A new system of composites: MWNT-mullite

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ABSTRACT

Carbon Nanotubes (CNTs) are attracting increasing interest as constituents of composite materials for a wide range of applications. MWNT (multi-walled CNT)-ceramics composites are in the beginning of research. The mechanical properties of MWNTs-SiO_2 composites were studied in our previous work. The aim of recent work is to develop new systems of composites and extend the potential application of advanced engineering ceramics. In this paper, MWNTs-mullite composites were firstly fabricated with HP (hot-pressing) and SPS (Spark plasma sintering). The microstructures of the composites were observed by FESEM (Field emission scanning electronic microscopy), furthermore, the mechanical and electrical properties of the composites were tested. The work is in progress to prepare new composites that could benefit from the properties of the nanotubes, paving the way for further research in the MWNTs-ceramics composites.

Keywords: multi-walled carbon nanotubes, composites, mullite, fabrication, properties

1 INTRODUCTION

Carbon Nanotubes (CNTs) are attracting increasing interest as constituents of composite materials for a wide range of applications [1-3]. Many applications of CNTs used as reinforcing additive fibers in polymers and metals have been proposed. [4,5] MWNT (multi-walled carbon nanotubes)-ceramics composites are in the beginning of research.[6-8] Fabrication and mechanical properties of MWNTs-SiO_2 composites were studied in our previous work .[9] Mullite ceramics has excellent mechanical properties, and is becoming increasingly important in electronic, optical, and high-temperature structural applications. To develop new systems of composites and extend the potential application of mullite and other advanced engineering ceramics, in the present work, MWNTs-mullite composites were firstly fabricated with HP (hot-pressing) and SPS (Spark plasma sintering). In this paper, the microstructures, the mechanical and electrical properties of the composites were discussed.

2 EXPERIMENTAL PROCEDURE

The multiwalled carbon nanotubes (purity>95%, dia. 20~40nm) fabricated by catalytic pyrolysis of hydrocarbon were kindly provided by Shenzhen NANO Tech. Port. Co. Ltd (China).

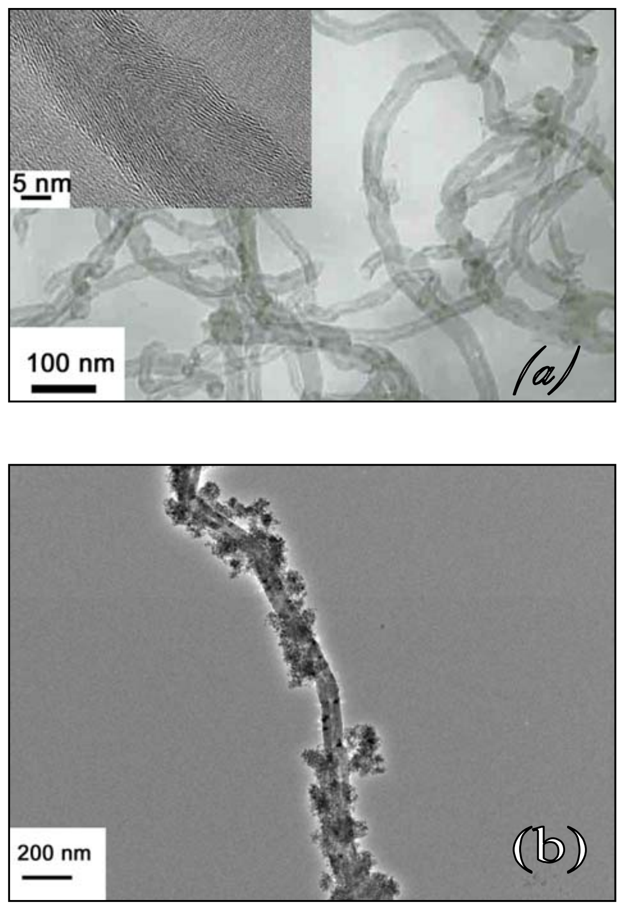

Fig.1 TEM images of MWNTs and MWNTs coated with mullite precursors

An in-situ chemical precipitation method for the synthesis of MWNTs-mullite composite powders has been reported[10]: (1) stable multi-walled carbon nanotubes (MWNTs) aqueous suspension with a 1.0 wt.% concentration was obtained with a very small quantity of dispersant; (2) Precursor of ceramics were synthesized in the suspension and densely deposited on the surface of MWNTs successfully by a simple and effective in-situ precipitation method. Transmission electron microscopy (TEM) was performed to observe the MWNTs (Fig. 1a) and the attachment of amorphous mullite precursor nanoparticles to the MWNTs. As shown in Fig.1a, the MWNTs have diameters ranging from 20 to 40 nm, lengths about tens of microns (μm), and the inner diameter is around 5 nm. The inserted HRTEM image clearly shows that nantotube is multi-walled, with approximately 15~25 walls of graphitized carbon layer. In Fig. 1b, it's obvious that the amorphous mullite precursor layer with the average particle size of 10nm is densely decorated on the wall of MWNTs. And the MWNTs are dispersed very well in the suspension.

Dense compacts of the composite powders were sintered with HP (hot-pressing, Ar atmosphere, at 30MPa in a graphite die with a diameter of 50mm at 1200, 1300, 1400, 1500, 1600 °C) and SPS (Spark plasma sintering, vacuum, with pressure 30MPa in a graphite die with a diameter of 50mm at 1100, 1200, 1300, 1400 °C).

The phase composition of the powder and composites was identified by X-ray diffraction (XRD) (Model D/max 2550V, Japan). Densities of the sintered samples were measured using the Archimedes technique. The transmission electron microscope (TEM) (Model JEM-2010) was performed to observe the micrographs of the CNTs and the mixed powders were observed**.** Field emission scanning electron microscope (FESEM) (Model JSM-6700, Japan) was used to observe the fracture surface. Composites with 5vol.%MWNTs were tested for illustration of bending strength (σ_f) that was measured by three-point method with a span of 30 mm and a crosshead speed of 0.5 mm min^{-1} (Model INSTRON-1995). The fracture toughness, K_{1C}, was evaluated by the single-edge notch beam method (Instron-1195, notch width: 0.25 mm, the notch depth: 3 mm) with six samples each data.

3 PHASE CONSTITUTION

The X-ray diffraction pattern of the MWNTs, the in-situ synthesized composite powders of MWNTs coated with mullite precursor and the dense solid composite samples (sintering temperature⩾1200 °C) were shown in Fig. 2. It's clear that the mullite precursor coated on the MWNTs has been completely transformed into mullite phase, and the MWNTs were not injured in the sintering process.

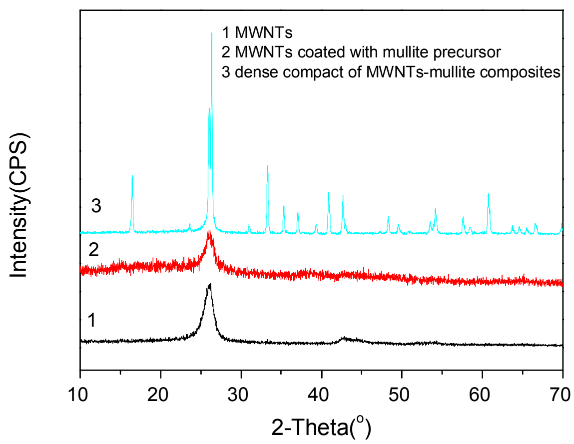

Fig.2: XRD of the MWNTs, the in-situ precipitated powders and the sintered compacts

4 DENSITY AND SINTERING TEMPERATURE

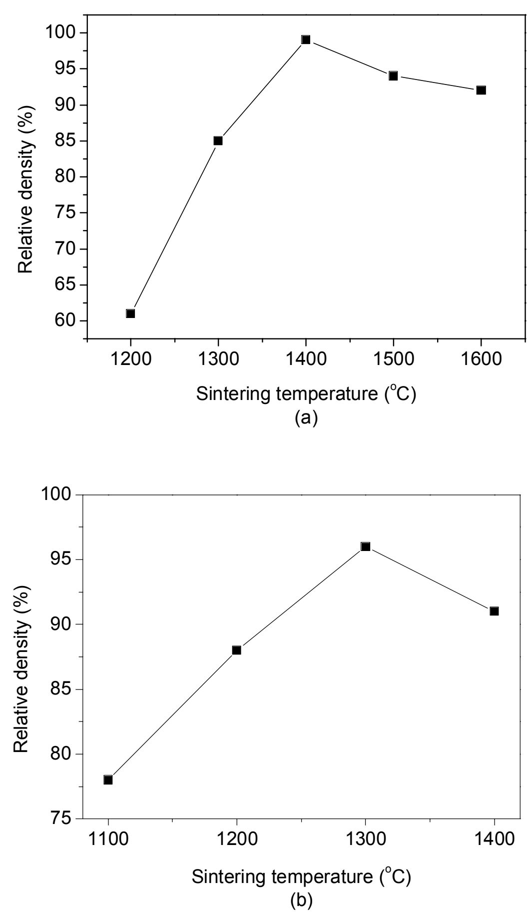

Fig.3: Relative density of 5vol.% MWNTs–mullite composites vs temperature (a) HP 1h in Ar; (b) SPS 3min in vacuum

The fully dense compact of the in-situ synthesized composite powders with HP (hot-pressing) at 1400 °C) and SPS (Spark plasma sintering) at 1200 °C. The sinter temperature is much lower than that of the traditionally mixed composite powders. [11] As shown in Fig.3, the relative densities of the 5vol.%MWNTs-mullites composites linearly increase before the peak and then decreases with the increase of sintering temperature. Data of density of all the MWNTs-composites are lower than monolithic mullite. That indicates that MWNTs may hinder the densification of mullite matrix during sintering. Furthermore, due to the tangled CNTs configuration resulted from the Van Der Wall's force between CNTs, it is difficult to homogeneously disperse CNTs in the matrix. Therefore, with the increase of CNTs volume content, more CNTs clusters existed and the relative density of the composites decrease conspicuously.

5 MICROSTRUCTURE AND PROPERTIES

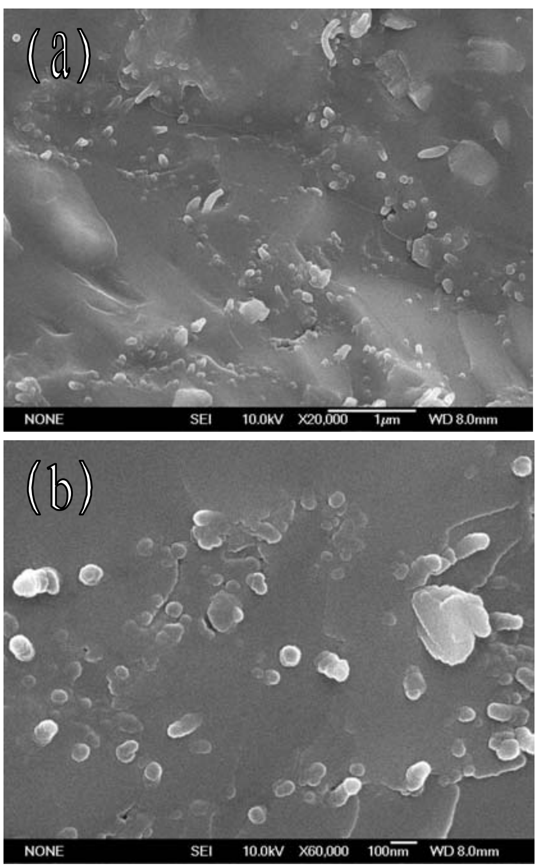

Fig.4 Images of the fracture surface of HP sintered sample of the 5vol.% MWNTs–mullite composites

Fracture surfaces of the composite sintered at 1400 °C (HP) were examined by Field emission scanning scanning electron microscopy (FESEM). MWNTs were reasonably well distributed in the mullite matrix as shown in Fig.4a. A number of MWNTs were observed pulled out (indicated by arrows in Fig.4b) from the mullite matrix. The nanotubes clearly survived from the processing and 1400 °C HP sintering.

FESEM was also performed to observe the microstructure of the dense solid composites sintered by SPS at 1200 °C (Fig.5a, b). Fig.4 shows that microstructure of the composites made from the SPS process is dense and containing no visible air pore and MWNTs are dispersed rather homogeneously in the matrix.

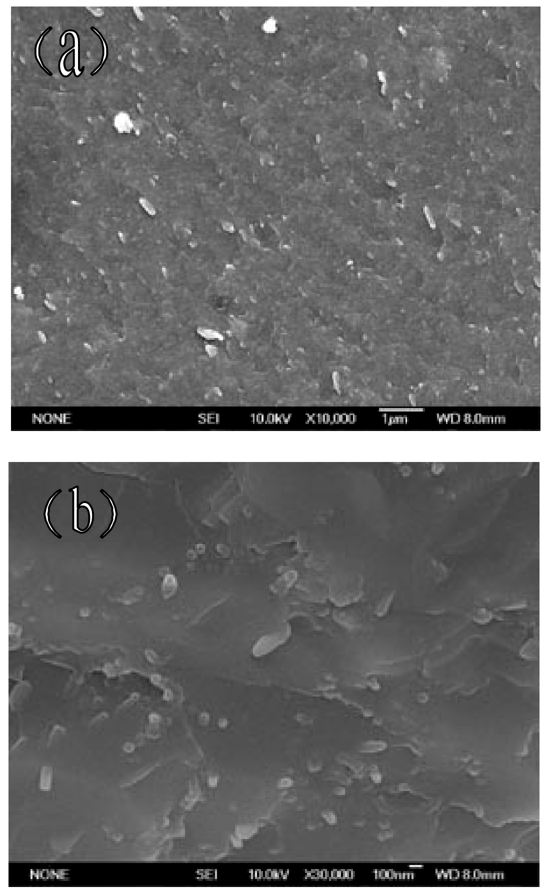

Fig.5Images of the fracture surface of SPS sintered sample of the 5vol.% MWNTs–mullite composites

The fracture toughness value of the 5 vol.% MWNTs-mullite composites is 3.8 MPa $m^{1/2}$,after sintering at 1400 °C, while it was 2.0 MPa $m^{1/2}$ for monolithic mullite made from the same process. This is about 90% increase in fracture toughness for the composite compared with the mullite. The bending strength of the composite is 380 MPa, and that of monolithic mullite is 216 MPa. This is about 80% increase in bending strength for the composite compared with the mullite. A similar improvement on SPS pressed composite was obtained.

The mullite-ceramics are insulating ($\sigma<10^{-14}$S/cm), the electrical conductivity σ of the 5vol% MWNTs-mullite composites (HP or SPS) is 0.02S/cm whereas the traditionally mixed MWNTs reinforced composites are insulating ($\sigma<10^{-6}$S/cm) [10] close to the mullite. That indicates that with the in-situ precipitation process the mullite precursor is uniformly and densely coated on MWNTs and the MWNTs are dispersed very homogeneously in the matrix and form an electrical conducting net.

6 SUMMARY

A new system of composite: multi-walled carbon nanotubes (MWNTs)-mullite ceramic matrix composites were fabricated and he mechanical and electrical properties of the composites were investigated.

It's obviously that MWNTs are dispersed very homogeneously in the matrix.microstructure of the dense solid composites a It was found that when the sample was sintered at 1400°C, the addition of 5 volume percent MWNTs led to 90% increase in bending strength and 80% increase in fracture toughness respectively, compared with the monolithic mullite. The electrical conductivity σ of the 5vol% MWNTs-mullite composites (HP or SPS) is increased greatly compared to monolithic mullite that indicate the MWNTs form an electrical conducting net.

In summary, novel dense MWNT-mullite composites have been fabricated by Hot-pressing process and Spark plasma sinter process. The introduction of CNTs can enhance the mechanical and electric properties of mullite matrix effectively.

Acknowledgements

This work was financially supported by the foundation of Shanghai Major Program (Grant No. 04DZ14002) and the Shanghai Nano Project (Grant No.0352nm053).

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