due to the shear force during ball milling. On the other hand, CNTs were shortened [20] and CNT clusters were broken down by shearing force. Then, CNTs were gradually embedded inside the Al powders through plastic deformation of the Al matrix [17] under the impact of the balls in the preliminary stage of ball-milling.

From the OM microstructure of the CNT/Al composites at different ball-milling times (Fig. 5), the entangled CNTs (the black blocks, as shown by the arrows) became less with increasing the ball-milling time from 2 to 8 h. The aluminum powders got thinner as ball milling time increasing (Fig. 3) and the high surface area and flat morphology of powders could provide more sites for CNT dispersion and thus were beneficial to the uniform distribution of CNTs [21]. The distribution of the CNTs in the composites changed from 6 h ball-milling to 12 h ball-milling. A network structure of CNTs around the Al powders was formed after 6 h ball-milling (Fig. 5c). As ball mill time increasing, the Al powders got thinner and CNTs were embedded into the matrix at the Al particle edge zone. Thus, CNT dispersed as a style of strip distribution.

The change in the dispersion style of CNTs is attributed to the deformation of the mixture powders. The mixture powders were flattened gradually by shearing force during ball-milling (Fig. 2), resulting in greatly increased specific surface areas of aluminum powders. In the preliminary stage of ball-milling some CNTs were distributed at the original powder boundaries. As the ball-milling time increased, the CNTs were gradually separated and dispersed into the Al powders (Fig. 3), and finally a uniform dispersion of the CNTs was achieved when ball-milled for an appropriate time (6 h). However, if further extending the ball-milling time, high energy ball-milling could change the structures of CNTs [22] and brought more impurities like Al_2O_3 and Fe. The thinner the flaky

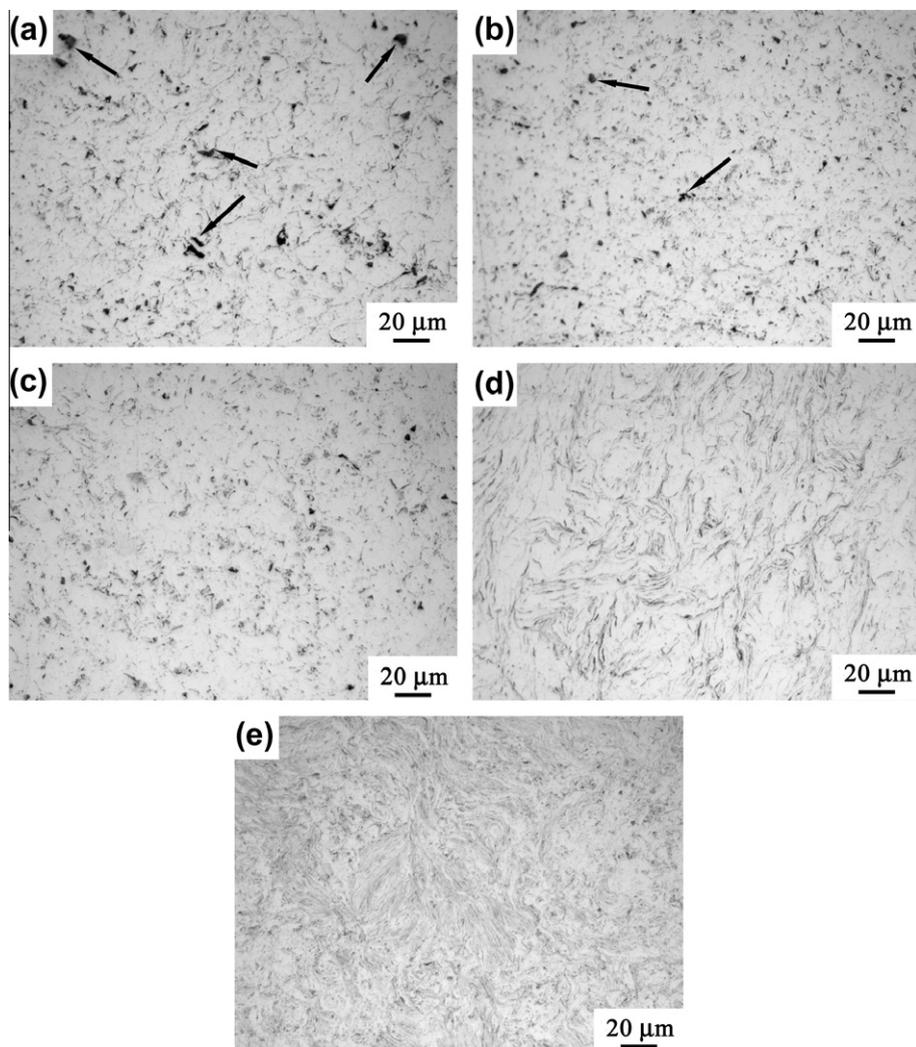


Fig. 5. OM microstructure of 0.5 wt.% CNT/Al composites with different ball-milling times: (a) 2 h, (b) 4 h, (c) 6 h, (d) 8 h, and (e) 12 h.

Table 1

Raman spectra characteristics of CNTs in ball-milled mixture powders with different milling times.

Milling time (h)	0	2	4	6	8	12
I_G/I_D ratio	0.85	0.82	0.77	0.71	0.62	0.53

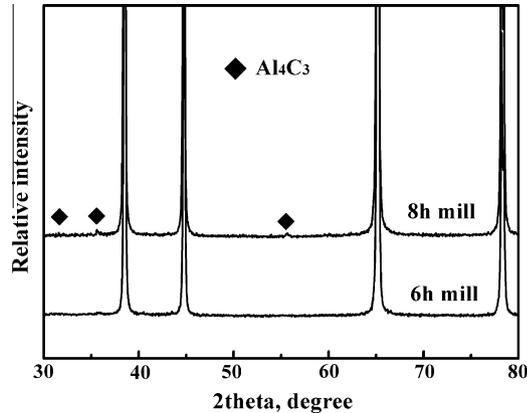


Fig. 6. X-ray diffraction results of the CNT/Al composite milled for different time.

aluminum particle was, the larger surfaces areas was, which would then lead to more Al_2O_3 . Too much Al_2O_3 would reduce the bonding of Al powders and decrease the ductility of the Al matrix, which would adversely affect the mechanical properties of the composites.

To assess the damage to the CNTs during ball-milling, Raman spectroscopic measurements were carried out. G band and D band of the CNTs are typically located at around 1580 cm^{-1} and 1350 cm^{-1} , respectively. Usually, the damage degree of the CNTs is characterized by the I_G/I_D ratio [23–25], and the calculated I_G/I_D value is shown in Table 1. It can be seen that the I_G/I_D ratio decreased with increasing the ball-milling time, indicating that the damage degree of the CNTs became more serious after extended ball-milling time, though the CNTs were more uniformly dispersed in the Al matrix. Therefore, in order to obtain good mechanical properties, ball-milling should be controlled in an appropriate duration to achieve a uniform dispersion of the CNTs and to reduce the damage to the CNTs. Actually, when the ball-milling time was longer than 6 h, the improvement of the dispersion uniformity was not obvious, but the CNT damage became more serious.

Fig. 6 shows XRD results of the CNT/Al composites at ball-milling time of 6 h and 8 h. It was indicated that the intensity of the

Al_4C_3 phase was increased as the ball mill time increased from 6 h to 8 h. Fig. 7 shows the TEM images of 0.5 wt.% CNT/Al composites at different ball-milling time. Structural changes of the CNTs could be observed in the CNT/Al composites ball milled for 6 h and 8 h due to strong mechanical and heat effects during ball-milling and hot-pressing processes, respectively. The typical wall layers were reduced and the fracture of the CNTs was found in the composite which were ball-milled for 6 h (Fig. 7a). For the CNT/Al composite with 8 h ball milling (Fig. 7b), few Al_4C_3 with a length of $\sim 50\text{ nm}$ was detected in the matrix near the CNTs. The inset in Fig. 7b is an enlargement of the brittle phase Al_4C_3 . This indicates that a small number of the CNTs reacted with the Al matrix to form brittle phase Al_4C_3 . Kuzumaki et al. [26] reported that the CNTs were stable in the Al matrix and did not form carbide as long as they were high-quality and low defect tubes. However, ball-milling caused the damage to the CNTs, thereby reducing the stability of the CNTs.

Fig. 8 shows the CNT distribution in the CNT/Al composite with 6 h ball-milling. The CNTs were found to be singly dispersed, and while some CNTs were distributed along the grain boundaries (as shown by black arrows), the others were located at the interior of the grains (as shown by white arrows). The distribution of CNTs at the grain boundaries exerted an effective pinning on the boundaries, contributing to the generation of much finer grains in the composites [27]. Further, no micro-void was found at the CNT–Al interfaces. Thus, the load could be efficiently transferred from the matrix to the CNTs, producing an effective strengthening.

Fig. 9 shows the stress–strain curves of the CNT/Al composites as well as the Al with various ball-milling times. The mechanical properties of both reinforced and unreinforced Al are listed in Table 2. For the Al matrix, increasing ball-milling time results in increased strength, however the elongation decreased quickly. Especially, zero elongation was obtained for the matrix milled for 12 h, which mainly due to the impurities of Al_2O_3 and Fe. For the composites, variations of the ultimate tensile strength (UTS) and yield strength (YS) of the composites with ball-milling time are similar with that of the unreinforced matrix. However, unlike the matrix, the elongation increased first and then decreased with increment of ball-milling time. At the same ball-milling time, the relative increments of UTS and YS of the composites relative to the matrix materials are showed in Fig. 10. By deducting the strengthening contribution from microstructure changing of matrix, the strengthening of CNTs increased first as the ball-milling time increased to 6 h (The YS and UTS were improved by 42.3% and 18.4%, respectively.), and then decreased when further increasing the ball-milling time.

The mechanical properties of the CNT/Al composites are mainly affected by four factors: matrix strength, interface reaction, disper-

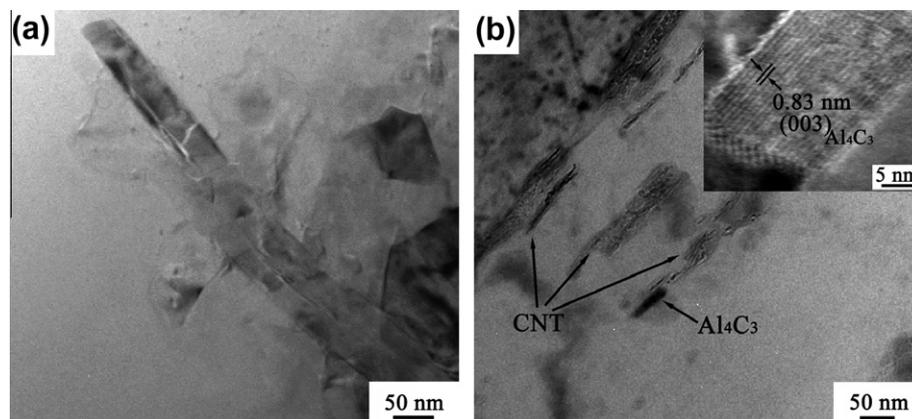


Fig. 7. TEM images of 0.5 wt.% CNT/Al composites with different ball-milling times: (a) 6 h and (b) 8 h.

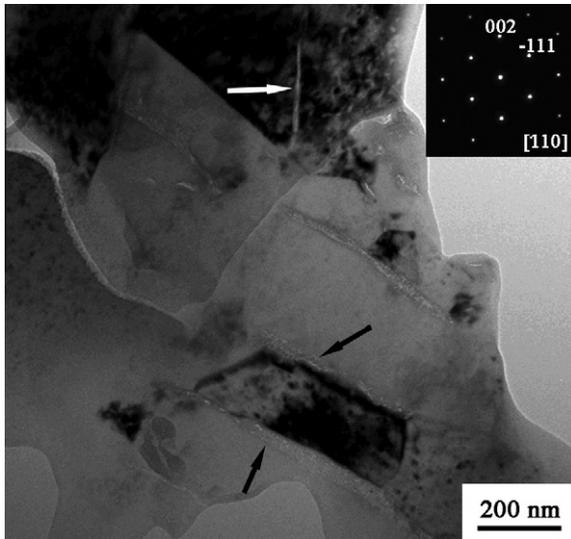


Fig. 8. TEM image showing CNT distribution at grain boundaries (denoted by black arrows) and within grains (denoted by white arrow) in CNT/Al composite with 6 h ball-milling, note [110] diffraction spots of Al matrix on the left and right of CNT (denoted by white arrow) are the same.

sion of CNTs and damage of CNTs. Increasing the ball-milling time results in more uniform dispersion of the CNTs and tighter bonding between the CNTs and Al, so the UTS and YS of the CNT/Al composites increased as the ball-milling time increased. Although the mechanical strength of the composites was improved, compared with that of the matrix material in the whole ball-milling process, the relative increments of UTS and YS slightly decreased at 8 h ball-milling and obviously decreased at 12 h ball-milling. This is because the strengthening of the composites by CNTs was improved first with the good dispersion of the CNTs, however, the improvement of dispersion uniformity was not obvious after 6 h ball-milling. Further increasing the ball-milling led to more serious damage to the CNTs, even the interface reaction between the damaged CNTs and Al matrix (Fig. 7b), resulting in reduced mechanical properties of the CNT/Al composites.

The elongation of the CNT/Al composites is mainly affected by the following factors: ductility of matrix, dispersion of CNTs, and damage of CNTs. Good dispersion of CNTs can increase the elongation of the composites. After 6 h ball-milling, as the ball-milling time increased further, the improvement of dispersion uniformity was not obvious, but the damage of CNTs increased (Fig. 5) and the impurity incorporation increases. They all led to a decrease in the ductility of the composites. So the elongation increased first and then decreased after 6 h ball-milling.

Fig. 11 shows the fractographs of the composites at different ball-milling times. Although the composite fabricated with 2 h ball-milling had lots of CNT clusters (Figs. 3a and 5a), no obvious

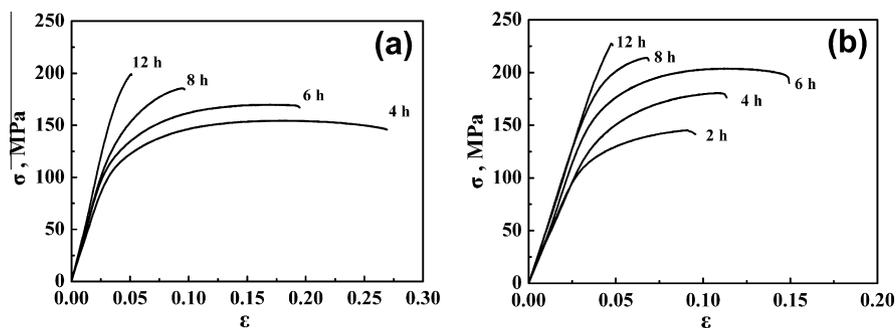


Fig. 9. Tensile properties of CNT/Al composites with different ball-milling times.

Table 2
The mechanical properties of matrix and composites.

Milling time (h)	Sample	YS (MPa)	UTS (MPa)	Elongation (%)
4	Matrix	98 ± 5	153 ± 7	23 ± 2
	Composite	128 ± 7	177 ± 8	6 ± 1
6	Matrix	104 ± 5	170 ± 5	14 ± 1
	Composite	148 ± 5	206 ± 8	7 ± 2
8	Matrix	115 ± 5	185 ± 7	5 ± 1
	Composite	156 ± 6	217 ± 7	3 ± 1
12	Matrix	–	195 ± 4	–
	Composite	–	220 ± 5	–

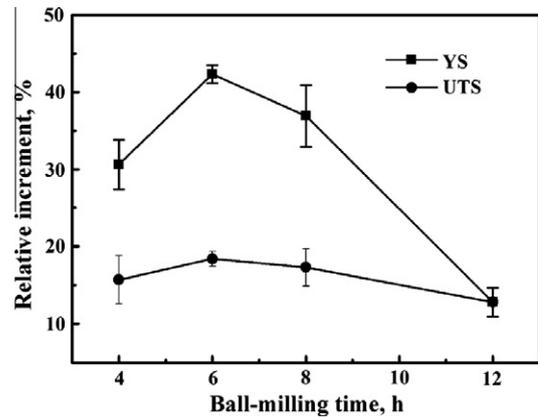


Fig. 10. Relative increments of UTS and YS of CNT/Al composites relative to Al matrix.

holes were observed on the fracture surface (Fig. 11a), and the fracture surface was characterized by small dimples and large tear ridges (Fig. 11b). As the ball-milling time increased to 6 h, the CNT/Al composite exhibited a relatively flat fracture surface (Fig. 11c), which was characterized by flat dimples with different sizes (Fig. 11d). However, with further increasing the ball-milling time to 12 h, the impurity and serious interface reaction decreased the ductility of the composites, resulting in brittle fracture feature (Fig. 11e), and nearly no dimples was observed on the fracture surface (Fig. 11f).

It is generally accepted that the mechanical properties of the composites is closely related to the interfacial bonding status [28]. Highly-magnified FE-SEM images of the fracture surface showed that for the composite with 2 h ball-milling, lots of entangled CNTs appeared on the fracture surface (Fig. 12a), whereas for the composite with 6 h ball-milling, no entangled CNTs were found on the fracture surface, and pulled-out single CNT was observed, as

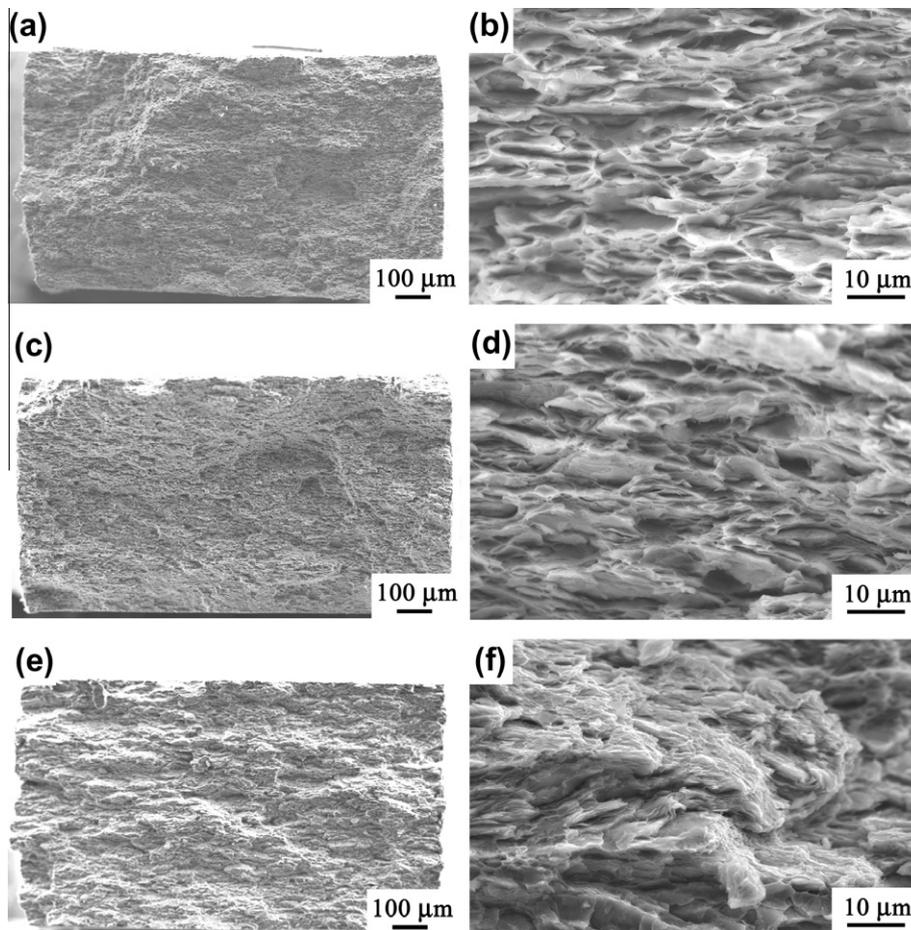


Fig. 11. Fractographs of CNT/Al composites with different ball-milling times: (a and b) 2 h, (c and d) 6 h, and (e and f) 12 h.

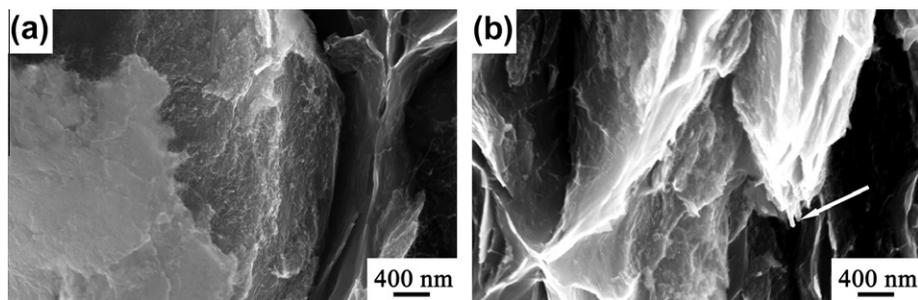


Fig. 12. FE-SEM fractographs of CNT/Al composites with different ball-milling times: (a) 2 h and (b) 6 h.

shown by the arrow in Fig. 12b, with the Al matrix being adhered to the surface of the pulled-out CNTs, suggesting that the CNTs were dispersed completely and had a strong interfacial bonding with the Al matrix.

Strengthening efficiency [29] is commonly used to evaluate the load transfer efficiency of reinforcement. By comparison, the strengthening efficiency of the CNTs reported in this study exceeds those reported by other researchers. For example, Esawi et al. [30] observed that a 2 wt.% CNT/Al composite fabricated through ball-milling for 3 h followed by hot extrusion and annealing at 500 °C exhibited an enhancement of ~21% in tensile strength compared with pure aluminum with the same process history. However, the content of CNTs in their study is three times higher than that in this study. Furthermore, Choi et al. [14] reported that the YS of

1.5 vol.% CNT/Al composites was improved by about 42% compared with the matrix material, the strengthening efficiency of CNTs is also lower than that achieved in this study. This is attributed to optimized ball-milling time in this study. It is believed that an optimized ball-milling time is beneficial to achieving a uniform dispersion of the CNTs and reducing the damage to the CNTs, thereby producing maximum strengthening of the CNTs to the Al matrix.

4. Conclusions

1. Ball-milling was beneficial for the dispersion of CNTs in the Al matrix and the strengthening of the Al matrix, however, extended ball-milling time (8–12 h) caused serious damage to the CNTs.

2. The CNT/Al composite with 6 h ball-milling exhibited a good interfacial bonding between CNTs and Al matrix, some CNTs were distributed along the grain boundaries and the others were located inside the grains.
3. The strengthening of CNTs was improved as the ball-milling time increased to 6 h, and then decreased with further increasing the ball-milling time. The yield strength of the CNT/Al composite with 6 h ball-milling increased by 42.3% compared with the Al matrix with the same processing history.

Acknowledgements

The authors gratefully acknowledge the support of (a) The National Key Basic Research Program of China under Grant Nos. 2011CB932603 and 2012CB619600 and (b) The National Natural Science Foundation of China under Grant No. 50890171.

References

- [1] Iijima S. Helical microtubules of graphitic carbon. *Nature* 1991;354(6348):56–8.
- [2] Popov VN. Carbon nanotubes: properties and application. *Mater Sci Eng R* 2004;43(3):61–102.
- [3] Wong EW, Sheehan PE, Lieber CM. Nanobeam mechanics: elasticity, strength and toughness of nanorods and nanotubes. *Science* 1997;277(5334):1971–5.
- [4] Hout Y, Tang J, Zhang HB, Qiant C, Feng YY, Liu J. Functionalized few-walled carbon nanotubes for mechanical reinforcement of polymeric composites. *ACS Nano* 2009;3(5):1057–62.
- [5] Thostenson ET, Ren ZF, Chou TW. Advances in the science and technology of carbon nanotubes and their composites: a review. *Compos Sci Technol* 2001;61(13):1899–912.
- [6] Peigney A, Laurent CH, Flahaut E, Rousset A. Carbon nanotubes in novel ceramic matrix composites. *Ceram Int* 2000;26(6):677–83.
- [7] Pan FS, Zhang DF. Aluminum alloy and application. Beijing: Chemical Industry Press; 2006.
- [8] Deng CF, Wang DZ, Zhang XX, Li AB. Processing and properties of carbon nanotubes reinforced aluminum composites. *Mater Sci Eng A* 2007;444(1–2):138–45.
- [9] Kwon HS, Estili M, Takagi K, Miyazaki T, Kawasaki A. Combination of hot extrusion and spark plasma sintering for producing carbon nanotube reinforced aluminum matrix composites. *Carbon* 2009;47(3):570–7.
- [10] Ma PC, Siddiqui NA, Marom G, Kim JK. Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review. *Composites: Part A* 2010;41(10):1345–67.
- [11] Perez-Bustamante R, Estrada-Guel I, Antunez-Flores W, Miki-Yoshida M, Ferreira PJ, Martinez-Sanchez R. Novel Al-matrix nanocomposites reinforced with multi-walled carbon nanotubes. *J Alloys Compd* 2008;450(1–2):323–6.
- [12] Esawi A, Morsi K, Sayed A, Tacher M, Lanka S. The influence of carbon nanotube (CNT) morphology and diameter on the processing and properties of CNT-reinforced aluminium composites. *Composites: Part A* 2011;42(3):234.
- [13] Esawi A, Morsi K, Sayed A, Tacher M, Lanka S. Effect of carbon nanotube (CNT) content on the mechanical properties of CNT-reinforced aluminium composites. *Compos Sci Technol* 2010;70(16):2237–41.
- [14] Choi HJ, Shin JY, Min BH, Park J, Bae DH. Reinforcing effects of carbon nanotubes in structural aluminum matrix nanocomposites. *J Mater Res* 2009;24(8):2610–6.
- [15] Ma PC, Wang SQ, Kim JK, Tang BZ. In-situ amino functionalization of carbon nanotubes using ball milling. *J Nanosci Nanotechnol* 2009;9(2):749–53.
- [16] Wang L, Choi H, Myoung JM, Lee W. Mechanical alloying of multi-walled carbon nanotubes and aluminium powders for the preparation of carbon/metal composites. *Carbon* 2009;47(15):3427–33.
- [17] Esawi A, Morsi K. Dispersion of carbon nanotubes (CNTs) in aluminum powder. *Composites: Part A* 2007;38(2):646–50.
- [18] Poirier D, Gauvin R, Drew RAL. Structural characterization of a mechanically milled carbon nanotube/aluminum mixture. *Composites: Part A* 2009;40(9):1482–9.
- [19] Ci LJ, Ryu ZY, Jin-Phillipp NY, Ruhle M. Investigation of the interfacial reaction between multi-walled carbon nanotubes and aluminum. *Acta Mater* 2006;54(20):5367–75.
- [20] Smart SK, Ren WC, Cheng HM, Lu GQ, Martin DJ. Shortened double-walled carbon nanotubes by high-energy ball-milling. *Int J Nanotechnol* 2007;4(5):618–33.
- [21] Jiang L, Fan GL, Li ZQ, Kai XZ, Zhang D, Chen ZX, et al. An approach to the uniform dispersion of a high volume fraction of carbon nanotubes in aluminum powders. *Carbon* 2011;49(6):1965–71.
- [22] Wang Y, Wu J, Wei F. A treatment method to give separated multi-walled carbon nanotubes with high purity, high crystallization and a large aspect ratio. *Carbon* 2003;41(15):2939–48.
- [23] Delhaes P, Couzi M, Trinquost M, Dentzer J, Hamidou H, Vix-Guterl C. A comparison between Raman spectroscopy and surface characterization of multiwall carbon nanotubes. *Carbon* 2006;44(14):964–74.
- [24] Casiraghi C, Ferrari AC, Robertson J. Raman spectroscopy of hydrogenated amorphous carbons. *Phys Rev B* 2005;72(8):085401/1–085401/14.
- [25] McGuire K, Gothard N, Gai PL, Dresselhaus MS, Sumanasekera G, Rao AM. Synthesis and Raman characterization of boron-doped single-walled carbon nanotubes. *Carbon* 2005;43(2):219–27.
- [26] Kuzumaki T, Miyazawa K, Ichinose H, Ito K. Processing of carbon nanotube reinforced aluminum composite. *J Mater Res* 1998;13(9):2445–9.
- [27] Liu ZY, Xiao BL, Wang WG, Ma ZY. Singly dispersed carbon nanotube/aluminum composites fabricated by powder metallurgy combined with friction stir processing. *Carbon* 2012;50(5):843–52.
- [28] Tham LM, Gupta M, Cheng L. Effect of limited matrix-reinforcement interfacial reaction on enhancing the mechanical properties of aluminum–silicon carbide composites. *Acta Mater* 2001;49(16):3243–53.
- [29] Kim KT, Eckert J, Menzel SB, Gemming T, Hong SH. Grain refinement assisted strengthening of carbon nanotube reinforced copper matrix nanocomposites. *Appl Phys Lett* 2008;92(12):121901/1–1/3.
- [30] Esawi A, Morsi K, Sayed A, Gawad AA, Borah P. Fabrication and properties of dispersed carbon nanotube–aluminum composites. *Mater Sci Eng A* 2009;508(1–2):167–73.