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Microstructure and properties of carbon nanotube/zirconia composite

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Abstract

Sintering and hot pressing have been used for preparation of monolithic ZrO_2 and zirconia–carbon nanotube (CNT) composite. The effect of the processing route and the CNT's addition on the microstructure, fracture/mechanical and electrical properties of the zirconia has been investigated at room temperature. The microstructure of the sintered and hot-pressed monolithic ZrO_2 consists of a submicron-sized grains. The matrix of the ZrO_2–CNT composite consists of a grains with even smaller size (approximately 140 nm) with relatively well dispersed carbon nanotubes. The hardness and the indentation toughness of the sintered monolithic zirconia are 1297 kg/mm^2 and 8.01 MPa m$^{0.5}$ and of the hot-pressed monolithic zirconia 1397 kg/mm^2 and 6.24 MPa m$^{0.5}$, respectively. The addition of the CNT's decreased the hardness and indentation toughness to 830 kg/mm^2 and 5.6 MPa m$^{0.5}$ however the electrical resistivity decreased significantly in comparison to the monolithic zirconia to the value of 0.1 Ω cm.
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Keywords: Nanocomposites; Mechanical properties; Electrical properties; Failure analysis

1. Introduction

During the last decade, there has been a steady increasing interest in development of advanced ceramic composites with improved mechanical and physical properties by incorporating second phase particles/whiskers into the ceramic matrix.[1,2] The discovery of carbon nanotubes has generated in recent years considerable interest in their use as reinforcements or functionalizing elements in different materials, including ceramics, due to their high Young's modulus (∼1500 GPa), high tensile strength (∼100 GPa), high aspect ratio, as well as high electrical conductivity and good thermal conductivity.[3] Single-wall and multi-wall nanotubes (SWNT, MWNT) and different processing routes have been used for preparation of CNTs/ceramic composites including sintering + post-hot isostatic press (HIP), hot press (HP), etc.[4–8] Recently spark plasma sintering (SPS) has been applied which reduce the risk of the carbon nanotubes' damage thanks the low sintering temperature and short sintering time.[6]

A number of authors reported improved mechanical and functional properties in the case of ceramic/CNT composites compared to the monolithic material.[6–8] According to the results of Zhan et al.[6] CNT/ceramic nanocomposites exhibit thermoelastic properties with a potential to use them as promising thermoelastic materials. The investigations focused mainly on alumina-based ceramic composites and only limited work was devoted to further systems based on silicon nitride or zirconia.[9–11]

Zirconia (3Y-TZP) is a very promising material for many structural applications due to their high mechanical properties. Zirconia or/and zirconia-based composites are interesting multifunctional materials for many further applications as solid oxide fuel cells, oxygen sensors and ceramic membranes due to their good high-temperature stability, high breakdown electrical field or large energy bandgap.[12]

The aim of the present contribution is to investigate the influence of the processing route and carbon nanotube addition on the microstructure, mechanical, fracture and electrical properties of zirconia.

2. Experimental procedure

The starting materials were ZrO_2 powder (TZ-3Y, Tosoh, Japan) and carbon nanotube (1.07 wt.%). The monolithic zirconia was prepared by sintering and hot pressing. The specimen

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in the form of discs with diameter of 20 mm were die pressed and than sintered at the temperature of 1400 °C/60 min and hot pressed at the temperature of 1300 °C/30 min. Carbon nanotubes (also called hollow nanofibres, HTF150FF, Electrovac, Austria) with an average diameter of 80–150 nm, specific surface area in a range of 20–100 m^2/g, Young's modulus ∼ 500 GPa, tensile strength ∼ 7 GPa and electrical resistivity of 10^{-3} to 10^{-4} Ω cm have been used. A water-based mixture was prepared with dispersant (DODECYLE MARANIL), CNTs, ZrO_2 and a polyvinylbutryl binder (MOWITAL B30T). The dispersion was primarily done using ultrasonics and a magnetic stirrer. After the dispersion, the mixture was subsequently spray dried. Specimens in the form of discs with a diameter of 10 mm and 20 mm were die pressed and after this hot pressed at 1300 °C/30 min.

The density of the experimental materials has been measured using the Archimedes method. XRD analysis (Phillips, X-pert) has been used for the determination of the phase composition of the experimental materials. Specimens for microstructure examination were prepared by diamond cutting, grinding, polishing and thermal etching. The microhardness (Leco instruments) and hardness were studied by Vickers indentation method at loads from 0.25 N to 150 N. Indentation toughness testing was carried out for estimation of the toughness of the materials at 150 N using a Vickers indenter and the Shetty equation.[13]

The microstructure and the fracture surface of the materials have been studied using scanning electron microscopy (SEM). The specimens were thermally etched at a temperature of 1250 °C and microfractography was used for analysis of the fracture lines and surfaces of the specimens.

The electrical resistivity was measured at room temperature using a four-point method. Specimens with the dimension of 1.5 mm × 1.5 mm × 10 mm were cut from the centre of the hot-pressed samples for these measurements.

3. Results and discussion

The sintering and hot-pressed monolithic zirconia exhibits nearly full density but the density of the ZrO_2–CNT composite was lower due to the porosity in the composite connected mainly with the clusters of the carbon nanotubes present in its microstructure. XRD analysis revealed that the experimental materials consist of mainly *t*-ZrO_2, however a small amount of monoclinic zirconia and yttrium oxide carbide has also been found, too.

In Fig. 1 the microstructure of the monolithic hot-pressed zirconia and the composite is illustrated at lower magnification. The monolithic sintered and hot-pressed zirconia consists of a very low, submicron/nanometer-sized grains with randomly occurring defects in the form of very small-sized pores with dimensions of approximately 100–200 nm, mainly in the sintered material (Fig. 2a and b). The average grain size of the ZrO_2 in the sintered and hot-pressed zirconia is 190 nm and 162 nm, respectively. The size distribution in both materials is similar as it is illustrated in Fig. 3. The microstructure of the composite consists of similar or an even smaller grained matrix (Fig. 2c) with relatively well dispersed CNTs) in the matrix, Fig. 1b (pores with their shape/orientation indicating the locations of the burned out CNTs during the thermal etching. The lower grain size of the zirconia together with the lower density of the composite compared to the monolithic material are evidence that the CNTs may hinder the sintering behavior of the zirconia-based composite.

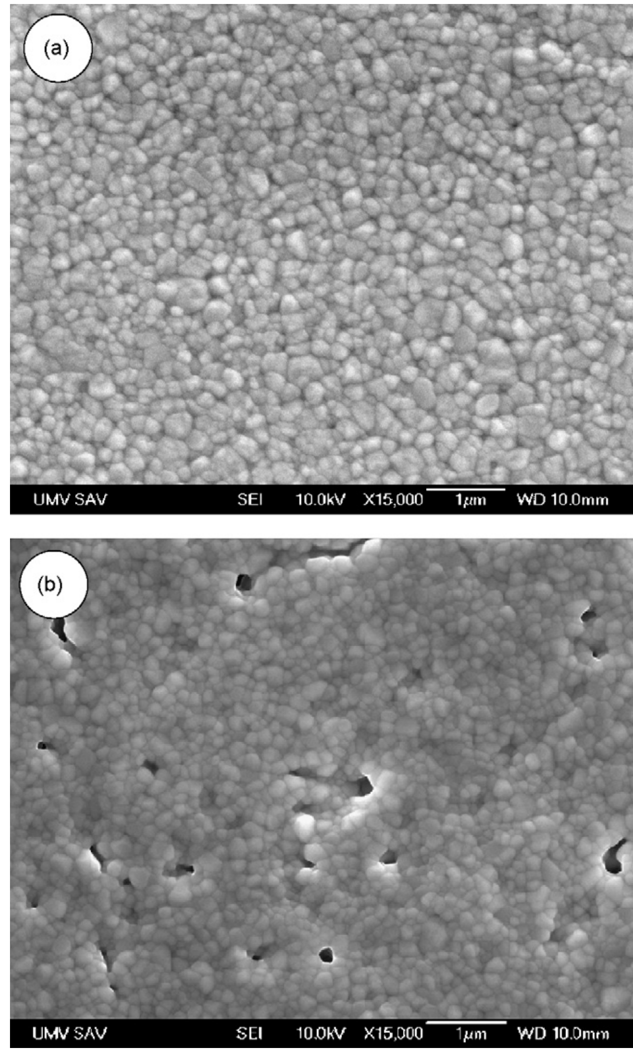

Fig. 1. Microstructure of the hot-pressed zirconia (a) and CNT–zirconia composite (b), SEM, thermally etched. Pores with their shape/orientation indicating the locations of the burned out CNTs during the thermal etching.

Relatively high amount of clusters of the CNTs have been found on the polished surface and fracture surface of the samples indicating that the mixing procedure has to be improved (Fig. 3). The size of the clusters varies from a few microns up to approximately 20 μm and porosity was always connected with these clusters (Fig. 4).

In Table 1 the basic properties such as the hardness and indentation toughness is presented together with the values of the electrical resistivity for the monolithic zirconia and for the composite. The hardness is increasing and the indentation toughness is decreasing with the decreasing grain size of the monolithic zirconia. The hardness and indentation toughness decreased after addition of CNTs to the zirconia. On the other hand the electri-

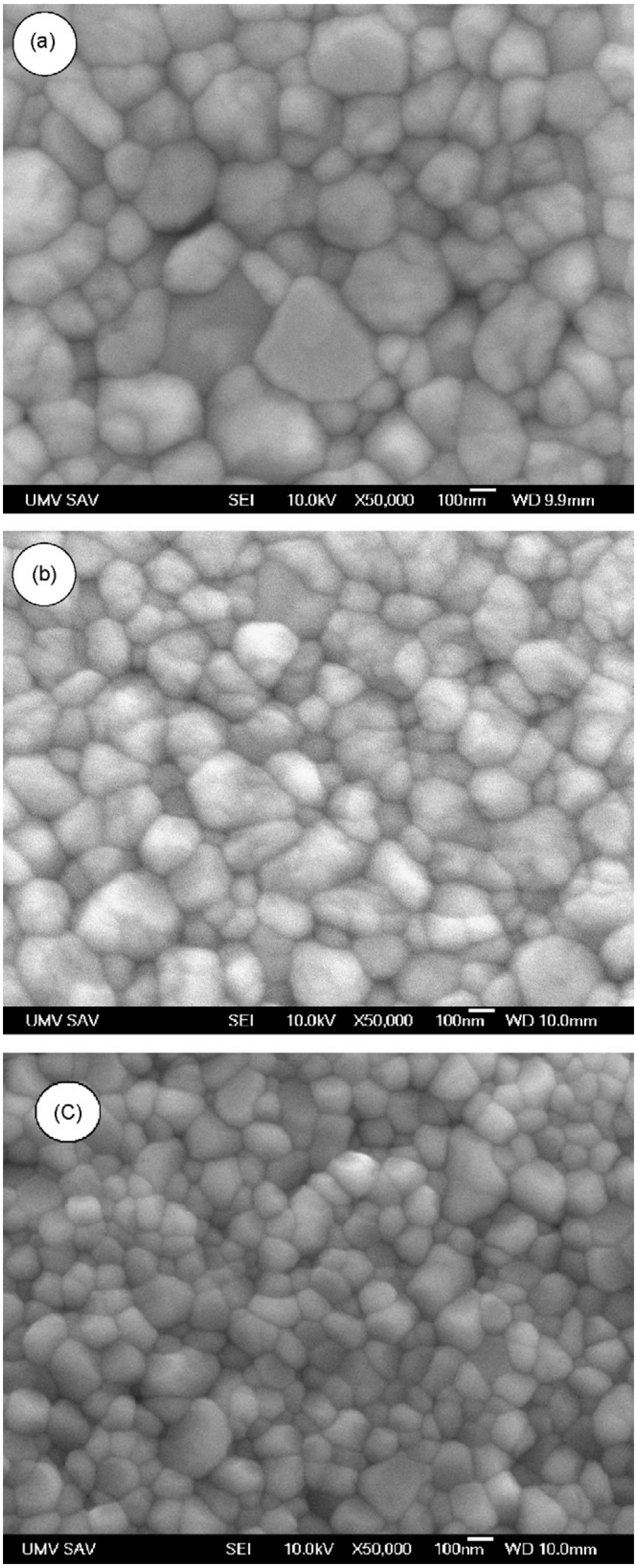

Fig. 2. Microstructure of the sintered (a) and hot-pressed (b) monolithic zirconia and the hot-pressed CNT–zirconia composite (c). Thermally etched.

cal resistivity decreased significantly from a very high value of approximately 10^{12} (the exact value was not possible to measure because of the high resistivity and the limitations of our measurement equipment) to a value of 0.105 Ω cm.[14]

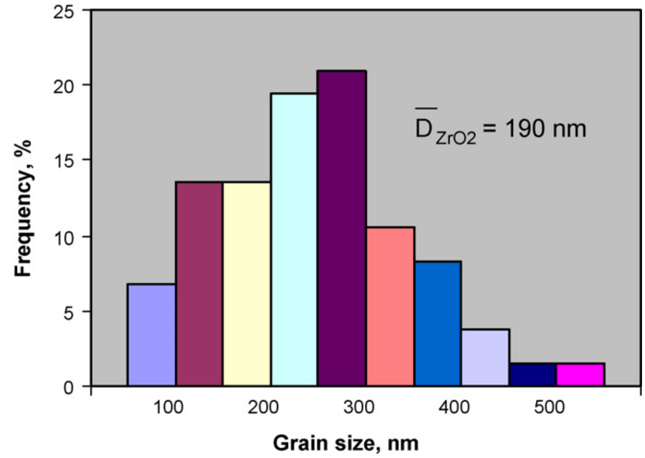

Fig. 3. Grain size distribution of the ZrO_2 grains in the sintered zirconia.

Characteristic indentation size effect has been found during the hardness test in all investigated materials as it is illustrated in the case of the hot-pressed monolithic zirconia in Fig. 5.

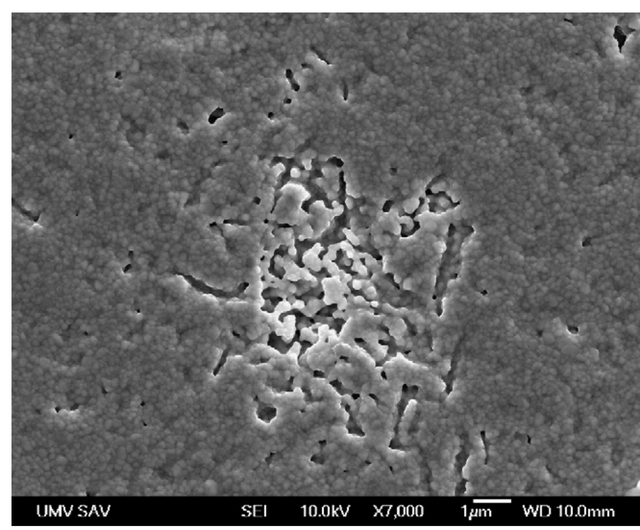

Fig. 4. Cluster of a CNTs in the composite.

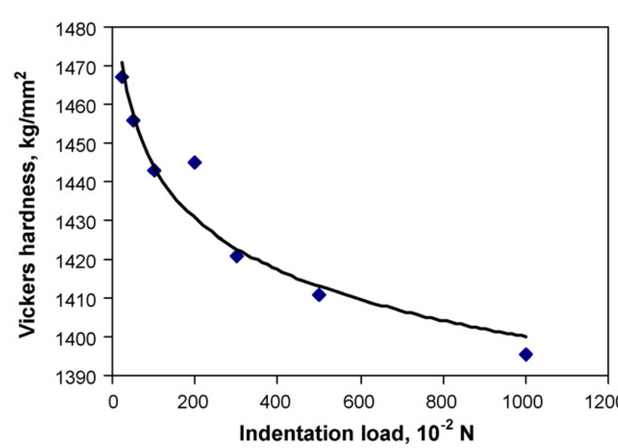

Fig. 5. Influence of the indentation load on the hardness of hot-pressed zirconia.

Table 1
Properties of the investigated materials

Material	Properties				
	Density (g/cm^3)	Grain size ZrO_2 (nm)	HV1 (kg/mm^2)	K_{IC} indentation ($MPa\,m^{0.5}$)	Electrical resistance (Ω cm)
ZrO_2–S	6.02	190	1297 ± 30	8.01 ± 0.15	–
ZrO_2–HP	6.05	162	1395 ± 26	6.24 ± 0.1	ca. 1.0×10^{12}
ZrO_2–CNT	5.22	144	830 ± 28	5.60 ± 0.15	0.105 ± 0.05

The fracture mechanisms in the bulk zirconia material are mainly intergranular with a very low roughness of the fracture lines/surface, only apparent at the nanometer scale (Fig. 6a). No toughening mechanisms have been revealed on the fracture lines/surfaces in this system. The composite reinforced by CNTs exhibits a slightly different behavior with more rough fracture line/surfaces with crack deflection at the larger singular CNTs (Fig. 6b). The crack deflection is similar to the crack deflection in whisker reinforced ceramics and represents one of the toughening mechanisms in similar systems which can improve the fracture toughness of the composites. Beside the crack deflection, crack bridging and CNTs pull-out was often detected on the fracture surface of the failed composite, however the pull-out length were usually short (Fig. 6b).

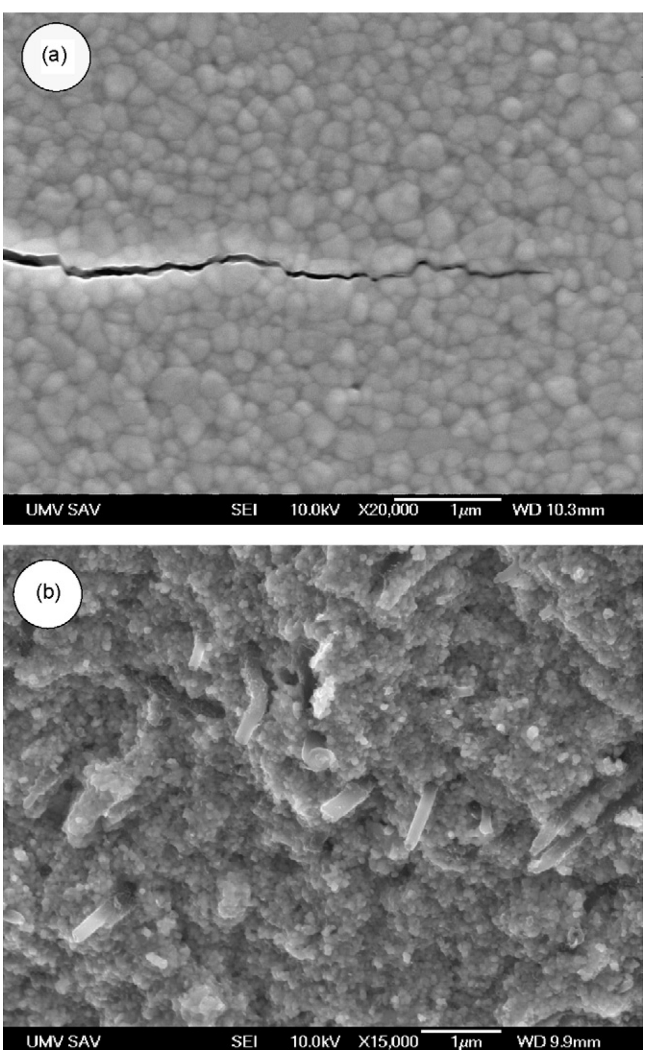

Fig. 6. Fracture line in the hot-pressed monolithic zirconia (a) and fracture surface of the zirconia + CNTs composite (b).

Comparing the results of the present investigation to the results of a similar study we need to mention two main differences in the processing step. In our investigation we used CNFs with different geometry, with higher diameter and with lower aspect ratio, compared to the CNTs in the similar investigations on ZrO_2–CNT systems. The second difference was in the way of sintering of the mixture, we used hot pressing, while similar investigations have used spark plasma sintering (SPS) or pressureless sintering + post-HIP treatment.

The thermoelectric properties of 10 vol.% single-wall carbon nanotube/3Y-TZP composite produced by SPS have been studied by Zhan et al.[6] According to these results, the electrical resistivity increased from approximately 0.02 Ω cm to approximately 0.5 Ω cm when the temperature increased to 545 K. The further increasing of the testing temperature resulted in the slight decrease of electrical resistivity.

Sun et al.[7] studied the mechanical and fracture behavior of MWCNT/3Y-TZP composites containing form 0.1 wt.% to 1.0 wt.% of MWCNTs and SWCNTs prepared by SPS. They found a negative influence of the CNTs addition, on the hardness of the composites and no influence (at 0.5%) or also negative influence on the fracture toughness. Comparing the influence of the SWCNTs and MWCNTs addition on the facture toughness they found that the MWCNT are more effective in the toughening. However they used the indentation technique for the toughness measurements which is useful only for comparison purposes, but cannot be considered a true material property and also tends to over estimate the K_{IC} value as described by Quinn and Brandt.[15]

Cha[16] used a new process for fabrication of MWCNT/alumina nanocomposites based on a molecular level mixing process and SPS. They investigated the effect of the MWCNT addition on the hardness and fracture toughness of the nanocomposites. According to the results the CNT/alumina nanocomposites show homogenously distributed CNTs strongly bonded to the alumina matrix. The nanocomposites thus exhibited an enhanced hardness and toughness compared to monolithic materials, which according to the authors is based on the load sharing and bridging mechanisms of CNTs in the alumina matrix.

The results of the present investigation are in a very good agreement with the results of Ukai et al.[8] as regards the influence of the CNTs addition on the electrical properties of zirconia. Using the coarse CNTs (carbon fibres) in our investigation we found a balanced electrical conductivity and mechanical properties for the CNT–zirconia composite. The electrical resistivity was in our case even lower compared to the results of Ukai et al., indicating the potential of the whisker like nanotubes for improving the functionality of the ceramics.

Dense MWNT/barium aluminosilicate glass composites have been fabricated by Ye et al.[17] using hot pressing. The incorporation of the CNTs improved the bending strength and the fracture toughness measured by single-edge-notch-beam (SENB) method. Bridging and pull-out was found as main toughening mechanisms responsible for the toughness improvement.

Xia et al.[18] in their review paper discussed the possibilities of toughening in carbon nanotube reinforced ceramic composites. According to their results debonding occurs at atomic scale in the CNTs/ceramic composites and imperfect nanotubes may provide more effective load transfer and can contribute to the enhanced strength and toughening. They found a new crack-resisting mechanism of CNT collapse in "shear bands" which was not observed in large-scale composites.

As regards the mechanical properties our investigation show that even the use of coarse whisker like CNTs are not effective for the toughening of the zirconia ceramic matrix at the current volume used. On the other hand we have to note that on the fracture surface/line we found frequently different toughening mechanisms mainly in the form of crack deflection at the CNTs and the reason of the low calculated indentation fracture toughness was the low hardness. A more reliable technique (e.g. SEVNB ref.) has to be used for the measurement of the fracture toughness on fully dense composites to obtain information concerning the true effect of the CNTs on the fracture toughness. The lower hardness of the composite compared to the monolithic material is dependent on the residual porosity which remains in the material after the sintering, similar to that observed in other investigations.[5] Together with the porosity, the clusters of the CNTs are characteristic processing defects present in our material and presented in all contributions dealing with similar composites. This indicates the still present difficulties at the preparation of defect free CNTs–ceramic composites but also the potential for the improvement of their functional and mechanical properties.

4. Conclusions

- Monolithic zirconia and carbon nanotube/zirconia composite have been prepared by sintering and hot pressing.
- The hardness of the sintered monolithic zirconia was lower and the indentation toughness higher in comparison to the hot-pressed material.
- The hardness and the indentation toughness degreased after the addition of the CNTs to the hot-pressed zirconia by approximately 30% and 10%, respectively.
- The electrical resistivity of the composite decreased by approximately 13 orders of magnitude in comparison to the monolithic zirconia.
- Microfractography of the fracture lines/surfaces of the composite revealed the potential of reinforcement of the zirconia by CNTs in the materials prepared by optimized processing route.

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