Transition in micro/nano-scale mechanical properties of ZrO2/multi-wall carbon nanotube composites

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ZrO2/multi-wall carbon nanotube (MWCNT) composites were consolidated using a spark plasma sintering technique. Micro- and nano-scale mechanical properties of sintered composites with various MWCNT contents were investigated using X-ray diffraction and instrumented indentation techniques. Transitional behavior in the hardness and elastic modulus of the composites was observed and attributed to the contrasting effects of the MWCNT addition; i.e., beneficial effects such as inhibition of crystal growth and phase transition and detrimental effects due to the agglomerated MWCNTs.

Key-words : ZrO2/CNT composite, Spark plasma sintering, Nanoindentation, Phase transition, Micro/nano-scale mechanical property

1. Introduction

Zirconia is well-known material that is used in many structural applications due to its superior mechanical properties. Zirconia and zirconia-based composites are interesting multifunctional materials for many applications as solid oxide fuel cells, oxygen sensors and ceramic membranes due to their good high-temperature stability, high breakdown electrical field and large energy bandgap. However, applications of zirconia are limited due to the reliability issue owing to the low fracture toughness and poor crack growth resistance, commonly observed in the ceramic system. In order to overcome such drawbacks, the mechanical and physical properties of zirconia-based composites have been widely studied. In recent years, there has been increasing interest in the development of carbon nanotube (CNT) reinforced composites to incorporate the exceptional properties of CNTs. Particularly CNTs have been considered as reinforcement in a ceramic-based nanocomposite system to enhance the fracture toughness utilizing their uniquely attractive mechanical and physical properties. It is evident that adding an appropriate amount of CNTs to ceramic-base materials can improve the mechanical properties. Ma et al. prepared CNTs/SiC composite powder via mixing nano sized SiC with 10% CNTs and then consolidated it using a hot press technique. They reported a 10% enhancement on both the strength and the fracture toughness in comparison with the monolithic SiC. Chang et al. fabricated alumina matrix composites containing 5 to 20 vol.% of multi-wall carbon nanotubes (MWCNTs). An improvement of 24% in fracture toughness compared to that of single-phase alumina was found. Also, Zhan et al. fabricated fully dense nanocomposites of single-wall CNTs with nanocrystalline alumina matrix at sintering temperatures as low as 1150°C by spark-plasma sintering (SPS) technique. They reported that a fracture toughness of 9.7 MPa m^1/2, nearly three times that of nanocrystalline alumina, could be achieved. Recently, the interesting phase transformation of zirconia in ZrO2/CNT composites was reported, and it is not yet clear how CNT inclusion affects the phase transition of the ZrO2 matrix during sintering or under stress condition.

In the present study, commercial ZrO2 powders and MWCNT composite were used as raw materials. These were consolidated by SPS to synthesize the MWCNT-reinforced ZrO2 composites. The effects of MWCNT contents on the transitional behaviors of ZrO2/CNT composites was investigated using X-ray diffraction and instrumented indentation techniques. Transitional behavior in the hardness and elastic modulus of the composites was observed and attributed to the contrasting effects of the MWCNT addition; i.e., beneficial effects such as inhibition of crystal growth and phase transition and detrimental effects due to the agglomerated MWCNTs.

2. Experimental Procedure

Commercially available 3 mol% yttria-stabilized zirconia (3YSZ) powder and MWCNTs (Applied Carbon Nanotechnology Co., Ltd., Korea) were selected as starting powders. To obtain the homogeneous MWCNTs and 3YSZ mixtures, the MWCNTs were dispersed mechanically by high energy ball milling with ZrO2 balls in an ethyl alcohol and surfactant solvent for 2 h. The
dispersed MWCNTs and ZrO₂ powder were mixed using an ultrasonic mixing technique. At that time, the ZrO₂ powder was added gradually to the ultrasonically dispersed MWCNTs alcohol suspension. The mixed content of MWCNTs in the ZrO₂ matrix varied from 0 to 1, 3, 5 and 10 vol.%. Finally, the mixed slurry of 3YSZ and the MWCNTs was dried in an oven to obtain the composite powders. Consolidation of the mixture of MWCNTs and ZrO₂ was conducted using an SPS system (FAST composite powders. The SPS sintering experiments with the prepared powders were conducted in a vacuum at 1300°C for a holding time of 3 min with a heating rate of 100°C min⁻¹. The pressure load was initially 30 MPa, which increased linearly to 60 MPa after the temperature reached 1300°C.

The sintered disc-type specimens were cut at 5 mm in thickness and polished using SiC paper and a diamond suspension. The densities of the sintered sample were measured using the Archimedes method. The microstructure was observed using a scanning electron microscope (SEM, S-4800, Hitachi). The mean grain size of all of the samples was measured statistically from the fractured surface. Raman spectroscopy (RDX, D8-Discovery, Bruker) was used to investigate the microstructure of the sintered composite. The micro-scale hardness was measured using a micro Vickers indenter (AA V-504, Mitutoyo) under a 30 N maximum load with dwell time of 5 s on a highly polished surface. In order to characterize nano-scale mechanical properties such as hardness and the elastic modulus, hundreds of indentations were performed for each sample using the instrumented nanoindentation system (TI-850, Hysitron). Nanoindentation was carried out under load control mode with maximum load of 1 mN and loading rate of 100μN sec⁻¹.

3. Results and discussion

With the above mentioned sintering condition, it was found that the parameters for SPS are sufficient to obtain the fully packed composites at all MWCNT contents. Details of the sintering behavior had been reported elsewhere. The density of the pure 3YSZ sintered in this study is in good agreement with the reported density of pure zirconia (6.04 g·cm⁻³). Based on the density and particle sizes of the sintered composites depicted in Table 1, it is evident that adding MWCNTs slightly reduces the density compared to the density of pure ZrO₂. Additionally, the grain size of the sintered specimen significantly decreases with an increasing MWCNT content from about ~230 nm in the pure ZrO₂ to about ~150 nm in the 5 vol.% MWCNTs. This observation indicates that an addition of CNTs play a role in impeding particle growth during the sintering process.

Figure 1(a) shows an XRD pattern of the monolithic 3YSZ and the ZrO₂/MWCNT composites. The sintered specimen is mainly the tetragonal phase ZrO₂ (t-ZrO₂) with a minor contribution from the monoclinic phase. A slight decrease of peaks corresponding to the tetragonal phase was observed when increasing the MWCNT content. It suggests the possibility that the ZrO₂ crystallinity might be degraded due to the increased MWCNT content. Interestingly, no peaks for monoclinic phase ZrO₂ (m-ZrO₂) was observed (from 20 = 20 to 30°) for the particular 5 vol.% MWCNT composites. Indeed, it has been reported that CNT can result in the phase transition in the various ZrO₂ composite system. Bocanegra-Bernal et al. recently reported experimental evidence of transformation in ZrO₂ for zirconia-toughened alumina (ZTA)/0.01 wt % MWCNT composites solidified by the pressureless sintering in air using graphite as a bed powder. Additionally, it was reported that CNT is favorable to the transition from m-ZrO₂ to cubic phase ZrO₂ (c-ZrO₂) and to the stabilization of c-ZrO₂. Considering possibility of the phase transition triggered by the CNT inclusion, our observation indicates that the presence of MWCNTs at particular content indeed affects phase transformation from t-ZrO₂ to m-ZrO₂. Additionally, it is interesting to note that the crystal size estimated form the half width of the peaks in XRD spectra [shown in Fig. 1(b)] revealed the smallest crystal size at 5 vol.% MWCNT composite. In contrast to the particle size measured form the fractured SEM micrographs, the crystal size increased again after a 5 vol.% MWCNT content when the MWCNT content increases further. It is evident that the MWCNTs plays a crucial role in evolution of atomic structure of ZrO₂-based composite sintered by the SPS technique.

Figures 2(a) and 2(b) show the typical failure mode after micro-Vickers indentation with a maximum load of 9.8 N. Discrete micro cracks were observed for lower CNT contents composites as shown in Fig. 2(a), while severe surface spalling was observed in the 10 vol.% MWCNT specimen [Fig. 2(b)]. The debonded MWCNTs bundles from the matrix were observed on the fracture surfaces, which have been commonly observed in composite with high CNT content. The fracture mode for a high MWCNT content is mainly intergranular failure due to the

Table 1. Density and the mean grain size of ZrO₂/MWCNT composite sintered by SPS

| Composition     | Density (g·cm⁻³) | Particle size (nm) |
|-----------------|------------------|--------------------|
| ZrO₂            | 6.07             | 230                |
| ZrO₂/1% MWCNTs  | 6.03             | 210                |
| ZrO₂/3% MWCNTs  | 5.29             | 190                |
| ZrO₂/5% MWCNTs  | 5.98             | 150                |
| ZrO₂/10% MWCNTs | 5.76             | 150                |
presence of MWCNTs at the grain boundary. The presence of these nanotube agglomerates (or clusters) has been reported by many researchers.12) A thermodynamic explanation based on the free volume of isotropic particles and particles with a high aspect ratio, which promotes the dimixion of both phases, has been suggested. However, these fracture failure was not observed in the composite with 10 vol.% MWCNT contents after nano-indentation due to relatively small plastic deformation [Fig. 2(c)]. The sintered composites were indented at 100 points in each selected area using a diamond indenter. The nanoscale hardness values and elastic moduli were calculated from each force-displacement curve. The distributions of the measured nano-scale hardness and elastic modulus are shown in Fig. 3. The most homogeneous distribution of hardness is found in monolithic ZrO$_2$ [Fig. 3(a)], in which there is a sharp peak and the distribution width is the narrowest. The height of this peak decreases as additional MWCNT content gradually increased. In other words, the distribution width of hardness on the sintered samples gradually increased with the increasing MWCNT content. The deterioration of hardness and non-uniform distribution of the composites might be due to weak interfacial bonding and small MWCNT agglomeration existing as flaws and cracks in the ZrO$_2$ matrix. Interestingly, the hardness distribution decreases at first, and then slightly increases at 5% MWCNT content. A similar trend is observed in the elastic moduli shown in Figs. 3(f)–3(j). The most uniform distribution of elastic modulus can be found in the pure ZrO$_2$ specimen. This uniform distribution gradually decreased with increasing MWCNT content except for the composite with 5% MWCNT content. This interesting phenomenon could be attributed to a decrease in the grain size and pure t-ZrO$_2$ matrix due to the presence of MWCNTs at the grain boundary.

We note that both micro-scale Vickers hardness and nanoscale hardness have an identical trend as a function of MWCNT content, even if the grain sizes were refined after MWCNT addition, as shown in Fig. 4. The most significant decrease was

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**Fig. 2.** (a) SEM micrographs of cracks in the indented ZrO$_2$/3 vol.% MWCNTs. (b) Surface spalling observed after micro Vickers indentation on ZrO$_2$/10 vol.% MWCNT composite. The insets in (a) and (b) shows the indentation impressions for each composite, respectively. (c) A scanning probe microscopy image of the indented ZrO$_2$/10 vol.% MWCNT composite surfaces after nano-indentations.

**Fig. 3.** Distribution of nanoscale hardness and elastic modulus for the pure ZrO$_2$ [(a) and (f)], 1 vol.% [(b) and (g)], for 3 vol.% [(c) and (h)], 5 vol.% [(d) and (i)], and 10 vol.% [(e) and (j)] MWCNT-reinforced composites, respectively.

**Fig. 4.** Micro- and nano-scale hardness and the elastic moduli as a function of MWCNT content in the ZrO$_2$/MWCNT composites consolidated by SPS.
observed at a 3 vol.% MWCNT addition. The deterioration of hardness might be caused by MWCNT agglomeration and a weakening of interfacial bonding when grains are warped and twinned by the MWCNTs. Therefore, the direct contact area and bonding force of the grains decrease with increasing MWCNT content. However, a significant increase in the nano-scale hardness and a slight Vickers hardness improvement are observed with the addition of 5 vol.% MWCNTs. It is reasonable that the strong interface connections between the MWCNT and zirconia results in pullout resistance, bridging the crack gaps and hindering the crack propagation by exploiting MWCNTs elasticity, leading to an improved elastic modulus and hardness. In addition, L. Shen et al. reported that the alterations are probably due to phase transformation of the composite at this concentration. The phase transformation produces residual stresses in the composite that are responsible for the apparent increase in elastic modulus. Cleary, adding MWCNTs to zirconia slows down the grain growth, which can partially contribute the increased hardness by the Hall-Petch effect.

4. Conclusions

In this study, fully dense 3YSZ matrix composites containing 0, 1, 3, 5, and 10 vol.% MWCNTs were consolidated using an SPS technique. All the composite powders was successfully sintered to almost full densification at 1300°C with a soaking time of 3 min under 60 MPa. Micro- and nano-scale mechanical properties of the composites with various MWCNT contents were investigated using a micro-Vickers indenter and an instrumented nano-indentation technique. Decreases in hardness and elastic modulus has been found when increasing the MWCNT content despite the full densification of the composite except for the 5 vol.% MWCNT content. Additionally, the addition of MWCNTs reduced the grain size of sintered composites significantly, and the smallest crystal size was observed when the MWCNT content reached 5 vol.%. The pure tetragonal phase of the ZrO2 matrix with 5 vol.% MWCNT content suggests that the smallest crystal size and a phase transformation impeded by MWCNT inclusions at this particular concentration is one reason why the hardness and elastic modulus has been enhanced.

Acknowledgements This research was supported by a 2014 Yeungnam University Research Grant. This research was also supported by the National Natural Science Foundation of China (Grant No. 51172248).

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