



Synthesis of zirconia nanoparticles on carbon nanotubes and their potential for enhancing the fracture toughness of alumina ceramics

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ARTICLE INFO

Article history:

Received 28 January 2008

Accepted 29 March 2008

Available online 10 April 2008

Keywords:

A. Zirconia

A. Carbon nanotube

A. Alumina

B. Mechanical property

ABSTRACT

Nanoparticles of zirconia (ZrO_2) were in situ synthesized on the surface of carbon nanotubes by means of liquid phase reactions and a proper heat treatment process. The size of the nanoparticles could be controlled by the amount of zirconium source materials in a solution and its reaction times. In this study, the size of the nanoparticles ranged from several nanometers to twenty nanometers. It was particularly noted that the synthesized zirconia possessed a cubic structure (c-phase) which generally existed as a stable form of zirconia crystals at high temperatures (above 2370 °C) as well as a form of zirconia that could be used for enhancing the fracture toughness of alumina ceramics. Experimental results showed that the mechanical properties of alumina ceramics mixed with in situ synthesized nanoparticles on the surface of carbon nanotubes were much better than that of pristine nanotubes or zirconia nanoparticles alone. The existence of the nanoparticles on the surface of nanotubes results in improving the dispersion and bonding properties of the nanotubes in alumina matrix environment. The fracture toughness of CNT/ ZrO_2 alumina ceramics was also improved by the mechanism of bridging effect.

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1. Introduction

Zirconia (ZrO_2) is one of the important materials used in the industry because of its high melting point, high mechanical properties, low thermal conductivity and high ionic conductivity. ZrO_2 has three polymorphs, they are (i) monoclinic (m-phase, below 1170 °C), (ii) tetragonal (t-phase, between 1170 and 2370 °C) and (iii) cubic (c-phase, above 2370 °C). With the decrease of temperatures to 2370 °C and 1170 °C, the structures of ZrO_2 will transform from c-phase to t-phase and m-phase, respectively. The high temperature phases (t- and c-phases) of ZrO_2 could be used as reinforcement for toughening alumina through three major mechanisms: they are phase transformation, second phase conversion, and micro-cracking. In order to obtain high temperature stable c- and t-phases of ZrO_2 at room temperature, it is necessary to incorporate other dopants into the crystal lattice, these dopants include CaO, MgO, Y_2O_3 , CeO_2 , Mg_3N_2 , Si_3N_4 , AlN, etc [1–3]. The stabilization of ZrO_2 can be achieved after it is sintered into a nitrogen environment provided either by molecular nitrogen or by solid nitrides [4]. Wang et al. [5] have reported that t- ZrO_2 would be

obtained by carburizing pure m- ZrO_2 powder at 1500 °C. Previous studies on the oxidation of ZrC powder also indicated that the microstructure of cubic ZrO_2 containing a certain amount of carbon, which suggested that carbon plays an important role in stabilizing cubic ZrO_2 [6,7].

Multiple applications have been expected for carbon nanotubes (CNTs) since they were discovered by Iijima in 1991 [8], notably as part of a new class of extraordinary strong material and therefore many research works have been currently devoted [9] to their incorporation into a metal-, ceramic-, or, more commonly, polymer-matrix. The composites were generally prepared by mixing the desired quantity of single- or multi-walled carbon nanotubes (SWNTs and MWNTs, respectively) with the matrix, which was either dissolved or suspended in a liquid medium, before further treatments. Many researchers have aimed at using CNTs to enhance the mechanical properties of composites. In the case of ceramic materials, two concluding remarks have been made to date. Some researchers have claimed that [10–14] CNTs seems to be effective toughening reagents for brittle materials, i.e. to produce bridging effect when the ceramics is subjected to a tensile load, which result in enhancing its fracture toughness. In addition, CNTs could also enhance the tribological behaviour of ceramics as the CNTs are relatively hard materials [15]. However, both the high aspect ratio (mostly more than 1000) and the small diameter (no more than one hundred nanometers) of CNTs induce many

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difficulties to satisfactorily disperse them within the matrix due to an agglomeration effect, particularly when the matrix material was in the granular form such as ceramic powder. It would be pernicious to both of the mechanical and physical properties of the composites. To resolve such problems, Peigney et al. [16,17] have proposed the use of in situ synthesis of CNTs within the oxide powder. In the obtained composite powder (with Al_2O_3 , MgAl_2O_4 or MgO matrix), SWNTs and MWNTs should be homogeneously distributed.

It was noticed that there were many inconsistent results reported as for the effects of CNTs in alumina ceramics. For example, Siegel et al. [13] have found the increase of fracture toughness of alumina ceramics by 24% with the addition of 10 vol% of CNTs. Laurent et al. [18] have claimed that no prospective reinforcement and toughening effect was observed by adding bundles of CNTs into $\text{Fe-Al}_2\text{O}_3$ composites. Zhan et al. [10] prepared composites by blending alumina powder and SWNTs and then sintered by means of spark-plasm sintering (SPS). The fracture toughness of the composites was measured using the Vickers-indentation method. An exciting result of the fracture toughness ($9.7 \text{ MPa m}^{0.5}$) was obtained with addition of 10 vol.% of SWNTs which should be three times, respectively, higher than that of common alumina ceramics. The efficient toughening effect was attributed to the advantages of SWNTs and low sintering temperature during SPS which would correspondingly decrease the demolishment to the SWNTs at high sintering temperatures. However, Sheldon et al. [19] and Padture et al. [20] have argued that the reliability of these results. Recently, Fan et al. [21] prepared a MWNTs/ Al_2O_3 composites with the volume content of MWNTs was 12%. By means of the direct measurements with single-edge V-notched beam specimens, the fracture toughness of the composites increased to $5.55 \pm 0.26 \text{ MPa m}^{0.5}$, 1.8 times that of pure Al_2O_3 , and the flexure strength varied slightly.

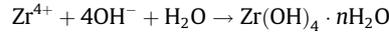
Luo et al. [22,23] added CNTs during the process of preparing ZrO_2 and obtained ZrO_2 nanoparticles made up of the cubic phase. It revealed that the addition of CNTs would be propitious to the transition from monoclinic ZrO_2 to cubic ZrO_2 and to the stabilization of cubic ZrO_2 at room temperature. The results suggested that it would be possible to toughen alumina ceramics by cooperative addition of CNTs/ ZrO_2 with the nanometer zirconia particles loaded on surfaces of the CNTs.

In this paper, ZrO_2 nanoparticles were in situ synthesized on the surfaces of CNTs and then applied to alumina ceramics. The toughness of resultant alumina ceramics mixed with CNTs was also investigated. Alumina ceramics would be modified by the complex effects of ZrO_2 nanoparticles and CNTs.

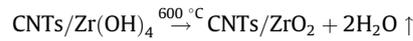
2. Experimental

2.1. Materials preparation

CNTs were prepared by chemical vapor depositing (CVD) and treated in boiling HF for 2 h to remove the amorphous carbon on the surfaces of CNTs, and then rinsed continuously into chemically neutral with deionized water. High purified CNTs were obtained after drying. The CNTs were added into deionized water with about 0.3 wt% of sodium dodecyl sulfonate (SDS) as a surfactant. The suspension of CNTs in deionized water was then sonicated to produce well dispersed CNTs in water. ZrCl_4 was added in the suspension with a proper concentration which could be adjusted according to the CNTs content in the suspension. The mass ratio of ZrCl_4 to CNTs was 4:40. The more ZrCl_4 added, the more the ZrO_2 nanoparticles prepared. Enough amount of dense ammonia was added into the suspension with strongly stirring, and a large amount of zirconium hydroxide gel formed instantaneously



The gel particles with about 2 μm of diameters were percolated and rinsed continuously to chemically neutral with deionized water. After being dried at 200–300 °C to remove the crystallization water, $\text{Zr}(\text{OH})_4$ powders on CNTs were prepared. The mixed powders were then calcined at 600 °C for 2 h under argon protection and transformed into the mixture of ZrO_2 and CNTs in which ZrO_2 particles were loaded on the surfaces of CNTs



The amount and sizes of the ZrO_2 particles were controlled by adjusting the addition of the zirconium source (i.e. ZrCl_4). The products at two different stages (i.e. before and after calcination at 600 °C) of the in situ synthesis were tested by means of X-ray diffraction (XRD).

The mixture of ZrO_2 and CNTs was added into alumina for toughening by different ways: mechanical mixing and blending in liquid. The blending with different contents were sintered under a pressure of 50 MPa at 1500 °C in vacuum ($\leq 6.67 \times 10^{-2}$ Pa). The samples containing different ZrO_2 /CNTs content were prepared for mechanical property tests.

In order to compare effects of the proposed manufacturing process of ZrO_2 /CNTs with pure CNTs and ZrO_2 on the mechanical properties of the prepared ceramic composites, four different kinds of alumina ceramics specimens were prepared for the tests (see Table 1).

2.2. Mechanical property tests

From the sintered plates with a diameter of 20 mm, prismatic bar specimens with the dimension of 16 mm (L) \times 4 mm (H) \times 2 mm (W) were cut for a flexural strength test (three-point bending) according to GB/T 6569-1986 (testing method for flexural strength of high performance ceramics). The fracture toughness tests were carried out with identical specimens but with a notch of 2 mm deep on an edge of the specimen by the same method according to JIS R1607-1995 (testing methods for fracture toughness of fine ceramics). The fracture toughness K_{IC} was calculated by

$$K_{\text{IC}} = \frac{LP}{WH^{3/2}} \times F$$

$$F = 2.9 \left(\frac{C}{H}\right)^{1/2} - 4.6 \left(\frac{C}{H}\right)^{3/2} + 21.8 \left(\frac{C}{H}\right)^{5/2} - 37.6 \left(\frac{C}{H}\right)^{7/2} + 38.7 \left(\frac{C}{H}\right)^{9/2}$$

Table 1
preparing conditions of the mechanical property testing specimens

Specimen	Preparing method
Alumina	Directly sintering with commercial alumina powders
Alumina + CNTs	CNTs treated with anionic surfactant and alumina treated with a cationic surfactant were blended for 15 min in deionized water under supersonic. The blending with a load of about 2 wt% CNTs was sieved and dried for sintering
Alumina + ZrO_2	Commercial nanometer ZrO_2 powders with proper amount of Y_2O_3 as a dopant were blended with suspension of alumina in deionized water under supersonic for 15 min. The blending with a load of 25 wt% ZrO_2 was sieved for sintering
Alumina + ZrO_2 /CNTs	CNTs treated with anion surfactant was added into suspension of ZrCl_4 (with Y_2O_3) in deionized water under supersonic for 15 min. Alumina with ammonia were added into the liquid. The blending was sieved and dried, and then calcined at 600 °C for 2 h in argon atmosphere. The loads of CNTs and ZrO_2 were about 1.5 wt% and 25 wt%, respectively

here L , H , and W are the dimension sizes of the specimens, respectively; P is the load at break of the specimens, and c the depth of the notch.

3. Results and discussion

3.1. Microstructures of the in situ synthesized products

The XRD (Cu $K_{\alpha 1}$ radiation) results of the in situ synthesized products are shown in Fig. 1. It is seen that the products before calcination ($Zr(OH)_4$) possess an amorphous transition form (see Fig. 1a), and the final products after calcination at 600 °C (ZrO_2) was in a cubic structure (see Fig. 1b). Meanwhile, Fig. 1a and b show also peaks responding to the CNTs structure. This result indicates that the structure of the in situ synthesized ZrO_2 particles was stabilized as cubic with CNTs existing at room temperature which was consistent with the previous studies [6,7,22,23].

The morphologies of the synthesized ZrO_2 nanoparticles on the surfaces of CNTs are shown in Fig. 2. Moreover, the size of the ZrO_2 nanoparticles could be controlled by adjusting the experimental

conditions such as the content of the zirconium source ($ZrCl_4$) in the liquid medium, synthesis reaction time. Fig. 3 shows the ZrO_2 nanoparticles on the surface of CNTs with different sizes synthesized under different zirconium resource concentrations. Therefore, the in situ synthesized ZrO_2 nanoparticles would be ideally used for enhancing the toughness of alumina ceramics.

3.2. Mechanical properties

The results extracted from the mechanical property tests are shown in Fig. 4. It should be mentioned that the results of the samples with zero ZrO_2 content shown in Fig. 4 were from samples obtained by blending pristine alumina and 2 wt% CNTs. The CNTs were same as that for ZrO_2 to be loaded on as mentioned previously in 2.1. As for the samples from pristine alumina, the flexural strength and fracture toughness tested were 302 ± 20 MPa and 3.56 ± 0.4 MPa $m^{0.5}$, respectively. It is seen that both of the flexural strength and fracture toughness of the alumina ceramics increase with the increase of the ZrO_2 content. Increasing the amount of ZrO_2 in the alumina ceramics, the higher the flexural strength cannot be obtained. In the present work, the highest flexural strength reached about 740 MPa that was about 120% higher than that of alumina ceramics with only using approximately 2 wt% of CNTs but without ZrO_2 . The fracture toughness increased rapidly with the increase the amount of ZrO_2 at first, then tended to be stable after the ZrO_2 exceeds 15 wt%, and reached the highest value of 7.8 MPa $m^{0.5}$ at about 25 wt% of ZrO_2 content. The peak value of the fracture toughness was about 53% higher than that of alumina ceramics with only use of 2 wt% of CNTs but without ZrO_2 , and about 119% higher than that of pristine alumina ceramics. Simultaneously, the flexural strength of the same samples were evidently improved compared both of the samples with 25 wt% and without zirconia.

It was worthy to be mentioned that the values of the fracture toughness tested in this work were somewhat highly estimated due to the blunt notch resulted from the current sample processing method taking into consideration of the fracture toughness of pristine alumina about 3.0–3.2 MPa $m^{0.5}$ [24]. The densities of the different samples are shown in Table 2. Both of the density and relative density of the alumina modified by CNTs/ ZrO_2 increased almost linearly with increasing zirconia loading.

The effects of modifying ways with CNTs and ZrO_2 (see Table 1) on the mechanical properties of prepared ceramic composites are shown in Fig. 5. It was noticed that the additions of either individual CNTs or ZrO_2 increased both the flexural strength and fracture toughness of the alumina composites, and moreover, the cooperative addition of CNTs and nanometer scale ZrO_2 loaded on the

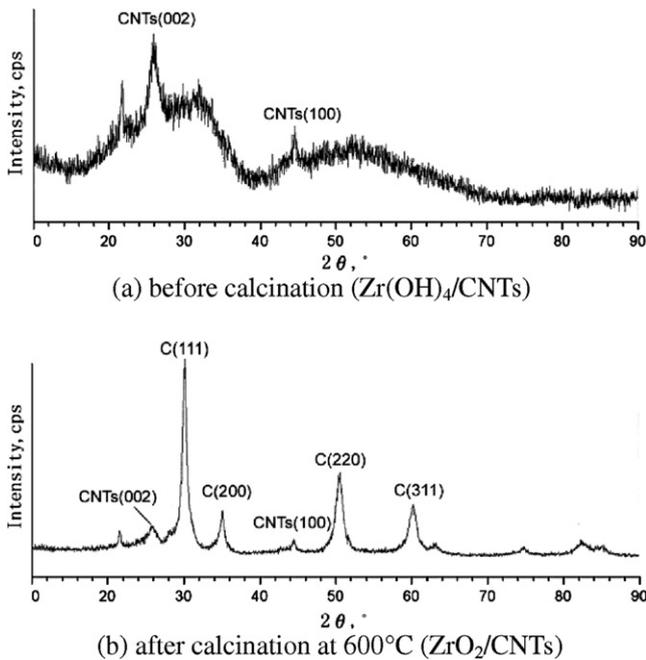


Fig. 1. The XRD spectrum of the in situ synthesized products at different stages.

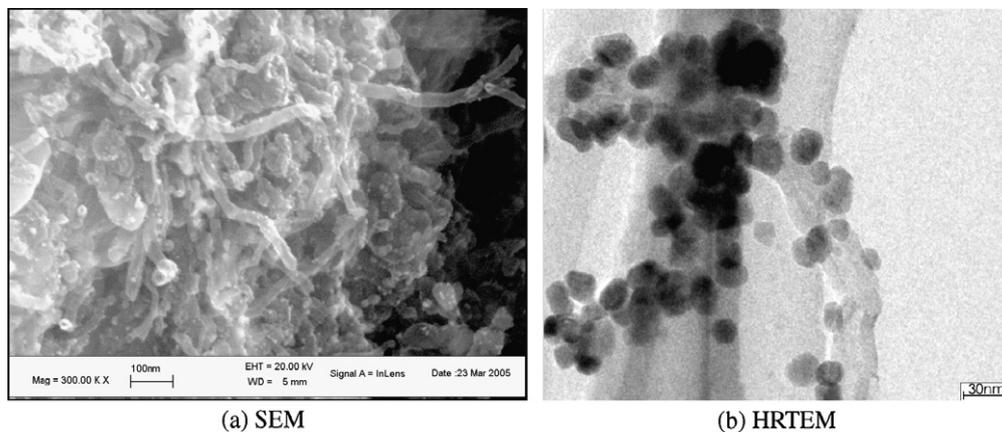


Fig. 2. The mixture of ZrO_2 and CNTs (a) and the morphology of ZrO_2 particles on the surfaces of CNTs (b).

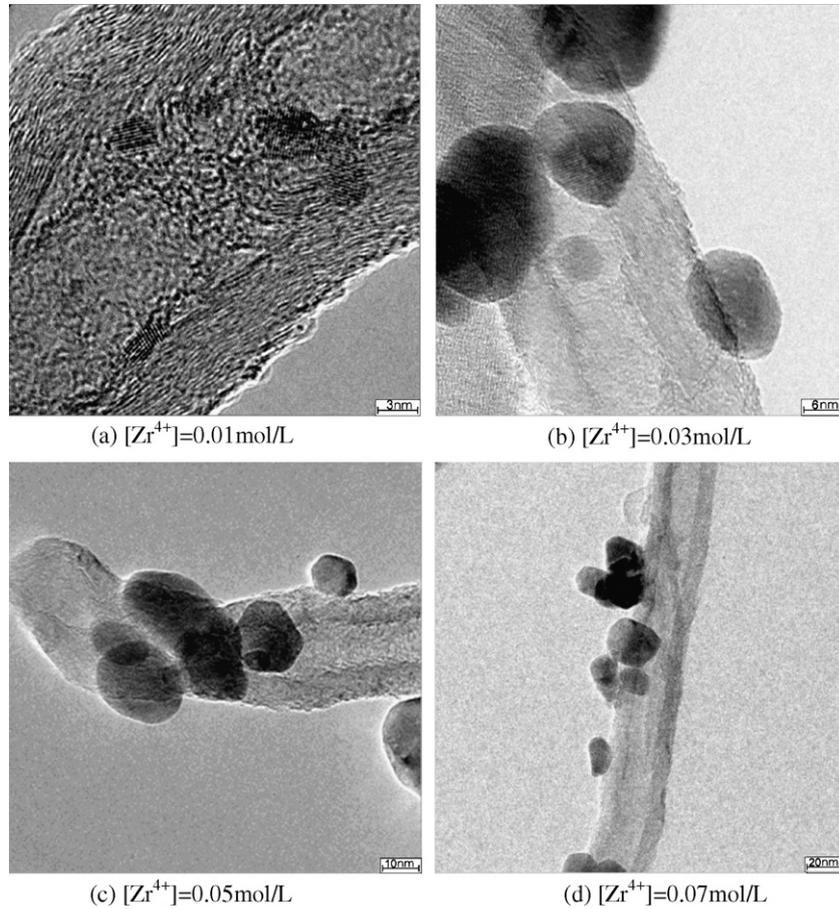


Fig. 3. Morphologies (HRTEM) of the ZrO₂ particles on CNTs with different sizes prepared with different Zr⁴⁺ concentrations.

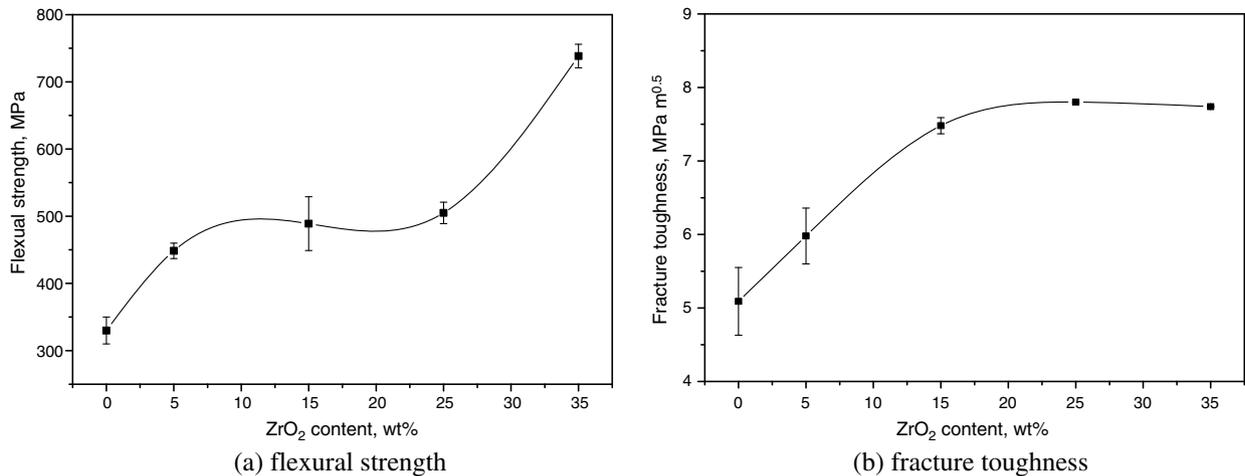


Fig. 4. Effects of the content of ZrO₂ loaded on surfaces of the CNTs on the mechanical properties.

Table 2
Measured and theoretic densities of the samples

ZrO ₂ content (wt%)	0	5	15	25	35	Pristine alumina
Measured (g/cm ³)	3.82	3.89	4.25	4.46	4.72	3.88
Theoretic (g/cm ³)	3.93	4.04	4.27	4.50	4.73	3.97
Relative (%)	97.2	96.3	99.5	99.1	99.8	97.7

surfaces of the CNTs would combine the beneficial effects of modification in alumina. Fig. 6 shows the fracture surfaces of the specimens after fracture toughness measurement which including

1.5 wt% of CNTs and 25 wt% of ZrO₂. The bridging effects of CNTs loaded by zirconia nanoparticles between two alumina grains and outcrops of CNTs are visual on the fracture surfaces. As shown in Fig. 5, the flexural strength and fracture toughness of the composites containing 1.5 wt% of CNTs and 25 wt% of ZrO₂ are 67% and 119% higher than that of the pristine alumina ceramics.

The fracture surface of the specimen was chemically analyzed by means of electron spectroscopy to confirm the surviving CNTs loaded with zirconia after the hot-press sintering, the result is shown in Fig. 7. It was mentioned that the fracture analyzed was

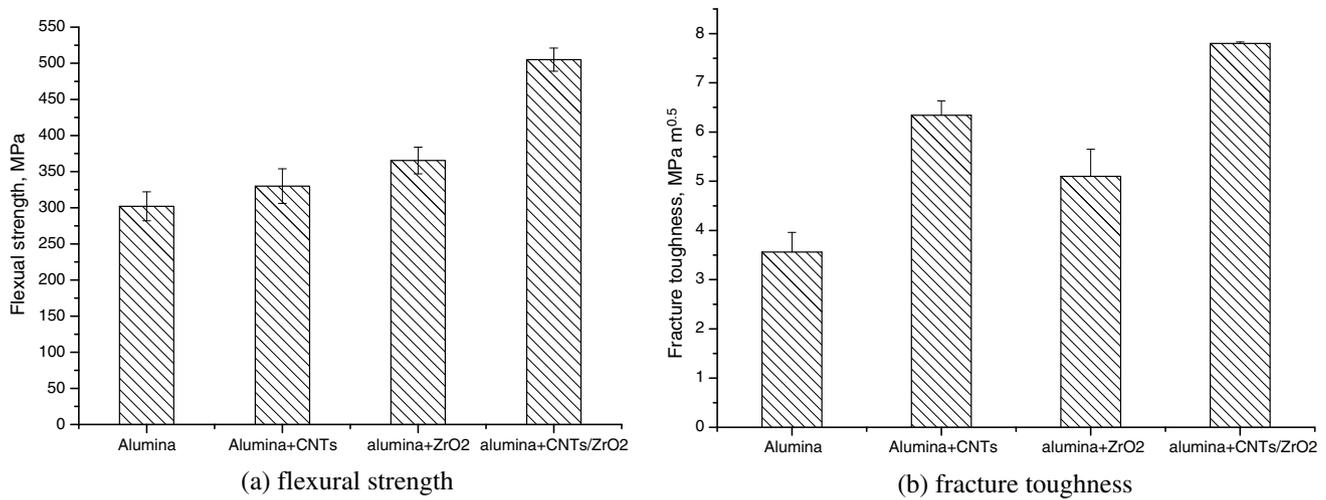


Fig. 5. Comparison of the mechanical properties of specimens prepared by different ways.

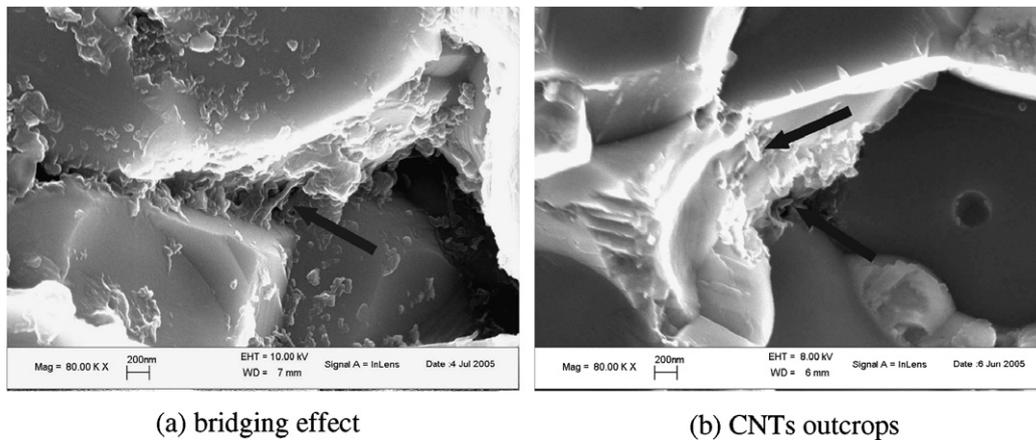


Fig. 6. Fracture morphologies of the alumina modified by CNTs/ZrO₂, SEM.

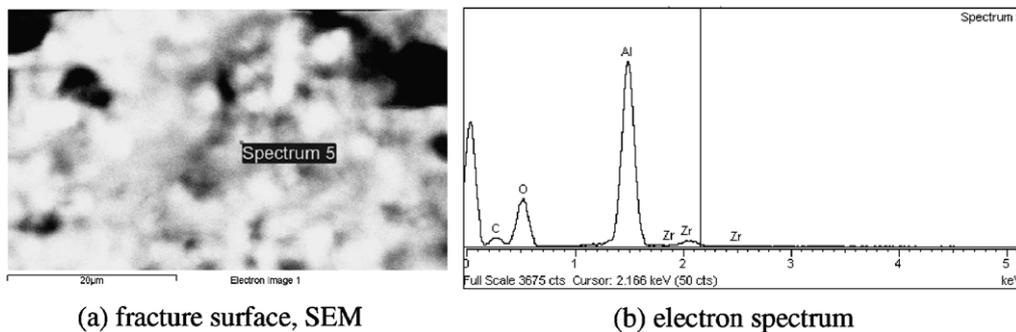


Fig. 7. Chemical analysis result of the specimen after mechanical test.

maintained the original status without any deposition in order to assure the correct chemical composition results and so that the image under SEM was somewhat unclear because of the dielectric characteristics of the ceramics composites.

From a crack growth resistance viewpoint, the fracture toughness of the zirconia toughening alumina (ZTA) materials was assumed to be the sum of the intrinsic toughness of the alumina matrix and the toughness increment due to several toughening mechanisms introduced by the zirconia particles: (1) phase transformation toughening [25–28]; (2) micro-cracking (intrinsically related to phase transformation) which then promoted a toughening effect through the permanent dilatation and reduced elastic mod-

ulus that they implied around the crack tip [26]; (3) internal stresses effects (as a result of thermal expansion differences between the two-phases) that induced compressive residual stresses within the alumina matrix [29]. The toughening effect of CNTs in ceramics was mainly attributed to two kinds of mechanisms, crack bridging and pullout on the fracture surfaces. Zhan et al. [10] proposed three critical factors to ensure the reinforcement of CNTs in ceramics. First, the properties of the individual CNTs must be optimized. Second, the CNTs must be sufficiently bonded to the matrix so that they actually carried the loads. Third, the load must be distributed throughout the nanotube to ensure that the outermost layer did not shear off.

In this work, the zirconia nanoparticles supported by CNTs may result in an enhance second phase toughening effect, and a good dispersion of CNTs could be reached and retained in the alumina matrix due to the separation among bundles of CNTs resulted from the ZrO₂ particles on the surfaces of CNTs (see Fig. 6). Moreover, the ZrO₂ particles on the surfaces of CNTs could efficiently improve the interaction between CNTs and alumina matrix by either chemical bonding or mechanical interlocking, and then facilitate the energy dissipation effect caused by CNTs during the crack propagation process. Simultaneously, the well dispersed CNTs with nanometer scale ZrO₂ particles on their surfaces effectively reinforced the alumina matrix. Therefore, both of the flexural strength and fracture toughness of the alumina ceramics composites modified by the synthesized CNTs/ZrO₂ were remarkably improved (see Fig. 5).

4. Conclusions

ZrO₂ nanoparticles were in situ synthesized by liquid–liquid two-phase method, and CNTs were applied as the templates for supporting the ZrO₂ nanoparticles. The amount and sizes of the ZrO₂ nanoparticles could be controlled by adjusting the zirconium source material content and the reaction time during the in situ synthesis process. The existence of CNTs was propitious for the formation of fine ZrO₂ particles and maintenance of their beneficial high temperature phase structure at room temperature. The products were added into the suspension of alumina in liquid medium for the preparation of alumina ceramics composites. Both of the flexural strength and fracture toughness of the composites increase with the increasing zirconia contained in the composites. The alumina ceramics composites contained 1.5 wt% CNTs and 25 wt% ZrO₂ displayed the flexural strength and fracture toughness of 505 MPa and 7.8 MPa m^{0.5}, respectively that were about 67% and 119% higher than that of pristine alumina ceramics. The in situ synthesized ZrO₂ nanoparticles on surfaces of CNTs could result in an enhance toughening effect and improve the interaction between CNTs and alumina matrix, and then both of the beneficial toughening effects of CNTs and ZrO₂ nanoparticles could be brought into play in alumina ceramics. Therefore, the toughening effects by addition of the in situ synthesized ZrO₂ particles on surfaces of CNTs were much better than that resulted from application of either CNTs or nanometer ZrO₂ powders individually.

Acknowledgements

Project is sponsored by the Foundation of National Natural Science, PR China (Grant No. 10332020) and the Innovation Fund for Outstanding Scholar of Henan Province, PR China (Grant No. 0521001000).

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