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Effect of mechanical alloying time and rotation speed on evolution of CNTs/Al-2024 composite powders

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Abstract: Carbon nanotubes (CNTs) reinforced aluminum matrix composites were fabricated by mechanical milling followed by hot extrusion. The commercial Al-2024 alloy with 1% CNTs was milled under various ball milling conditions. Microstructure evolution and mechanical properties of the milled powder and consolidated bulk materials were examined by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and mechanical test. The effect of CNTs concentration and milling time on the microstructure of the CNTs/Al-2024 composites was studied. Based on the structural observation, the formation behavior of nanostructure in ball milled powder was discussed. The results show that the increment in the milling time and ration speed, for a fixed amount of CNTs, causes a reduction of the particle size of powders resulting from MM. The finest particle size was obtained after 15 h of milling. Moreover, the composite had an increase in tensile strength due to the small amount of CNTs addition.
Key words: CNTs; Al matrix composite; mechanical milling; microstructure

1 Introduction

Particulate-reinforced metal matrix composites (MMCs) have the potential to provide tailored mechanical properties, for example, high specific stiffness, specific strength and creep resistance [1−3]. Among the various MMCs, Al-based MMCs have drawn greatest attention due to their low density and high specific strength. To meet the materials demanded by the aeronautic industry where lower mass and higher strength materials are desired, super-materials which are ultralight and have high hardness and high strength are expected.

Carbon nanotubes (CNTs), which were first discovered in 1991 [4], have superior mechanical properties with a tensile strength up to 150 GPa and an elastic modulus up to 1 TPa, as well as excellent thermal stability and electrical conductivity, exceeding that of conventional fibers [5]. All of these unimaginable characteristics render them potential reinforcement for the composite materials. Besides, the nanosized carbon tubes also provide superior dispersion strengthening to the composite structures. Al-MMCs reinforced by CNTs dispersion are an emerging area that is calling the attention of several research groups in the scientific community [6−8]. KUZUMAKI et al [9] prepared a small amount of CNTs reinforced Al matrix composite material and the strength of the material increased twice. DENG et al [10] mixed CNT and Al-2024 with mechanical milling followed by isostatic cool pressing and hot extrusion, and the tensile strength of the composite was improved by 35.7%. ZHAO et al [11] prepared CNTs/Al and found that CNTs could refine grains and increase tensile intensity and rigidity of the composite. However, agglomeration of the CNTs has been reported as a common problem which hinders the attainment of the desired properties because of low controllability of the zeta potential of metal particles and the large density gap between the metal and CNT. For

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this reason, the development of bulk fabrication methods for CNT−metal matrix composites was started on the basis of a mechanical mixing approach [8,9].

Efforts have thus been focused on finding effective dispersion techniques which can disperse the CNTs homogeneously within the matrix powders. The two techniques that have been investigated are sonication [12] and high energy ball milling [13−16]. Mechanical milling can make CNTs uniformly distribute in the matrix. In this work, the effect of ball milling time, rotation speed and the process control agents (PCA) content on the microstructure of aluminum composites prepared using BM were investigated, as well as the mechanical properties and CNT contents.

2 Experimental

The atomized Al-2024 alloy powder with ~4% Cu (mass fraction) and ~1.5% Mg as the primary alloying elements and CNTs (provided by Shenzhen Nanotech Port Company, whose purity was about 95% as claimed by the producer) with 10−20 nm in diameter and 5−15 μm in length were used as the starting material. The powder of these two materials was mixed together at a mass ratio of 1:99 (CNTs/Al-2024). The mechanical milling experiment was conducted using a Fritsch pulverisette 5 high-energy planetary milling apparatus. The SUS 304L milling tank and balls were selected as the milling medium. Milling parameters were selected with argon atmosphere protection at room temperature as follows: ball to powder ratio of 10:1, BM rotation speeds of 150, 200, 250, 300 and 350 r/min, milling time of 1, 5, 10 and 15 h. To prevent adhesion and welding of the powder to the tank walls and the balls, and to control the fracturing events, different contents of stearic acid ($CH_3(CH_2)_{16}COOH$) and methanol were added as PCA.

Consolidation of the composite powder was performed under vacuum using induction heating sintering. High strength heat-resistant stainless steel punches and dies with an inner diameter of 20 mm were used. The sintering temperature and pressure were 798 K and 400 MPa, respectively. The holding time at maximum temperature was 30 min and the average heating rate was about 25 K/s. The hot pressed billet was then hot-extruded at the 773 K by an extrusion ratio of 10:1 using graphite as lubricant.

The microstructure characterizations of milled powder and consolidated bulk materials were carried out by SEM (Apollo 300) operated at 25 kV. Phase identification was performed by RIGAKU RINT-2000 X-ray diffractometer with Cu K_α radiation and an image plate detector over the 2θ range of 20°−90° at 0.02° step size. The tensile test was carried out by Instron 5565 machine. For tensile testing, all of the samples were cut and polished into dog-bone-shaped specimens with a gauge length of 3 mm and a cross section of 1 mm× 1 mm. The operation of the testing machine was computer-controlled and the digital data of load and displacement from the gage section were recorded. Tensile specimens were tested at an quasi-static strain rate of 5×10^{-4} s^{-1}, with direct measurement of the displacement of the tensile gage section by infrared ray. Density was tested by Archimedes law.

3 Results and discussion

The morphologies of the starting powder are shown in Figs. 1(a) and (b) for Al-2024 and CNTs, respectively. The original Al-2024 powders are mostly spherical and show surface characteristic of gas-atomized powders, and the average particle size is about 20 μm. While almost overall CNTs intertwine with each other and aggregate together. From Fig. 1(b), a diameter of ~10−20 nm can be observed.

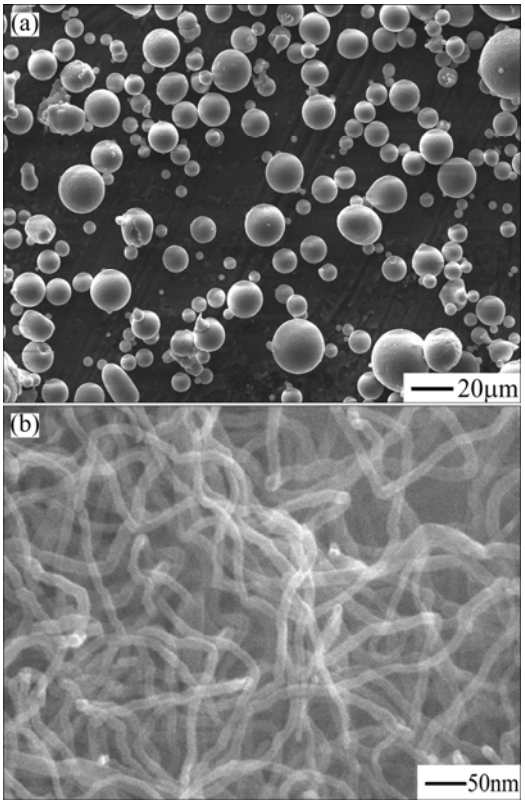

Fig. 1 SEM images of initial powder: (a) Al-2024; (b) CNTs

The SEM images in Fig. 2 show the powder size/morphological evolution with milling time for 1%CNTs/Al-2024 powder mixtures. It is found that the powder morphologies are significantly varied according to ball milling time. At the early stage of milling (5 h of milling), the composite powders get flattened by the ball-powder-ball collisions, as shown in Fig. 2(b). With

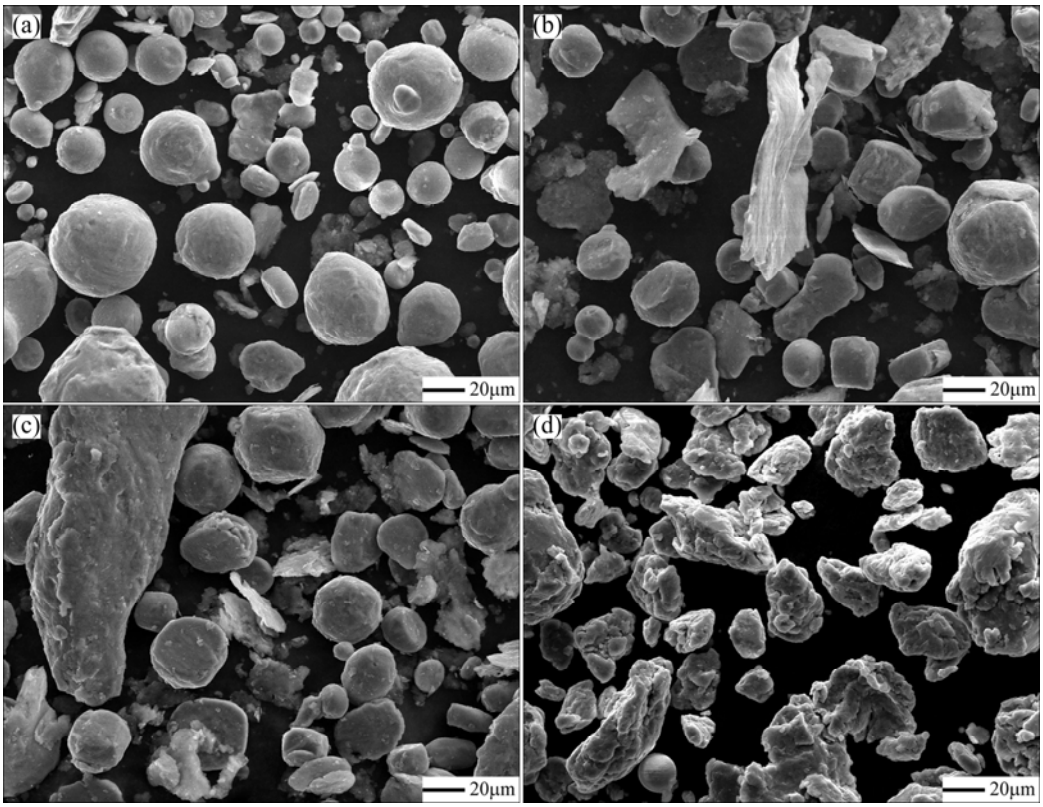

Fig. 2 SEM images of particle morphology and size change for 1%CNTs/Al-2024 powder composites with 1% stearic acid with different milling time: (a) 1 h; (b) 5 h; (c) 10 h; (d) 15 h

prolonged milling time, the flakes start to weld together forming large particles with a rough surface. This could be attributed to the cold welding between the particles resulting in the formation of condensations wherein several particles are held together loosely at point contact. Further milling results in severe plastic deformation of condensations and further reduction in particle size with continued milling. When the milling time reaches 15 h, the particle size stays in a stable value. In general, the size of the powder increases first and then decreases and finally stays in a stable value with the increasing of milling time.

This also can be confirmed by the XRD profile in Fig. 3. Intensity of the peak becomes lowering and broadening with the increase of the milling time. The reasons for these are the deformation, grain refinement and straining induced by the milling process, which can be got from the Scherrer formula as follows:

$$d = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

where d is the crystallite size; λ is the wavelength of the X-radiation used; B is the peak width at half the maximum intensity; θ is the Bragg angle [17].

It is well known that PCA can prevent particles from cold wedding. In this experiment, stearic acid and

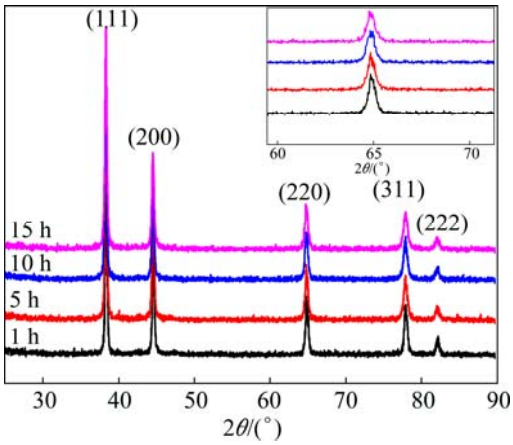

Fig. 3 XRD profiles of 1%CNTs/Al-2024 powder milled for different time

methanol were chosed to for comparison. From Fig. 4, it is observed that when adding 1% (volume fraction) methanol to 1%CNTs/Al-2024 powder, the powder becomes massy with 10 h of milling at 350 r/min, while the composites powder becomes some flakelets with 1% (mass fraction) stearic acid in it. Thus it can be seen that stearic acid works better than methanol for this composites powder.

Figure 5 shows morphological evolution with ball milling speed for 1%CNTs/Al-2024 powder with the

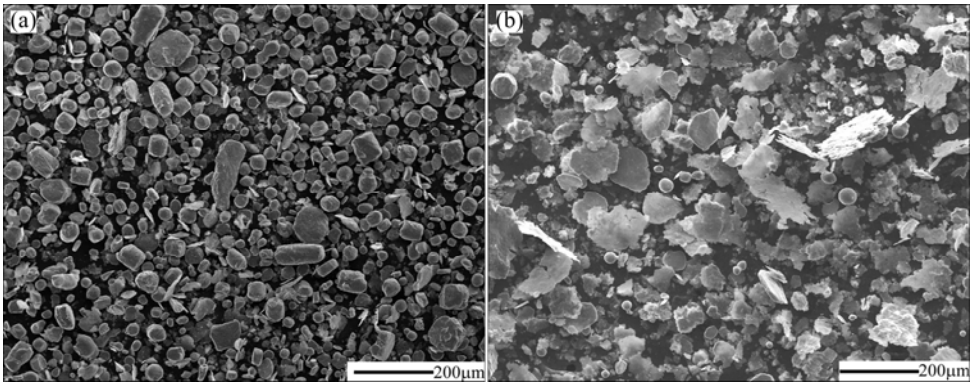

Fig. 4 SEM images of 1%CNTs/Al-2024 powder milled for 10 h at 350 r/min with 1% methanol (a) and 1% stearic acid (b)

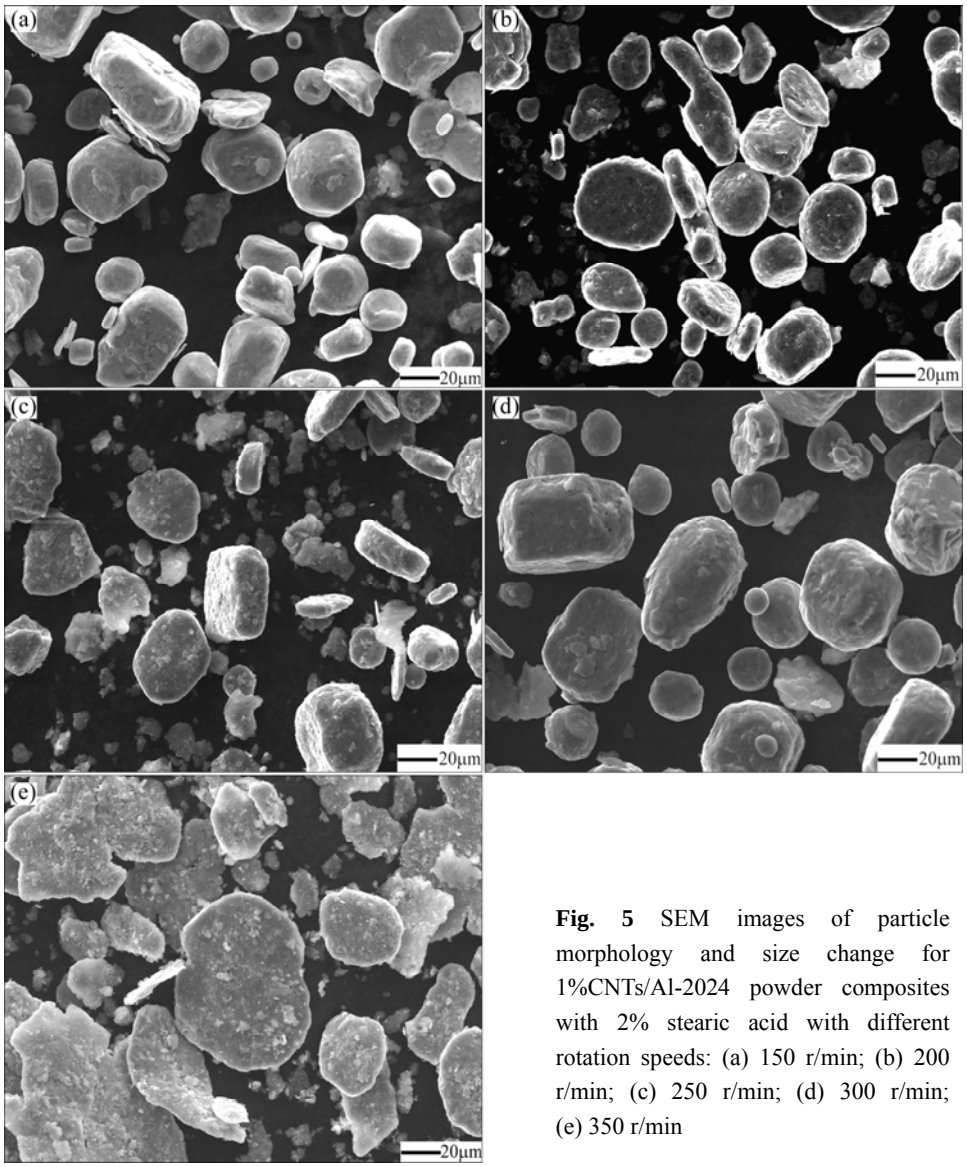

Fig. 5 SEM images of particle morphology and size change for 1%CNTs/Al-2024 powder composites with 2% stearic acid with different rotation speeds: (a) 150 r/min; (b) 200 r/min; (c) 250 r/min; (d) 300 r/min; (e) 350 r/min

addition of 2% stearic acid. The crushing effect of the composites powder becomes more obviously with the increase of ball milling speed and the powder becomes flakes when the speed reaches 350 r/min. Additionally, there are some small particles on the surface of the flakes. Therefore, 350 r/min is the optimal ball milling speed in this experimental.

Figure 6 shows that after adding 2% of stearic acid as PCA to the 1%CNTs/Al-2024 mixture, the particle morphology is predominantly flakes even after 10 h of

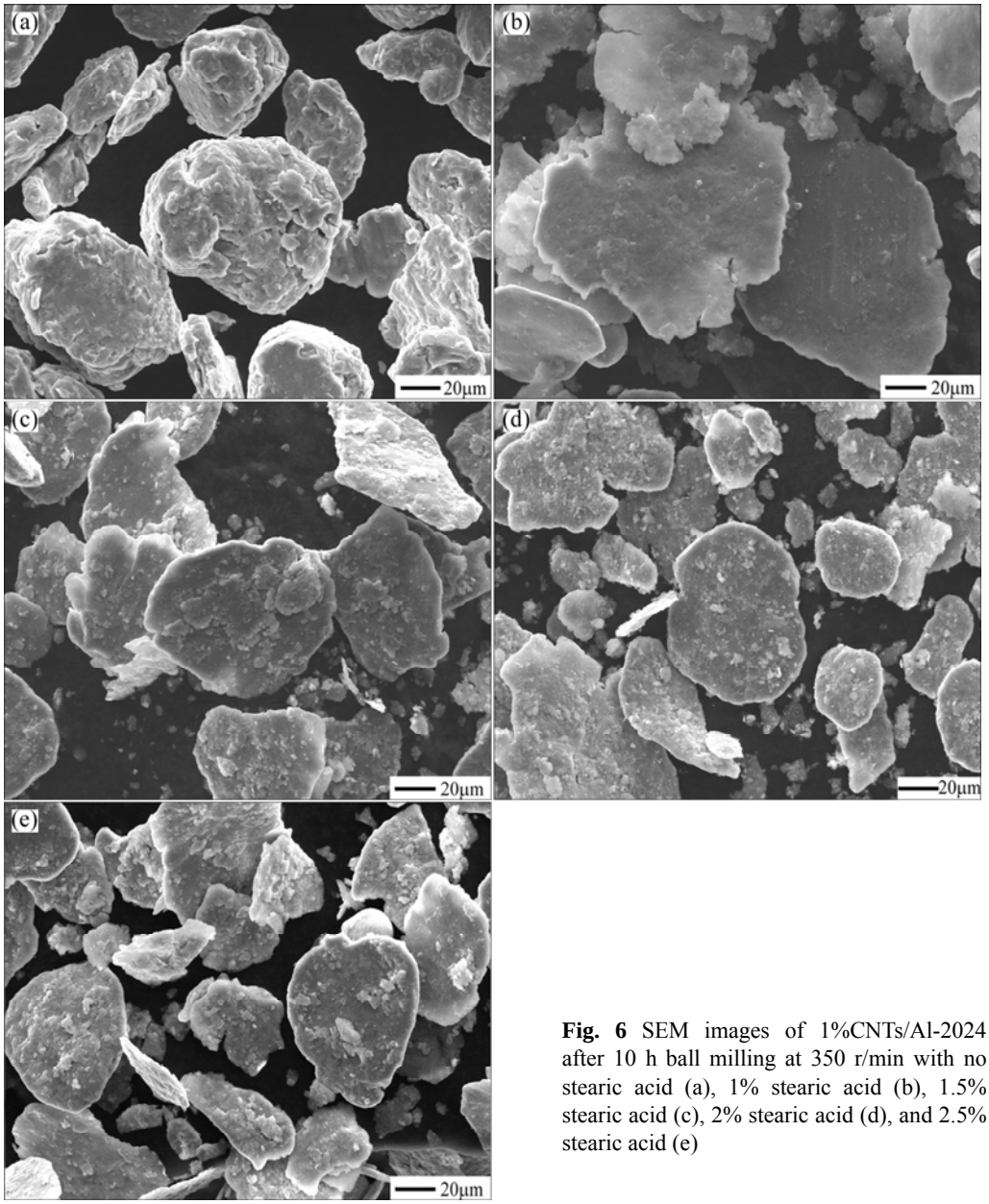

Fig. 6 SEM images of 1%CNTs/Al-2024 after 10 h ball milling at 350 r/min with no stearic acid (a), 1% stearic acid (b), 1.5% stearic acid (c), 2% stearic acid (d), and 2.5% stearic acid (e)

milling. Here the stearic acid hinders the cold-welding process. On the surface of the milled powder, bundles of entangled CNTs are found, as shown in Fig. 7(a), whereas Fig. 7(b) shows some CNTs dispersed on the surface of Al alloy powder. Carbon nanotubes are observed being embedded between the aluminum alloy particles that are being cold-welded, as shown in Fig. 7(c). These results suggest that it is possible to control the particle size and morphology at low carbon nanotube contents, which is also the subject of ongoing research.

The fractographs of the composite after the tensile test are shown in Fig. 8. The fracture surface displays a lot of dimples associated with ductile fracture, as shown in Fig. 8(a). The appearance of these dimples means that the joining between the Al-2024 particles is very strong. Figure 8(b) shows CNTs condensation in Al-2024 matrix. EDX analysis also certified this.

The effects of CNTs content on tensile strength and density are shown in Table 1. It is evident that with small amount of CNTs addition (1%), the tensile strength of the composite increases by 13.73% compared with Al-2024, while a large amount of CNTs addition reduces the tensile strength of the composites. This can be due to the fact that small amount of CNTs addition could fill up the microvoids resulting in the increase of the density and tensile strength of the composites. Nevertheless, high CNTs content will increase the agglomeration of CNTs in the mixed powders. The elongation of the composite decreases due to part of the CNTs aggregated in Al matrix. Further investigation is ongoing to improve the density of the bulk sample.

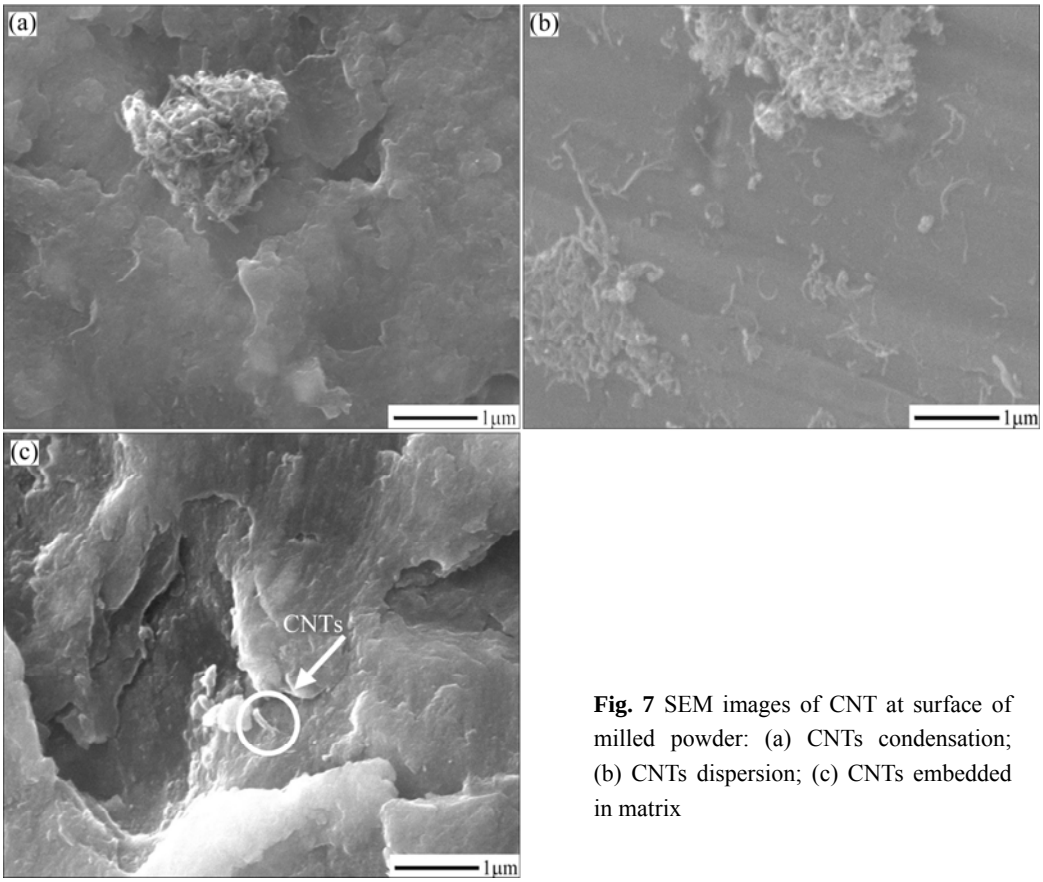

Fig. 7 SEM images of CNT at surface of milled powder: (a) CNTs condensation; (b) CNTs dispersion; (c) CNTs embedded in matrix

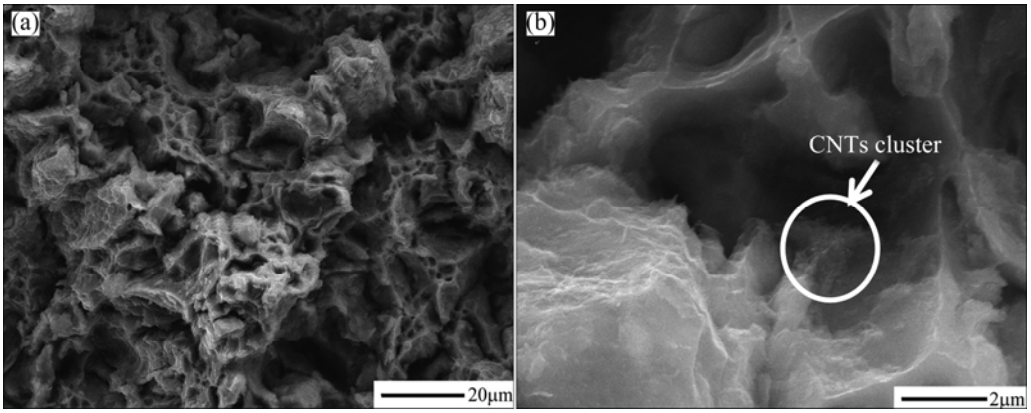

Fig. 8 SEM images of fracture surface of extruded 1%CNTs/Al-2024 after tensile test: (a) Low-magnification image; (b) CNTs condensation in Al matrix

Table 1 Mechanical properties of composites and matrix (350 r/min, 2% stearic acid and milled for 10 h)

Sample	ρ/%	σ_b/MPa	ε/%
Al-2024	97.1	203.9	7.75
1%CNTs/Al-2024	98.0	231.9	4.3
3%CNTs/Al-2024	95.0	176.9	2.88

4 Conclusions

1) Mechanical alloying is a promising technique for dispersing CNTs in Al-2024 alloy powder and controlling CNTs/Al-2024 powder morphology and size. It also delineates that ball milling time, rotation speed and PCA content can significantly influence particle morphology and size. The control of particle size is important for subsequent sintering/consolidation processes.

2) Adding 1% CNTs to the Al-2024 increases the tensile strength of the composite by 13.73% compared with Al-2024 while reduces the elongation and density slightly. Additional work is necessary to solve CNTs dispersion and pores in the Al matrix.

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球磨时间和转速对 CNTs/Al-2024 复合粉末变化的影响

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摘 要：通过机械球磨和热挤出的方法制备碳纳米管(CNTs)增强铝基复合材料。在 2024 铝合金中加入 1% CNTs，并在不同条件下进行球磨。通过 X 射线衍射仪(XRD)、场发射扫描电镜(FESEM)以及力学性能测试等方法对球磨过的粉末和块体材料的显微组织的变化和力学性能进行测试。研究碳纳米管浓度和球磨时间对 CNTs/Al-2024 复合材料显微组织的影响。通过对显微组织的观察，讨论粉末在球磨过程中的变形行为。结果表明：在 CNTs 含量相同的条件下，粉末颗粒尺寸随着球磨时间和转速的增加而减小，当球磨时间达到 15 h，粉末颗粒尺寸最小。由于 CNTs 的加入，铝合金复合材料的拉伸性能有所提高。

关键词：碳纳米管；铝基复合材料；机械球磨；显微组织

(Edited by Chao WANG)