JOURNAL OF MATERIALS SCIENCE 20 (1985) 1178–1184

Strength, fracture toughness and Vickers hardness of CeO_2-stabilized tetragonal ZrO_2 polycrystals (Ce-TZP)

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Dense Ce-TZP ceramics containing about 7 to 16 mol % CeO_2 were fabricated using fine powders prepared by the hydrolysis technique. The mechanical properties of these ceramics were evaluated. The bending strength of sintered bodies with 10 to 12 mol % CeO_2 content and small grain-size was about 800 MPa. Fracture toughness was measured by two different methods; a micro-indentation technique and the chevron notched beam technique. A high fracture toughness was obtained for sintered bodies with 7 to 10 % CeO_2 content and large grain-size. Fracture toughness and hardness were dependent on CeO_2 content and grain-size. These mechanical properties are discussed on the basis of the stability of the metastable tetragonal phase depending on CeO_2 content and grain-size.

1. Introduction

CeO_2-partially stabilized zirconia is considered a candidate material for toughened zirconia ceramics containing tetragonal polycrystals. It is well known that Y_2O_3-partially stabilized zirconia, called Y-TZP (Y_2O_3-stabilized tetragonal ZrO_2 polycrystals) is the representative toughned zirconia ceramic.

From the results of the phase relationship in ZrO_2–CeO_2 system, it is found that there exists an extensive solid solution region with tetragonal phase which is stable at near room temperature. [1, 2] From these phase relationships, it is expected that we can fabricate various kinds of toughened zirconia ceramics composed of the tetragonal phase containing widely different amount of CeO_2 content.

Since the Ce-TZP ceramics contain a range of CeO_2 content, it is interesting to study the dependence of mechanical properties on CeO_2 content in these ceramics in order to get more detailed information on stress-induced transformation toughening. Lange [2] demonstrated that CeO_2 alloying contributed to the transformation toughening in Al_2O_3–ZrO_2 alloyed with CeO_2 ceramics. Recently, Coyle *et al.* [3] reported the mechanical properties of CeO_2 doped ZrO_2 toughened ceramics. In this study, we fabricated dense Ce-TZP ceramics using fine powders prepared by the hydrolysis technique, and evaluated the mechanical properties of these ceramics. It is our purpose here to study the effect of the metastable tetragonal phase on the mechanical behavior of Ce-TZP ceramics.

2. Experimental procedure

Fine CeO_2–ZrO_2 powders containing different amounts of CeO_2 were prepared by the hydrolysis technique using a mixed solution of $ZrOCl_2$ and $CeCl_3$. The commercial grade $CeCl_3$ solution had a purity of 85%, containing 7% $LaCl_3$ and 8% $NdCl_3$. The $ZrOCl_2$ hydrous salt had a purity of 99.9%. The mixed solution was heated at 100° C for 50 h to obtain the hydrolysis product.

0022–2461/85 $03.00 + .12

TABLE I. Characteristics of Ce-TZP ceramics

Sample	CeO_2 content (mol%)	Crystalline phase	Lattice constants of ZrO_2 ss*		Bulk density ($g\,cm^{-3}$)
			a (nm)	c (nm)	
A	8.6	Tetragonal ZrO_2s.s. + a small amount of $(La, Nd)_2Zr_2O_7$	0.5116	0.5214	6.23
B	9.5	Tetragonal ZrO_2 s.s. + a small amount of $(La, Nd)_2Zr_2O_7$	0.5118	0.5218	6.26
C	10.8	Tetragonal ZrO_2 s.s. + a small amount of $(La, Nd)_2Zr_2O_7$	0.5121	0.5219	6.27
D	12.2	Tetragonal ZrO_2 s.s. + a small amount of $(La, Nd)_2Zr_2O_7$	0.5125	0.5220	6.28
E	15.8	Tetragonal ZrO_2 s.s. + a small amount of $(La, Nd)_2Zr_2O_7$	0.5125	0.5224	6.32
F	7.0	Tetragonal ZrO_2 s.s. + a small amount of $(La, Nd)_2Zr_2O_7$	0.5114	0.5212	6.22
G	11.0	Tetragonal ZrO_2 s.s. + a small amount of $(La, Nd)_2Zr_2O_7$	0.5124	0.5220	6.26

*ZrO_2 solid solution

The hydrolysis product, hydrous ZrO_2, was dried in a vacuum evaporator, and then calcined at 950° C. The calcined powders were wet-milled in ethyl alcohol for 24 h, and then dried in an evaporator. The powders were granulated through 32 mesh screen, and pressed into plate at 40 MPa, and then isostatically pressed at 300 MPa. The green compacts were sintered in air at 1400 to 1600° C for 2 h.

CeO_2 content was determined by analysis of the X-ray fluorescence. The bulk density was measured by a water displacement method. The lattice constants were measured by X-ray diffraction using Si as a standard material. Each sintered plate was cut into bar (0.3 cm by 0.4 cm by 4 cm) to measure bending strength and fracture toughness. The measurements of 3-point bend strength were performed using a 30 mm span and a cross head speed of $0.5\,mm\,min^{-1}$. The fracture toughness was evaluated by two different methods: a microindentation technique (MI) and the chevron notched beam technique (CNB) [4]. For the technique, a load of 490 N was applied to the specimen, and K_{IC} values were calculated by using the equation reported by Niihara *et al.* [5] For the CNB technique, chevron notches were machined with a 0.3 mm thick diamond saw. The notched specimens were annealed at 1200° C in air in order to relieve the residual stress introduced by the saw. Fracture toughness was measured in a 4-point bending test using a cross head speed of $0.1\,mm\,min^{-1}$. Microhardness was measured by applying a load of 294 N using a diamond Vickers indenter. The fraction of tetragonal-to-monoclinic transformation occurring during fracture was measured by means of X-ray diffraction analysis. The fraction was determined by comparing the tetragonal/monoclinic ratio of the broken surface with that of the polished surface.

3. Experimental results

3.1. Phase and microstructure

The characteristics of Ce-TZP containing different amount of CeO_2 content are listed in Table I. As the commercial grade $CeCl_3$ containing 15% $LaCl_3$ and $NdCl_3$ was used as the CeO_2 source, two crystalline phases were formed in the sintered bodies. The major phase was CeO_2–ZrO_2 solid solution with a tetragonal structure, and minor phase was a pyrochlore type compound, $(La, Nd)_2Zr_2O_7$. It is considered that pyrochlore type compound is formed by reaction between ZrO_2 and La_2O_3 (Nd_2O_3) in the sintering process.

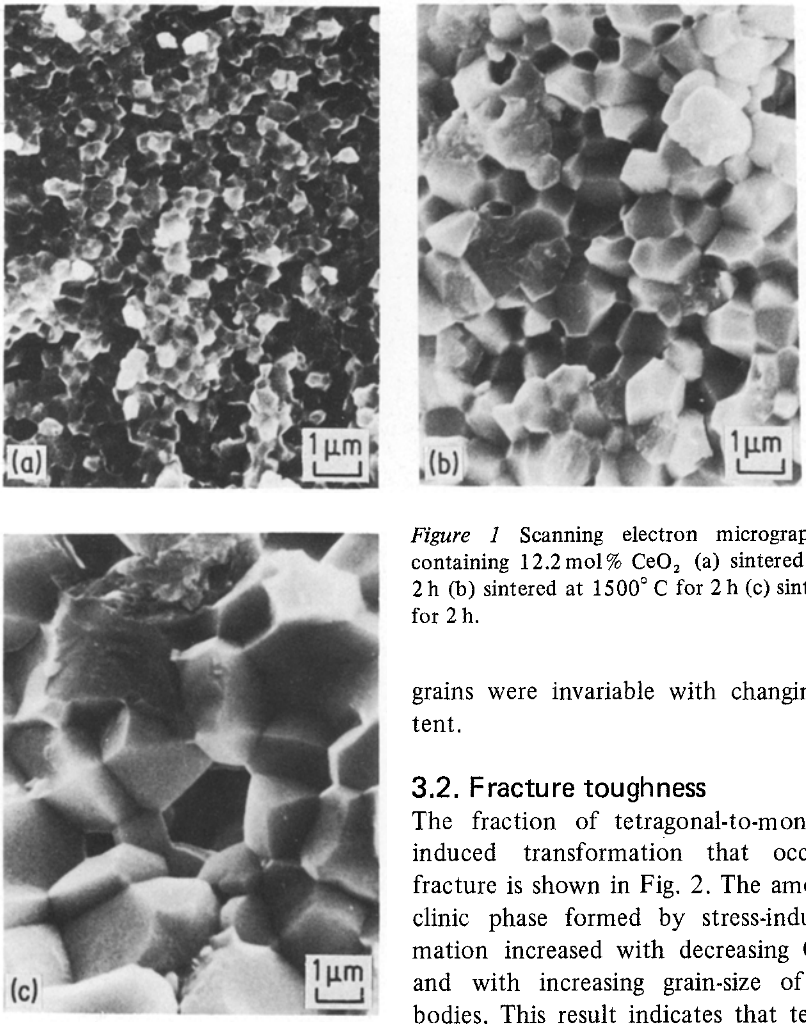

Figure 1 Scanning electron micrographs of Ce-TZP containing 12.2 mol% CeO_2 (a) sintered at 1400° C for 2 h (b) sintered at 1500° C for 2 h (c) sintered at 1600° C for 2 h.

The lattice constants of the tetragonal solid solution increased linearly with increasing CeO_2 content. This fact indicates that a homogeneous dispersion of CeO_2 is achieved for a wide range of CeO_2 contents. Since the bulk densities of Ce-TZP ceramics sintered at 1400° C, 1500° C and 1600° C were almost same as each other, the bulk densities of Ce-TZP sintered at 1500° C are listed in Table I. The bulk densities increased with increasing CeO_2 content, and reached more than 99% of the theoretical densities estimated by using lattice constants.

Scanning electron micrographs of Ce-TZP containing 12.2 mol % CeO_2 are shown in Fig. 1. The average grain-size was about 0.5, 1.0 and 2.5 μm, at temperatures of 1400° C, 1500° C and 1600° C, respectively. Results of SEM observation for Ce-TZP samples containing about 7 to 16 mol% CeO_2 revealed that the shape and size of grains were invariable with changing CeO_2 content.

3.2. Fracture toughness

The fraction of tetragonal-to-monoclinic stress-induced transformation that occurred during fracture is shown in Fig. 2. The amount of monoclinic phase formed by stress-induced transformation increased with decreasing CeO_2 content and with increasing grain-size of the sintered bodies. This result indicates that tetragonal large grains containing a small amount of CeO_2 are easily transformed to monoclinic phase under applied stress. The result of fracture toughness measured by the MI technique is shown in Fig. 3. Fracture toughness increased with decreasing CeO_2 content and with increasing grain-size. The dependence of fracture toughness on both CeO_2 content and grain-size corresponded excellently to the amount of monoclinic phase formed by stress-induced transformation as shown in Fig. 2.

Comparison of fracture toughness obtained from the MI and CNB techniques is shown in Fig. 4. The compositions of samples are given in Table I (F and G), and the average grain-size of each sample was 0.5 μm and 2.0 μm, respectively. K_{IC} values were plotted against the fraction of stress induced transformation. As seen in Fig. 4, the fracture toughness of samples F and G obtained from the MI technique varied extensively with CeO_2 content and grain-size. K_{IC}

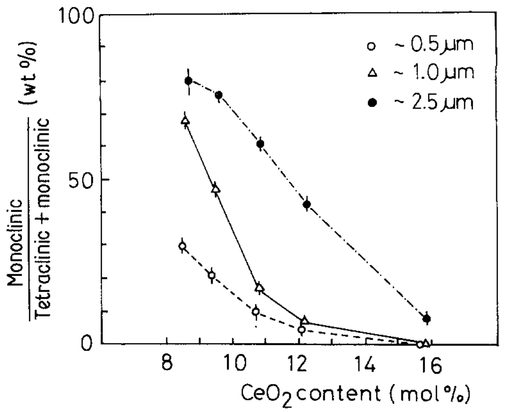

Figure 2 Dependence of stress-induced transformation on CeO_2 content and grain-size.

values corresponded to the amount of monoclinic phase formed by stress-induced transformation, which is the same as the result shown in Fig. 2 and Fig. 3. On the other hand, fracture toughness obtained from the CNB technique showed no significant dependence on CeO_2 content, grain-size or the amount of monoclinic phase formed by stress-induced transformation. The difference between K_{IC} values obtained from both techniques was significant for the samples having the large amount of monoclinic phase formed by stress-induced transformation.

3.3. Bending strength

The bending strengths of Ce-TZP containing different amounts of CeO_2 are shown in Fig. 5. The present results indicate that fracture strength was higher when the Ce-TZP ceramics contained about 10 to 12 mol% CeO_2, and their grain-size was smaller than about 1 μm. The fracture strength of sintered bodies containing less than 10 mol% CeO_2 strongly dependent on grain-size.

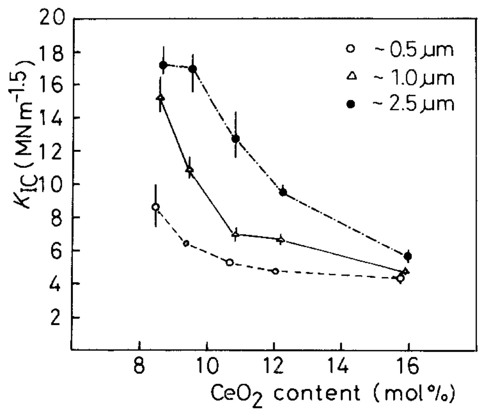

Figure 3 Dependence of fracture toughness on CeO_2 content and grain-size.

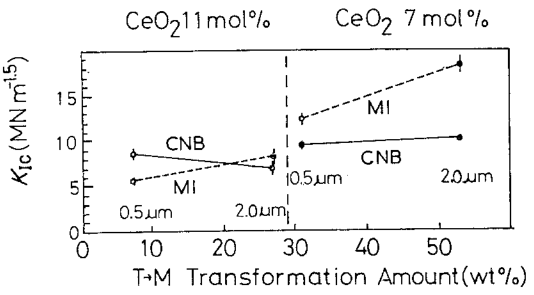

Figure 4 Fracture toughness obtained from two different test techniques; Microindentation technique (MI) and chevron notched beam technique (CNB).

Representative stress-strain curves obtained from 3-point bending strength measurement are illustrated in Fig. 6. The (F-1) sample showed a serrated stress–strain curve, which was due to significant plastic deformation prior to failure. The (F-2) sample showed a non-linear stress–strain relationship under a higher stress field, which was also due to weak plasticity. Both samples (G-1) and (G-2) showed a linear stress–strain relationship, which indicated that the fracture was brittle. The plastic deformation of Ce-TZP ceramics was due to decreasing CeO_2 content and increasing of grain-size. This plastic deformation was closely related to the stress-induced transformation. The plasticity was significant for the sintered bodies exhibiting large amounts of stress-induced transformation.

3.4. Vickers hardness

The Vickers hardness of Ce-TZP ceramics varied extensively with CeO_2 content and grain-size.

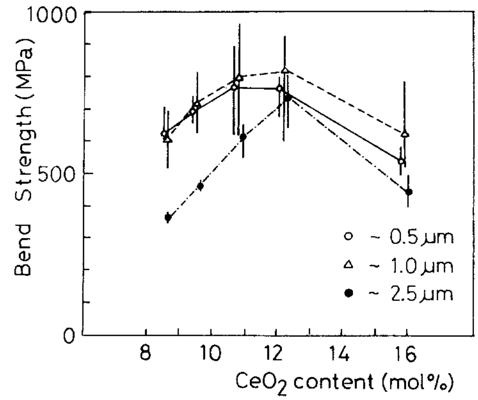

Figure 5 Bend strength of Ce-TZP containing different amount of CeO_2 content sintered at 1400, 1500 and 1600° C, respectively.

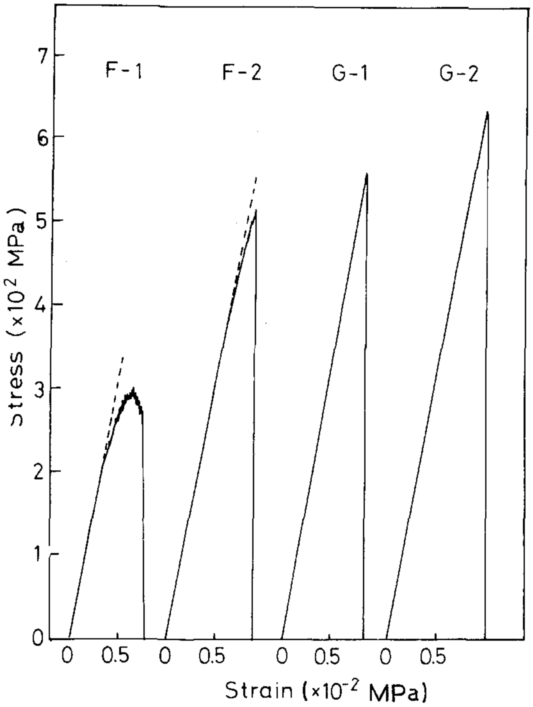

Figure 6 Stress–strain curves of Ce-TZP obtained by bending test. CeO_2 content, grain-size of sintered body and the amount of stress-induced transformation are 7 mol%, 2.0 μm and 60% for (F-1), 7 mol%, 0.5 μm and 35% for (F-2), 11 mol%, 2.0 μm and 28% for (G-1) and 11 mol%, 0.5 μm and 8% for (G-2), respectively.

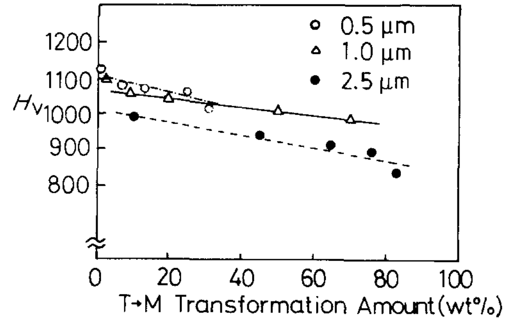

Figure 7 Relation between Vickers hardness and the amount of stress-induced transformation.

Vickers hardness decreased with decreasing CeO_2 content and with increasing grain-size. This result indicated that hardness was closely related to the stress-induced transformation. Fig. 7 represents the relationship between hardness and the amount of monoclinic phase formed by stress-induced transformation. Hardness decreased almost linearly with the increasing amount of monoclinic phase formed by stress-induced transformation.

4. Discussion

The present study revealed that the stress-induced transformation of Ce-TZP ceramics depended strongly on CeO_2 content and grain-size. As shown in Fig. 2, the amount of monoclinic phase formed by stress-induced transformation increased with decreasing CeO_2 content and with increasing grain-size. The previous studies on phase relationships in the CeO_2–ZrO_2 system indicated that transformation temperature from tetragonal to monoclinic phase increased with decreasing CeO_2 content, e.g. 600° C for 12 mol% CeO_2 and 270° C for 20 mol% CeO_2 [2]. This result suggested that the retained tetragonal phase containing a small amount of CeO_2 was more unstable than that containing a large amount. The grain-size effect on phase transformation has been studied on partially-stabilized zirconia (PSZ) and ZrO_2–Al_2O_3 composite materials by many investigators [6–8]. These studies revealed that the transformation temperature decreased with decreasing grain-size, which indicated that the retained tetragonal phase composed of small grains was more stable than that composed of large grains. The present result shown in Fig. 2 is well explained on the basis of the effect of CeO_2 content and grain-size on stress-induced transformation. Decreased CeO_2 content and increased grain-size lead to the elevation of martensitic transformation temperature, which corresponded to the reduction of stability of the retained tetragonal phase. Consequently, the tetragonal phase was easily transformed by applied stress.

The plastic deformation was characteristic of the mechanical behaviour of Ce-TZP ceramics. As shown in Fig. 6, plastic deformation occurred prior to failure in bending test. This behaviour is thought to be similar to the R-curve behaviour observed in Mg-PSZ where crack propagation was very stable [9]. It is expected that the plastic deformation of Ce-TZP ceramics was due to slow crack propagation. The present result shown in Fig. 6 indicated that the plastic deformation was remarkable in increasing the amount of stress-induced transformation. This result suggests that crack propagation is prevented and/or delayed by the shielding effect enhanced by a large number of transformed particles.

There was good correspondence between hardness and the amount of stress-induced transformation as shown in Fig. 7. Hannink and Swain [10] reported that a microstructural change occurred around the indent in Mg-PSZ. They observed the plastic deformation band formed by the stress-induced transformation of tetragonal precipitates. Hardness decreased with an increased amount of stress-induced transformation. This result suggests that the plastic deformation, which is introduced by the stress-induced transformation, is responsible for the decrease of hardness.

From the results of fracture toughness determined by two test techniques, as shown in Fig. 4, the values of K_{IC} obtained were quite different. The differences between the MI and CNB results were significant for sintered bodies exhibiting large amount of stress-induced transformation. As for the result of bending and indentation tests, the sintered bodies having a large amount of stress-induced transformation exhibited appreciably plastic deformation. It is expected that the differences of fracture toughness between the MI and CNB results is caused by this plastic deformation. In the MI technique, since the transformed particles around the indent deformed plastically, the cracks initiated at the indent had difficulty in extending. Therefore, K_{IC} values obtained from the MI technique were larger than that of the CNB technique, and K_{IC} values strongly depended on the amount of plastic deformation resulting from stress-induced transformation. The dependence of fracture toughness of Al_2O_3 on test technique and grain-size has been reported by Mussler *et al.* [11]. They reported that fracture toughness obtained by the notched beam technique is related to the initiation of crack, whereas fracture toughness obtained by the double cantilever beam technique is related to the crack propagation and reflects the R-curve behaviour of materials. The fracture toughness of Ce-TZP obtained from CNB is thought to be related to crack initiation rather than crack propagation, and not strongly influenced by the plastic deformation or R-curve behaviour.

According to the theory of transformation-toughening proposed by Lange [12], the increase of fracture energy contributed by stress-induced transformation is given by following equation.

$$\Delta G = V \times W$$

where V is the volume of tetragonal particles in the transformation zone, and W is the work per unit volume obtained by transformation. In Ce-TZP ceramics, as shown in Fig. 2, when CeO_2 content decreased and grain-size increased, V increased. Whereas, it is expected that W decreased with increasing V, because large grains of tetragonal phase containing small amounts of CeO_2 were so unstable that the energy required for transformation from tetragonal to monoclinic phase decreased. Consequently, it is expected that the increase of fracture energy is not so large as that of the amount of transformation from tetragonal to monoclinic phase. This consideration was confirmed by the experimental result of the fracture toughness obtained by the CNB technique. Namely, K_{IC} values obtained by the CNB technique were not so high as those expected from the large amount of tetragonal-to-monoclinic phase transformation.

5. Conclusions

The strength, fracture toughness and hardness of Ce-TZP ceramics containing about 7 to 16 mol% CeO_2 were evaluated. A bending strength of 800 MPa was obtained for sintered bodies containing about 10 to 12 mol% CeO_2. Fracture toughness and hardness were strongly dependent on CeO_2 content and the grain-size of the sintered bodies. These mechanical properties were well understood on the basis of the correlation with the amount of stress-induced transformation.

Plastic deformation, which was caused by the stress-induced transformation of the tetragonal particles, had a remarkable effect on the mechanical properties of Ce-TZP ceramics. It was considered that this plastic deformation resulted in the following behaviour; (a) The decrease of hardness with decreasing CeO_2 content and with increasing grain-size, (b) The differences in fracture toughness obtained from two different test techniques such as MI and CNB.

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Received 18 May
and accepted 2 July 1984