Preparation and electrical characterization of carbon nanotube /ZrO₂ composite ceramics

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Abstract. Carbon nanotubes (CNTs) in a kind of ideal reinforcements for structural materials, as well as the promising components to prepare multifunctional composites. In this paper, multi-walled carbon nanotube /ZrO₂ functional composite ceramics were investigated and successfully fabricated via the spark plasma sintering technique. The structures of nano-composite ceramics were characterized by XRD, SEM and EDS, and their mechanical and electrical properties were also studied. It was found that there is an increasing of 18% in ceramics toughness compared with pure ZrO₂ ceramics prepared by the same method. Interestingly, the results of the AC complex impedance spectra at 25~325 °C showed that the electrical resistance of the ceramics increased with the temperature under 150 °C, and will decrease dramatically when it is higher than 150 °C.

1. Introduction

Due to their high mechanical strength (strength and flexibility), excellent electrical and thermal conductivities, carbon nanotubes (CNTs) are not only ideal reinforcements for structural materials, but also promising components to prepare multifunctional composites. In recent years, much attention has been paid to the fabrication of novel CNT composites since the large scale production of multi-walled carbon nanotubes (MWNTs) has been realized. By far, various materials, including CNT-polymer composites [1-3], CNT-metal composites [4-6], and CNT-ceramic composites [7-10] have been successfully prepared. Comparing with polymer and metal matrix composites, CNT-ceramic composites are not extensively investigated, and most of them are SiO₂ [11-12], Al₂O₃ [8,13-15], SiC [7,16] ceramics matrix with CNT as a strengthening phase. However, because CNTs are usually not dispersed in the matrix and there is insufficient bonding across the nanotubes/host interface, the improvement in mechanical properties of these composites is not very satisfying. It is still a big challenge to fabricate ceramic matrix-CNT composites with high mechanical properties and other properties.

Zirconia is an important ceramic materials and has a broad range of applications, including catalysts, oxygen sensors, and fuel cells etc [17]. Zirconia and its composites have been studied extensively during the past years, but few covers the CNT/ZrO₂ ceramic composites. Sun et al [18] prepared 3 mol% yttria-doped zirconia matrix composites using multi-wall and single-wall carbon...
nanotubes as reinforcements, respectively. But their results showed that no prominent improvement on the mechanical properties, which results from the weak bond between 3Y-TZP matrix and CNTs. Here, a new method was introduced to prepare MWNT/ZrO$_2$ ceramic composites, and their mechanical and electrical properties were investigated.

2. Experimental procedure

2.1. Modifying MWNTs with ZrO$_2$ nanoparticles

MWNTs were kindly provided by Shenzhen NanoPort Company. The method of MWNTs coated with ZrO$_2$ nanoparticles was reported previously by our research [19]. The typical experimental procedure employed here was described as follows. First, the MWNTs were treated by concentrated nitric acid at 140 °C for 6 h, rinsed with distilled water and dried at 100 °C for 12 h. Second, 70 mg of acid treated MWNTs were added into vigorously stirred 30 mL of ZrOCl$_2$·8H$_2$O (0.03 M) aqueous solution. After being ultrasonicated for 0.5 h, the black solution was hydrothermal treated at 150 °C for 12 h. When it was washed and dried, the obtained products were denoted as A.

2.2. Preparation of MWNT/ZrO$_2$ composite powders

Some of the as-synthesized sample A was added into the mixed solution formed by ZrOCl$_2$·8H$_2$O, 3 mol% Y(NO$_3$)$_3$, and superfluous NH$_4$HCO$_3$. After stirring for 10 mins, the solution was first heated by microwave for 3 min and then dropped into ethanol to form a precipitation. The precipitation was calcined at 600 °C for 2 hours in a nitrogen atmosphere. A series of MWNTs/ZrO$_2$ composite powders with different content of sample A (0.5 wt%, 1 wt %, 3 wt %, 5 wt %) were prepared.

2.3. Fabrication of MWNT/ZrO$_2$ composite ceramics

The as prepared MWNT/ZrO$_2$ composite powders were sintered by spark plasma sintering (Dr. Sinter 2080 SPS apparatus) at 1150 °C for 3-4 min. A pressure of 15 MPa was applied at the beginning of the sintering process and it increased to 35 MPa after the temperature of 800 °C. After sintering, the obtained ceramics were denoted as ZrO$_2$-x wt% A (x is the content of A in the composite ceramics). For comparison, those acid treated MWNTs that without modification with ZrO$_2$ were used to prepare MWNTs/ZrO$_2$ composites followed the same procedure.

2.4. Characterization and properties measurement

The products were characterized by using X-ray powder diffraction (XRD, D/max 2550V) with Cu Ka radiation (1.5406 nm). The density of composite ceramics was measured by the Archimedes’ method. Hardness and fracture toughness were measure using a Vickers indenter (Akashi-A). Scanning electron micrographs were obtained using a Field Emission SEM (JSM-6700F, 15 kV). The impedance spectra (40 Hz to 6000 kHz) were measured at HP 4294 Impedance Analyzer.

3. Results and discussions

Figure 1 shows the X-ray diffraction patterns of pure ZrO$_2$ (a) and MWNT/ZrO$_2$ composites (b, c, d) with different contents of sample A. The most intense peaks of pure ZrO$_2$ (Figure 1(a)) correspond to the (101), (112), and (211) reflection of tetragonal ZrO$_2$ (t-ZrO$_2$, JCPDS card No. 79-1770), and a minor of monoclinic ZrO$_2$ (m-ZrO$_2$) are also detected. While in the curves of MWNT/ZrO$_2$ composites (b, c, d), they show that both t-ZrO$_2$ and m-ZrO$_2$ coexist in the composites and the t-ZrO$_2$ is dominant, but with the increase of sample A content, the quantity of m-ZrO$_2$ increases. It also found that it is very hard to elicit the characteristic peaks of the MWNTs, which mainly results from the low content of MWNTs in the composites.
The morphology of the MWNT/ZrO$_2$ composite powders was examined by TEM, as shown in Figure 2. The typical TEM micrograph in Figure 2(a) clearly shows that the surface of MWNTs was coated by zirconia particles and it is hardly to see the shell of MWNTs. EDS measurement was performed to investigate the composition of these nanoparticles. The EDS spectrum (Figure 2(b)) indicates that these particles anchored on the nanotubes consist of C, O, Zr and Y. The carbon peak come from the carbon nanotubes, and the peaks of Zr, Y and O are attributed to yttria-doped zirconia. So MWNTs coated with 3Y-ZrO$_2$ nanoparticles were successfully prepared by the method. The phases of ZrO$_2$ in the composites were mainly t-ZrO$_2$, and a minor of m-ZrO$_2$, but the more content of sample A in the composites, the more m-ZrO$_2$ were.

**Figure 1.** XRD patterns of pure ZrO$_2$ (a) and MWNT/ZrO$_2$ composite powders: (b) ZrO$_2$/1wt% A, (c) ZrO$_2$/3wt% A, and (d) ZrO$_2$/5wt% A.

**Figure 2.** TEM image (a), and EDS spectrum (b) of MWNT/ZrO$_2$ composite powders.

Table 1 shows the mechanical properties of MWNT/ZrO$_2$ composites. It can be seen that the hardness increased from 11.36 to 11.67 GPa, and the fracture toughness increased from 4.56 to 5.56 MPa·m$^{1/2}$ when the addition of A is 1 wt%. All the other samples’ mechanical properties decreased with the addition of A. When the weight content A is increased to 5%, the hardness and fracture toughness decreased by 50%. The decreases may result from the different phase of ZrO$_2$ in pure
zirconia and the composites. XRD patterns of zirconia and MWNT/ZrO\textsubscript{2} composite ceramics (Figure 3) reveals that ZrO\textsubscript{2} mainly exists in tetragonal phase in zirconia ceramics, while in the composites, m-ZrO\textsubscript{2} is dominant. It is estimated by the following relationship \cite{20}:

\[
V_m = \frac{P \chi_m}{1 + (P-1)\chi_m}
\]

where \(V_m\) is the volume fraction of m-ZrO\textsubscript{2}, and the volume fraction of t-ZrO\textsubscript{2} is given by \(V_t=1-V_m\).

\[P= 1.340, \quad \chi_m = \frac{I_m(111) + I_m(11\bar{1})}{I_m(11\bar{1}) + I_m(111) + I_m(10\bar{1})}\]

where \(I_x(l,m,n)\) represent the relative intensity diffraction from \((l,m,n)\) plane of x phase in XRD spectrum, the crystalline contents of t-ZrO\textsubscript{2} in Figure 3(a), (b) and (c) were 60.7 vol\%, 22.23 vol\% and 21.76 vol\%, respectively. Tetragonal ZrO\textsubscript{2} can improve the mechanical properties due to the transformation of t-ZrO\textsubscript{2} to m-ZrO\textsubscript{2}. The content of t-ZrO\textsubscript{2} in composites is far below that of pure zirconia ceramics, so their hardness and toughness decreased greatly. Comparing with the products in which MWNTs were not modified with ZrO\textsubscript{2}, the modified composites have better properties, which proved that after being coated with a layer inorganic species, the wettability of CNTs surface with the matrix has been improved.

**Table 1.** the mechanical properties of ZrO\textsubscript{2} and MWNT/ZrO\textsubscript{2} composites

| Specimens                  | Relative density (%) | HV(GPa) | \(K_Ic\) (MPa\(\cdot\)m\(1/2\)) |
|----------------------------|---------------------|---------|---------------------------------|
| ZrO\textsubscript{2}       | 96                  | 11.36   | 4.56                            |
| ZrO\textsubscript{2}/1wt%A | 96                  | 11.67   | 5.56                            |
| ZrO\textsubscript{2}/1.5wt%A | 95.3               | 9.233   | 3.64                            |
| ZrO\textsubscript{2}/3wt%A | 95.4               | -       | -                               |
| ZrO\textsubscript{2}/5wt%A | 94.5               | 5.47    | 2.28                            |
| ZrO\textsubscript{2}/0.5wt% acid treated MWNTs without modifications | 94.3 | 4.17 | 2.44 |

\[\text{Figure 3.} \text{ XRD patterns of 3Y-ZrO}_2 \ (a) \text{ and MWNT/3Y-ZrO}_2 \text{ composite ceramics: (b) 3Y-ZrO}_2/0.5\text{wt}\% A, and (c) 3Y-ZrO}_2/5\text{wt}\% A.}\]
Figure 4 is the SEM images of the fracture surface of 3Y-ZrO₂/0.5wt% A (a), and 3Y-ZrO₂/5wt% A (b). It is scarcely to see MWNTs in ZrO₂/0.5 wt% A due to the low content of MWNTs. With more addition of sample A, most MWNTs are located at the zirconia grain boundary. All the samples’ fracture surface exhibited intergranular fracture.

![Figure 4](image1.png)

Figure 4. SEM images of the fracture surface: (a) ZrO₂/0.5wt% A, and (b) ZrO₂/5wt% A.

The AC complex impedance spectra (40 Hz to 6000 kHz) of MWNT/ZrO₂ ceramics were investigated. The electrical resistivity of ZrO₂ ceramics at room temperature decreases after addition of ZrO₂ modified MWNTs, but it shows no regularity with increasing of the modified MWNTs. Figure 5 (a) is a typical AC complex impedance spectra of ZrO₂/1.5 wt% A at different temperature. A single semicircle is seen in the complex impedance, which means the grain boundary resistance dominates the overall impedance. The dependence of electrical resistivity on temperature (as shown in Figure 5 (b)) shows that the electrical resistance of the composite ceramics increases with the temperature under 150 °C, and decrease dramatically when it is higher than 150 °C. The further conductive mechanism is under way.

![Figure 5](image2.png)

Figure 5. (a) the AC complex impedance spectra of ZrO₂/1.5wt% A at different temperature, (b) the dependence of electrical resistivity in composites on temperature.

4. Conclusions

MWNT/ZrO₂ composite ceramics were successfully fabricated via the spark plasma sintering at 1150 °C. It was found that, no obvious incensement in mechanical properties was achieved after addition of ZrO₂ modified MWNTs, which is because more m-ZrO₂ was formed after sintering comparing with pure ZrO₂ ceramics. The results of the AC complex impedance spectra showed that the electrical resistance of the composite ceramics increased with the temperature under 150 °C, and will decrease dramatically when above 150 °C.
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