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Mechanical properties and microstructure of ZrO_2–SiO_2 composite

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ZrO_2–SiO_2 composite powder has been prepared by a wet chemical route using zirconyl chloride and fumed silica as starting materials and subsequently sintered by the hot-pressing method to obtain a ZrO_2–SiO_2 ceramic. The mechanical properties of the silica matrix have been much increased by the addition of 20 vol % zirconia. The microstructural features of the composite are observed by transmission electron microscopy (TEM) and high-resolution electron microscopy (HREM). The stabilibity of tetragonal zirconia in the matrix is attributed to the particle-size effect, and to the constraint effect of the silica matrix and that of the interphasic reaction layer. The increase in mechanical properties is discussed in relation to the residual stress and the enhanced elastic modulus caused by the incorporated ZrO_2 particles.

1. Introduction

The development of multiphase composite ceramics is one of the current research interests in the field of ceramic materials [1], including particle-dispersed multiphase ceramics, fibre (or whisker)-reinforced ceramic matrix composites, self-enhanced multiphase composed ceramics and gradient multiphase composed ceramics. The grain-boundary phase plays an important role in sintering and physical properties of ceramics. Recently, Guo [2] proposed the concept of stress design of a ceramic grain boundary, which was based on the investigation of the grain-boundary phases as interface and interphase of multiphase ceramics [3]. It is expected that, through the stress design of a grain boundary, ceramic composites possess the ability to transfer, consume or absorb the applied energy, in order to achieve strengthening and toughening of ceramics. One approach of stress design is the introduction of thermal residual stresses into the grain boundary. The system chosen for this study is a ZrO_2–SiO_2 composite where the residual stress arises from a high thermal expansion mismatch between ZrO_2 inclusions and the silica matrix ($\alpha \approx 10 \times 10^{-6}$ and $0.5 \times 10^{-6}\,°C^{-1}$ for zirconia and silica, respectively).

In the last two decades, the ZrO_2-containing ceramics have attracted a great deal of research interest because of their high fracture toughness, which has been attributed to the stress-induced transformation of tetragonal zirconia [4]. In the field of glass technology, however, ZrO_2 is used as a nucleating agent to make glass-ceramics. The preparation of ZrO_2-transformation toughened glass-ceramics containing up to 20 and 30 wt % ZrO_2 has been reported in the literature [5, 6]. Nogami and Tomozawa [7] have prepared the ZrO_2–SiO_2 glass-ceramics, and obtained a large increase in K_{IC} associated with the formation of t-ZrO_2 for the composition containing 60 mol % ZrO_2. On the other hand, Maschio *et al.* [8] were unable to achieve any appreciable toughening in the melt mixture of a powdered borosilicate glass with up to 19 wt % ZrO_2. The present work was concerned with the role of ZrO_2 addition in the mechanical properties of the silica-based materials. The stability of tetragonal ZrO_2 and microstructure of the composite were also investigated.

2. Experimental procedure

The gel, containing 20 vol % ZrO_2, 80 vol % SiO_2 (20ZS) was prepared by a wet chemical process using $ZrOCl_2$ solution and fumed silica as precursors. The concentrated ammonia was added to the homogeneous slurry under vigorous stirring, which was obtained by mixing the precursors with distilled water. The resulting gel was washed with distilled water and dried at 120 °C for 24 h, and then calcined at 700 °C for 120 min to obtain the composite powders of the ZrO_2–SiO_2 system.

The hot-pressing method was employed using a graphite die. The composite powder was sintered at 1350 °C for 1/2 h under a pressure of 20 MPa in a nitrogen atmosphere. Specimens were cut into bars (2.5 mm × 5 mm × 30 mm) for flexural strength and Young's modulus measurements (Instron-8501 tester); the three-point bending method with a span of 20 mm and a loading rate of $0.5\ mm\ min^{-1}$ was employed.

Fracture toughness was determined by the Vickers' indentation method for the polished samples. Indentation tests were performed employing a Vickers' microhardness tester and an indentation load of 4.9 N. At each indentation, the load was applied for 5 s and the lengths of diagonal and radial cracks were measured by an optical microscope. The fracture toughness, K_{IC}, can be approximately calculated by the relationship [7]

$$K_{IC} = 0.055\, H a^{1/2} (l/a)^{-1/2} \tag{1}$$

where H is the Vickers' hardness; a, l are the half-diagonal of the indent and the radial crack length, respectively. The pure silica sample was also investigated for comparison.

The phase composition was determined using an X-ray diffractometer (Rigaku Denki RAX-10) using CuK_α radiation. The microstructural features of the sintered samples were characterized by TEM (JEM-200CX) and HREM.

3. Results and discussion

Fig. 1 shows ZrO_2 particles, dispersed homogeneously in the silica matrix. The sizes of ZrO_2 and SiO_2 particles are about 5 and 40 nm, respectively. The XRD pattern of the ZrO_2–SiO_2 sample (Fig. 2a) reveals that the structure is still amorphous after the gel has been calcined at 700 °C and there is a broadened peak at $2\theta = 30.2^\circ$ which may indicate the ordering of t-ZrO_2 phase.

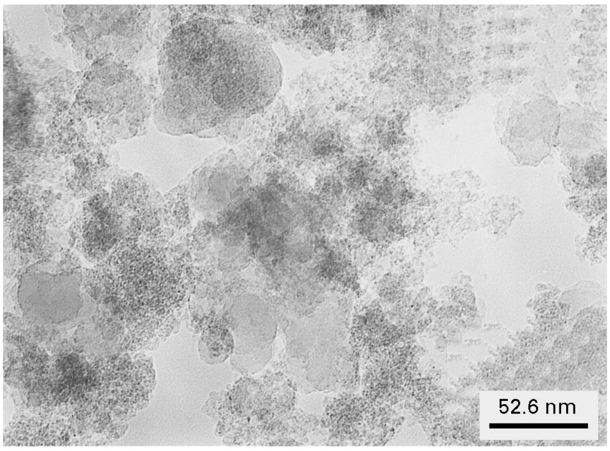

Figure 1 Transmission electron micrograph of ZrO_2–SiO_2 (20ZS) composite powder calcined at 700 °C for 2 h.

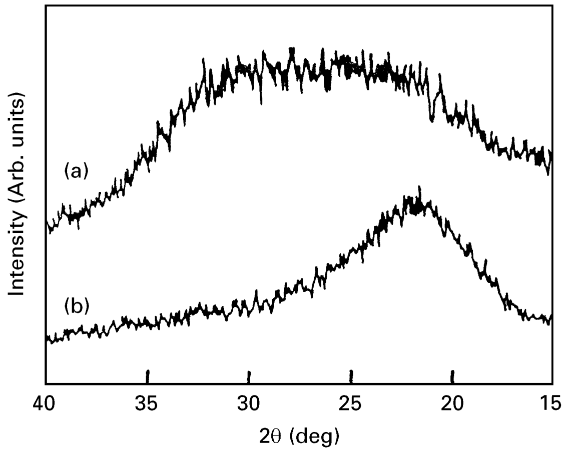

Figure 2 XRD patterns of (a) 20ZS composite powder calcined at 700 °C for 2 h, and (b) the sintered silica sample by the hot-pressed method.

The sintered density of SiO_2 and ZrO_2–SiO_2 composite, measured by the water displacement method, was 98.5% theoretical.

X-ray diffraction analysis (Fig. 3a) on the polished surface of samples indicated that the hot-pressed sample (20ZS) is composed of t-ZrO_2 and amorphous silica. There was no evidence of the formation of zircon ($ZrSiO_4$), and the crystallization of cristobalite from the amorphous silica, which is consistent with the results from the pure silica sample (Fig. 2b) sintered under the same conditions. The electron diffraction patterns also revealed that zirconia crystallizes as tetragonal phase (Fig. 4b) and the silica matrix remains amorphous (Fig. 4c). It is clear that the silica matrix has the ability to stabilize the zirconia as tetragonal phase at temperatures up to 1350 °C. It has been reported [9, 10] that conversion of tetragonal to monoclinic phase is noticeably inhibited by the presence of SiO_2 in the ZrO_2–SiO_2 system. The stability of t-ZrO_2 may be interpreted by the following factors. As proposed by Lange [11], the free energy change of the tetragonal-to-monoclinic (t → m) phase transformation, $\Delta G_{t\to m}$, can be described as

$$\begin{aligned}\Delta G_{t\to m} &= (\Delta G_c^m - \Delta G_c^t) + (\Delta G_s^m - \Delta G_s^t) \\ &\quad + (\Delta G_{se}^m - \Delta G_{se}^t) \\ &= -\Delta G_c + \Delta G_s + \Delta G_{se}\end{aligned} \tag{2}$$

where ΔG_c^m and ΔG_c^t, and ΔG_s^m and ΔG_s^t, and ΔG_{se}^m and ΔG_{se}^t are the chemical free energies, the surface free energies, and the strain free energies in the monoclinic and the tetragonal state, respectively. Altering the change in chemical free energy, $|\Delta G_c|$, can be accomplished by doping with additives such as Y_2O_3, CeO_2 etc. The change in chemical free energy, $|\Delta G_c|$, may be constant, because no additives were used in the present study. The surface free energy is inversely proportional to the grain size as expressed by

$$\Delta G_s = 6(\gamma_m - g_s \gamma_t)/d \tag{3}$$

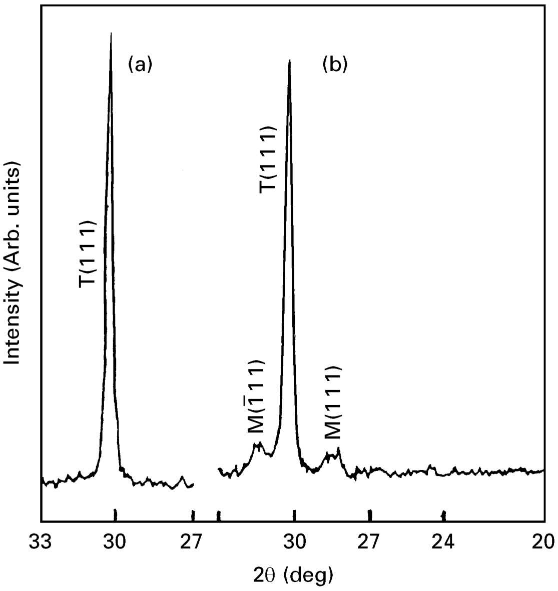

Figure 3 XRD patterns of (a) 20ZS sintered sample on the polished surface, (b) powders crushed and ground from the 20ZS sintered sample.

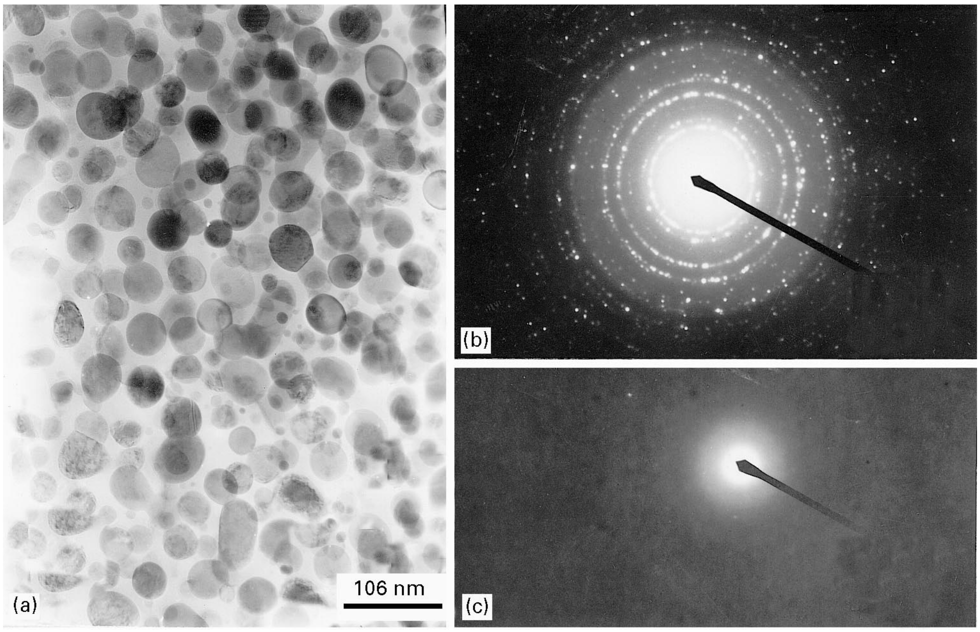

Figure 4 (a) Transmission electron micrograph of 20ZS sintered sample; electron diffraction patterns of (b) a zirconia grain, and (c) silica matrix.

where γ_m and γ_t are the specific interfacial energies in the monoclinic and the tetragonal state, d is the diameter of the t-ZrO_2 grain, $g_s = A_t/A_m$, and A_t and A_m are the interfacial surface areas. Therefore, the stability of t-ZrO_2 increases with decreasing grain size. Because the ZrO_2 particles are dispersed in the silica matrix, the grain growth of ZrO_2 is impeded due to the SiO_2 encasement. For instance, the average size of t-ZrO_2 particles is about 50 nm as determined from the transmission electron micrograph in Fig. 4a, which is in agreement with the value, calculated from the XRD pattern (Fig. 3a) using Scherer's formula, $d = K\lambda/\beta\cos\theta$, where d is the average particle size, β the line-width at half-peak intensity, and λ the wavelength. Furthermore, the presence of some smaller t-ZrO_2 grains in the sintered structure indicates that the growth of ZrO_2 grains is inhibited by the silica matrix. Thus, the t-ZrO_2 grains with smaller sizes are reasonably expected to be stable in the silica matrix. The change in the strain energy can be expressed as $\Delta G_{se} = E_c(\Delta V/V)^2/6$, where E_c and $\Delta V/V$ are the Young's modulus of the matrix and isotropic volume expansion by transformation, respectively. Compared with the stability of t-ZrO_2 for the pure zirconia ceramics, the stability of t-ZrO_2 in the silica matrix is enhanced by the strain energy.

From a purely chemical view, Nagarajan and Rao [9] assumed that a thin layer of $ZrSiO_4$ formed on the ZrO_2 particles may be responsible for the inhibition of the t → m transformation. As shown in Fig. 5a, we can see a high-resolution lattice image of a ZrO_2 particle (t-ZrO_2) surrounded by the amorphous silica matrix. A thin layer of interphase reaction (Fig. 5b) is found, which may be ascribed to the formation of Zr–O–Si bonds, because the formation of $ZrSiO_4$ could not be detected by XRD, or the content of $ZrSiO_4$ formed is beyond the resolution of XRD. The interphasic reaction layer plays a role in stabilizing ZrO_2 grains as tetragonal phase. Because the t → m transformation involves a positive change of volume and the t-ZrO_2 grains are constrained by the interphasic reaction layers, the t → m transformation is hindered.

From Table I we find the fracture strength and Young's modulus have been much raised by adding 20 vol % ZrO_2 particles in the silica matrix. The SiO_2 sintered sample is not able to give the fracture toughness under the same experimental conditions as those for the ZrO_2–SiO_2 samples; the measured mechanical properties of SiO_2 sintered sample are lower than the values of fused silica glass. It is argued that the lower values may be due to the presence of the porosity and to the surface damage caused by mechanical grinding. The strength will be higher when the SiO_2 sintered samples are polished. Generally, the toughening mechanisms in ceramics containing zirconia are related to the volume expansion and shear strain associated with the tetragonal to monoclinic transformation. There are two well-accepted mechanisms which have been discussed in great detail everywhere, i.e. stress-induced transformation toughening and microcrack toughening. In the preparation of $3ZrO_2 \cdot 2SiO_2$ glass-ceramics by the sol–gel process from metal alkoxides, Nogami and Tonozawa [7] reported that the higher fracture toughness was attributed to tetragonal →monoclinic ZrO_2 transformation toughening. In the present study, however, we found that zirconia is completely tetragonal phase in the sintered sample (Fig. 3a), and there are weak peaks of monoclinic phase present in the XRD profile (Fig. 3b) after the sintered sample ZrO_2–SiO_2 was crushed and ground to powders. This may mean that the tetragonal transformation is not the main

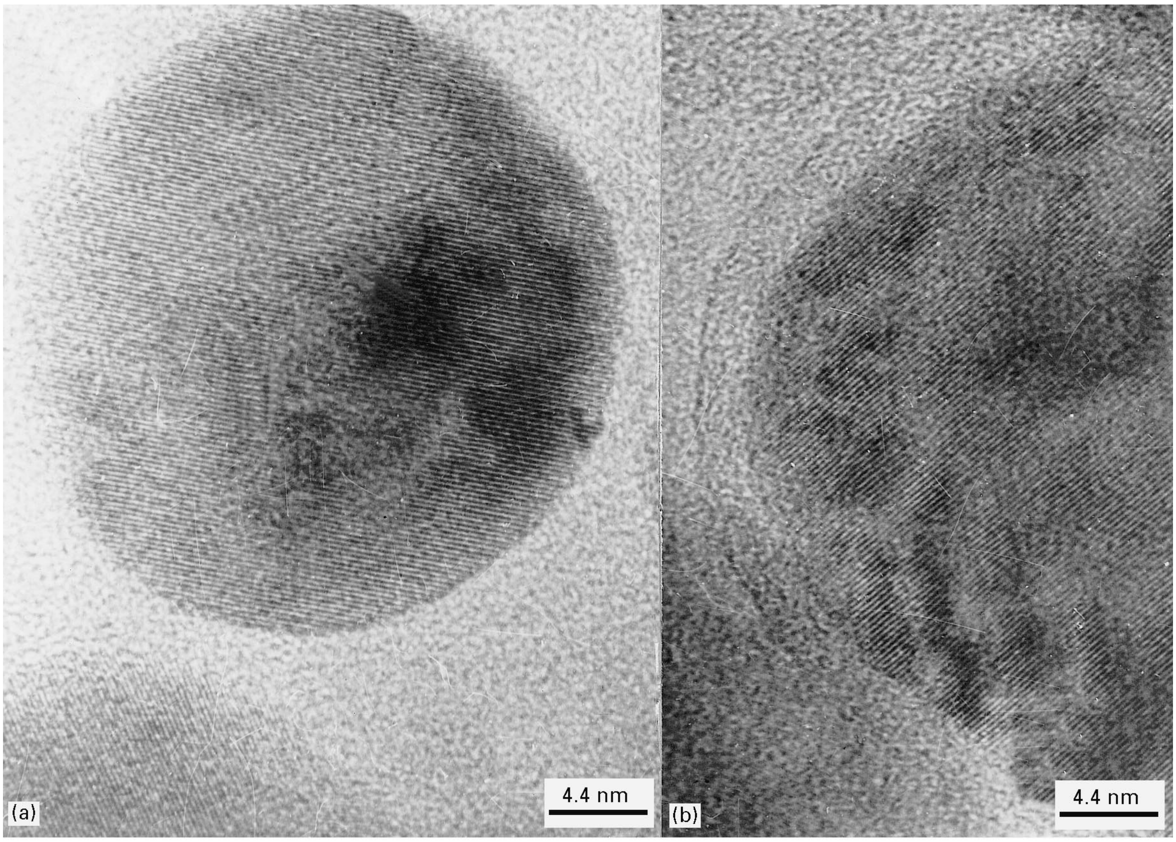

Figure 5 HREM micrographs of 20ZS sample, (a) t-ZrO_2 with a spherical grain dispersing in the silica matrix, and (b) interphasic reaction layer between the t-ZrO_2 and the silica matrix.

TABLE I Mechanical properties of sintered silica and ZrO_2–SiO_2 composite

Materials	Young's modulus (GPa)	Strength (MPa)	K_{IC} (MPa $m^{1/2}$)
SiO_2	49.5	54.8	–
ZrO_2–SiO_2	56.4	128.1	2.88

strengthening and toughening mechanism in the ZrO_2–SiO_2 system, because the t-ZrO_2 particles are smaller and only parts of the t-ZrO_2 grains with larger size can transform to monoclinic phase under the applied stress.

From another viewpoint, elastic modulus, *E*, may play an important role in the mechanical properties of the fabricated ceramics. On the basis of the Griffith equation

$$\sigma = (2E\gamma/\pi c)^{1/2} \qquad (4)$$

where σ is the mechanical strength, *E* the elastic modulus, γ the fracture surface energy, and *c* the length of the crack flaw, a higher *E* leads to a better mechanical strength. The Young's modulus increases when ZrO_2 is added, as listed in Table I, thus, the enhanced strength may be ascribed to the higher modulus of elasticity of zirconia dispersed in the silica matrix.

There is another toughening mechanism of particulate-enhanced ceramics which has been attributed to the residual stress (strain) field due to mismatch between the coefficients of thermal expansion (CETs) of the ceramic matrix and particulate. For a particulate-reinforced ceramic-matrix composite with $\alpha_p > \alpha_m$, such as TiB_2/SiC composite [12], the average thermal stresses in the particulates and matrix are in tension and compression, respectively. Similar to that of the TiB_2/SiC composite, the thermal residual stress field in ZrO_2/SiO_2 composite consists of two regions: the tensile stress region in the particulates and their vicinity in the matrix, and the compressive stress region in the bulk of the matrix. The residual stress at the surface layer of the composite is partially relaxed due to having a free surface, and the stress acting at the surface become compressive. Hence, the increase in both strength and toughness by adding zirconia may be partially due to such compressive stresses at the surface layer.

High-resolution electron micrographs provide atomic-level information on the interphase structure. The ZrO_2 particles embedded in the silica matrix are mainly spherical and dispersed homogeneously. Some abnormal grain growth of ZrO_2 particles through neck-connection (Fig. 6) is detected occasionally between two ZrO_2 particles which are adjacent to each other. Phase boundaries between ZrO_2 and amorphous silica are clear, as illustrated in Fig. 5a. However, interphasic reaction layers are observed in Fig. 5b and 7, which are ascribed to the formation of Zr–O–Si bonds, because no zircon has formed based on the XRD analysis mentioned above. The authors assumed that these interphasic reaction layers play an

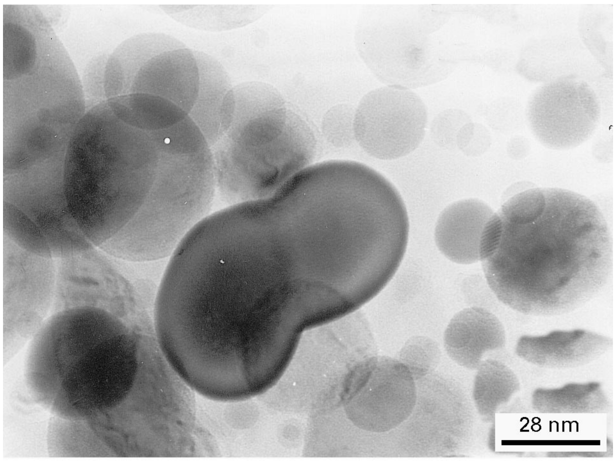

Figure 6 Illustration of abnormal growth of a zirconia grain.

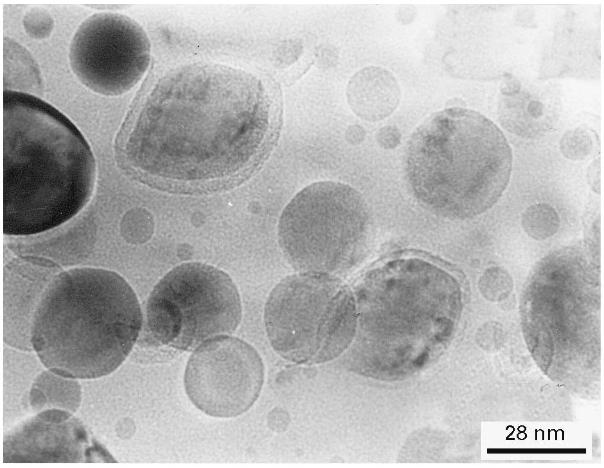

Figure 7 Image of the interphasic reaction layer around the t-ZrO_2 particle.

important role in controlling the physical properties of the ZrO_2–SiO_2 composite. One role is that the interphasic reaction layer makes a contribution to stabilizing the zirconia as tetragonal phase; the other is that the strong chemical bonding between ZrO_2 grains and the silica matrix will absorb the fracture energy and thus result in the enhanced mechanical properties of the composite.

4. Conclusions

1. The stability of tetragonal ZrO_2 is interpreted by the smaller size of ZrO_2 grains due to the encasement of silica, the constraint effect of the silica matrix, and the formation of Zr–O–Si interphasic reaction layer around the ZrO_2 particles.

2. Despite the fact that less conversion of t-ZrO_2 to m-ZrO_2 took place, the mechanical properties of silica were significantly increased by doping with 20 vol % ZrO_2 particles. The increase in mechanical properties was attributed to the residual compressive stress at the surface layer and the higher modulus of elasticity of zirconia dispersed in the silica matrix.

3. Transmission electron micrographs show the spherical ZrO_2 grains dispersed homogeneously in the silica matrix. It is revealed by HREM that the majority of the interphases between ZrO_2 and SiO_2 are clear, whereas some interphasic reaction layers are found, and occasionally abnormal growth of ZrO_2 grain too.

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