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ORIGINAL PAPER

Microstructural, mechanical and electrical properties of alumina-doped cubic zirconia (c-ZrO_2)

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Abstract The effect of Al_2O_3 content on microstructure, hardness, fracture toughness and electrical conductivity behaviours of c-ZrO_2 ceramics was investigated using high-purity commercial powder of 8 mol% yttria-stabilised c-ZrO_2 doped with up to 10 wt.% Al_2O_3. XRD results showed that the c-ZrO_2 specimens doped up to 0.3 wt.% Al_2O_3 revealed no Al_2O_3 peaks, indicating that Al_2O_3 was completely solubilised in the c-ZrO_2 matrix. However, when >0.3 wt.% Al_2O_3 was added, Al_2O_3 peaks started to appear, showing that overdoped Al_2O_3 was not solubilised in the c-ZrO_2 matrix. The introduction of Al_2O_3 significantly enhanced the hardness and fracture toughness of c-ZrO_2. The hardness and fracture toughness increased with increasing Al_2O_3 content. The maximum hardness and fracture toughness values reached 1,459±8 kg/mm^2 and 2.41±0.02 MPa/m$^{1/2}$, respectively, with the addition of 10 wt.% Al_2O_3, while these values were 1,314±11 kg/mm^2 and 1.5 ±0.03 MPa/m$^{1/2}$ for undoped c-ZrO_2. The increase of hardness and fracture toughness can be attributed to smaller grain size, the increment of Young's modulus of Al_2O_3-doped c-ZrO_2 and different expansion coefficients of c-ZrO_2 and Al_2O_3 grains. The electrical conductivity of the specimens was measured using a frequency response analyzer in the frequency range of 5–13 MHz and in the temperature range of 300–800 °C. It was seen that electrical conductivity slightly increased with increasing Al_2O_3 content up to 1 wt.%, and further increase in Al_2O_3 led to a decreased in the conductivity.

Keywords Cubic zirconia · Electrical conductivity · Hardness · Fracture toughness · Alumina

Introduction

Cubic zirconia is a fast oxide ionic conducter at high temperatures. Because of its high stability in both reducing and oxidising environments, the cubic zirconia has been used as an electrolyte material for solid oxide fuel cells and oxygen sensors. Despite these advantages, the room and high temperature mechanical properties of the cubic zirconia are rather low. Therefore, it is necessary to improve the mechanical properties of cubic zirconia to guarantee the lifetime and reliability of the solid oxide fuel cell system [1]. Generally, the properties of ceramics depend on the microstructure. Many researchers have shown [1–5] that dispersion of nano-sized particles into matrix grains is an effective technique for improving mechanical properties of ceramics without deteriorating electrical conductivity. In the present study, the effect of Al_2O_3 dopant in amounts up to 10 wt.% on the microstructure, hardness, fracture toughness and electrical conductivity behaviours of c-ZrO_2 ceramics was determined.

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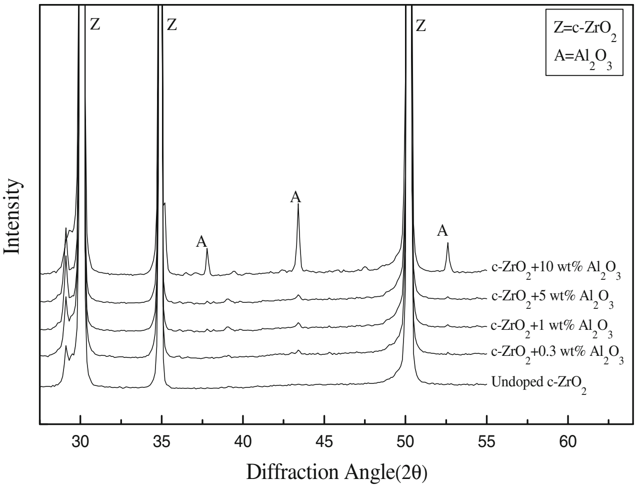

Fig. 1 X-ray diffraction patterns of various amount of Al_2O_3-doped c-ZrO_2. *Z* and *A* indicate c-ZrO_2 and Al_2O_3, respectively

Materials and procedures

The materials used in the present work were 8 mol% yttria-stabilised cubic zirconia (c-ZrO_2) powder, Tosoh, Japan and high-purity (>99.999%) alumina (α-Al_2O_3) powder, Sumitoma, Japan. The average particle sizes were 0.3 μm for c-ZrO_2 and 0.4 μm for α-Al_2O_3.

Colloidal processing was used for the mixing of powders in order to achieve a uniform distribution and homogeneous microstructure. The mixed powders were dried by rotary distillation, sieved through a 60-mesh screen to remove hard agglomerate particles and then die-pressed into disks by uniaxial pressing at 40 MPa in a steel die followed by cold isostatic pressing at 400 MPa. The specimens were sintered at 1,450 °C for 1 h.

For hardness and fracture toughness measurements, disk specimens were employed. The dimension of the disk specimen after polishing to a 1-μm diamond finish was 15 mm in diameter and 10 mm in thickness. Both hardness and fracture toughness were measured using a Vickers indenter. Indentations were made on polished specimens with a load of 20 kg held for 15 s. Ten tests were conducted for each specimen. The indentation fracture toughness was calculated using the formula proposed by Anstis et al. [6].

Scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometer attachment was used to characterize the microstructure of as-sintered specimens. Phase content was determined using XRD with CuKα radiation.

The electrical conductivity measurements were carried out with pellet specimens of 10-mm diameter and about

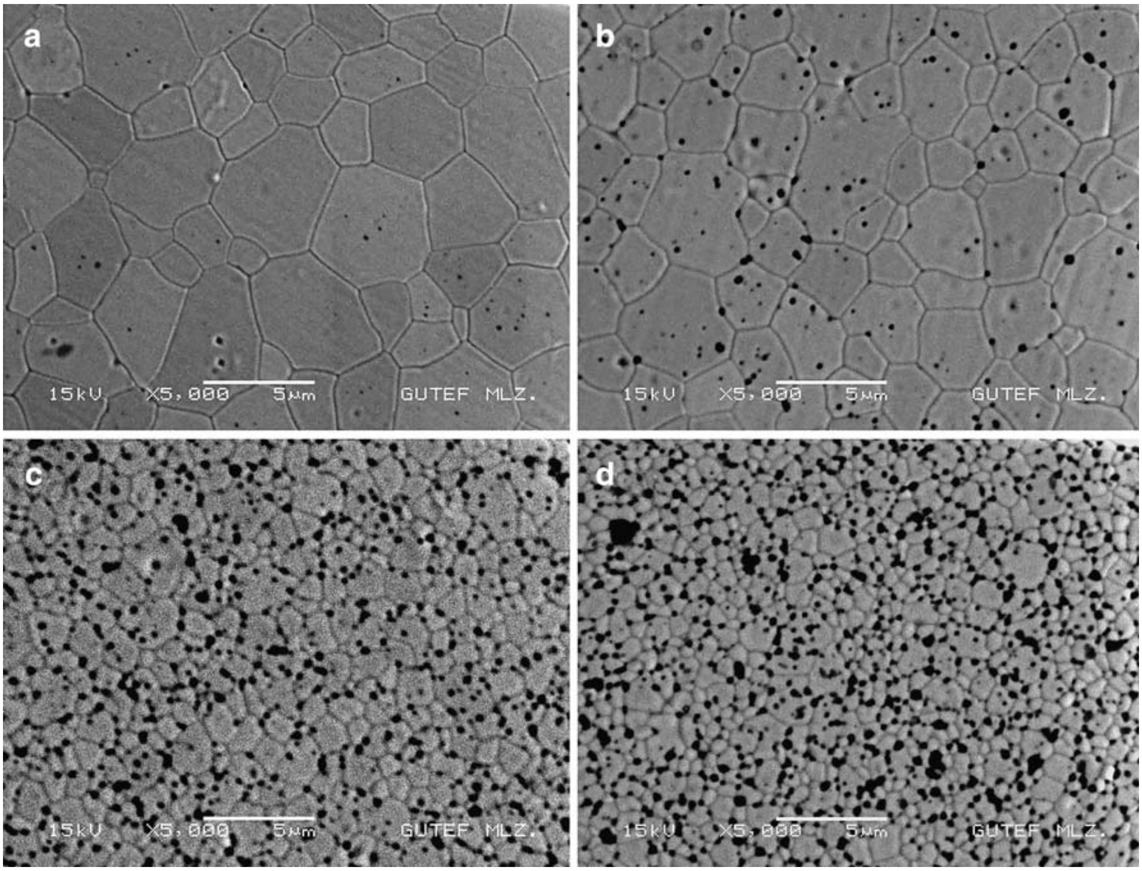

Fig. 2 The effect of Al_2O_3 addition on microstructure of c-ZrO_2 **a** undoped, **b** 1 wt.% Al_2O_3, **c** 5 wt.% Al_2O_3 and **d** 10 wt.% Al_2O_3

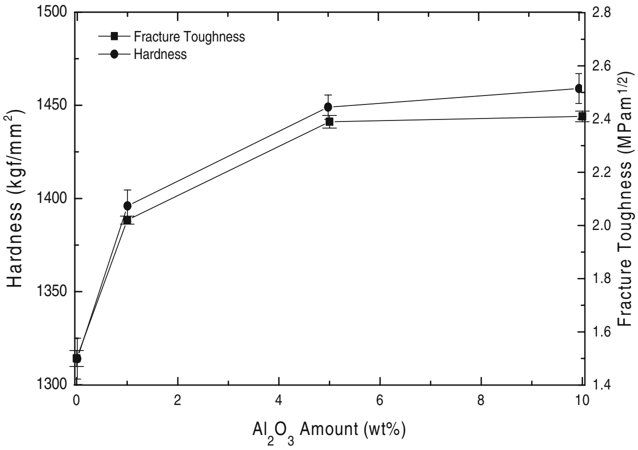

Fig. 3 The effect of Al_2O_3 content on hardness and fracture toughness of c-ZrO_2

2-mm thick. The two surfaces of each sintered pellet were slightly polished with abrasive paper, and platinum paste was applied to both sides of the specimens. The specimens were then dried in an oven at 100 °C to eliminate the solvent and annealed at 1,000 °C for 30 min to avoid an excessive shrinkage of the platinum electrodes. The temperature dependence of electrical conductivity was measured using a frequency response analyzer (Solartron Model 1260) in the frequency range of 5–13 MHz. Measurements were made in air and in the temperature range of 300–800 °C. The equilibrium time chosen before temperature change was 10 min.

Experimental results and discussion

XRD patterns from various amounts of Al_2O_3-doped c-ZrO_2 specimens are shown in Fig. 1. The c-ZrO_2 specimens doped up to 0.3 wt.% Al_2O_3 revealed no Al_2O_3 peaks, indicating that Al_2O_3 was completely solubilised in the c-ZrO_2 matrix and did not remain in the specimens as a secondary phase. However, when >0.3 wt.% Al_2O_3 was added, Al_2O_3 peaks started to appear, showing that over-doped Al_2O_3 was not solubilised in the c-ZrO_2 matrix, forming a secondary phase. These results were also confirmed by measuring the lattice parameter change of c-ZrO_2 with Al_2O_3 content [7].

The scanning electron micrographs of the c-ZrO_2 with and without Al_2O_3 are shown in Fig. 2. The Al_2O_3 particles can be visible for the specimens with Al_2O_3 content ≥1 wt.%. This suggests that only small part of the Al_2O_3 dissolved in the c-ZrO_2 matrix and the rest of Al_2O_3

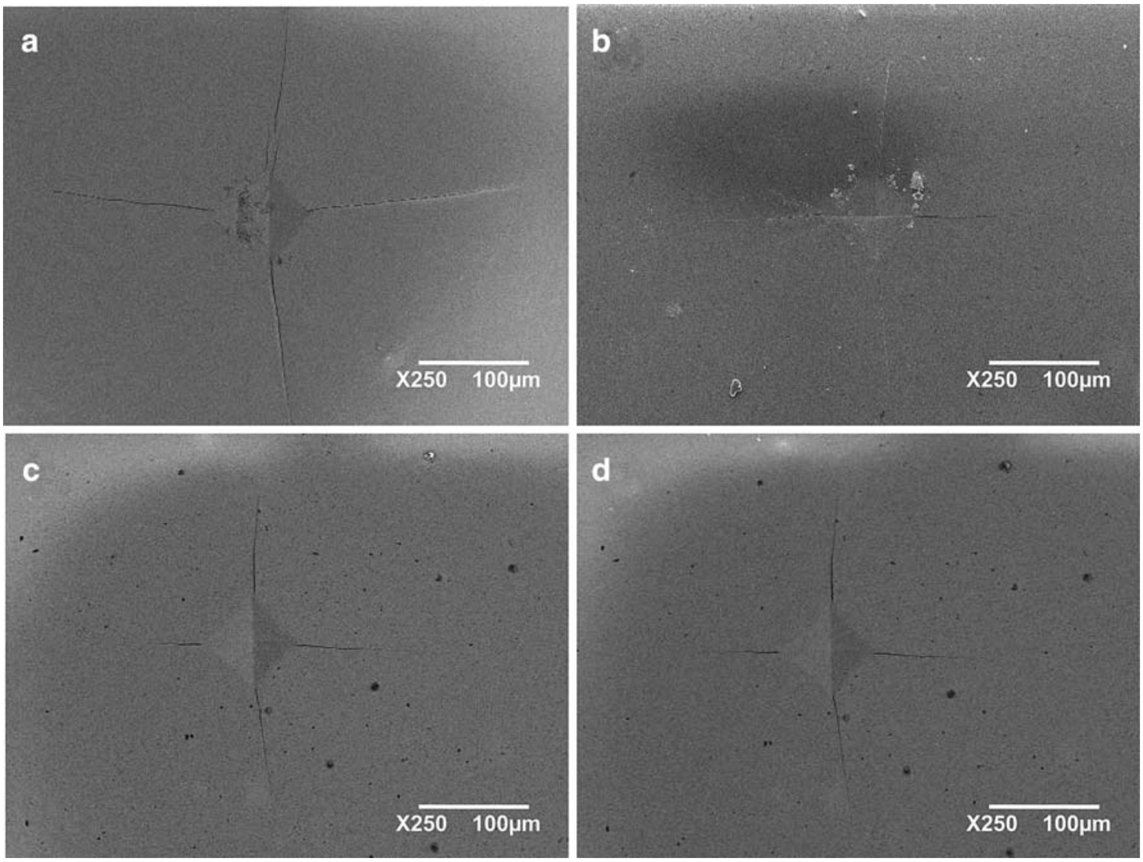

Fig. 4 SEM micrographs of Vickers indentations with different crack lengths in the c-ZrO_2 specimens doped with various amounts of Al_2O_3 **a** undoped, **b** 1 wt.% Al_2O_3, **c** 5 wt.% Al_2O_3 and **d** 10 wt.% Al_2O_3

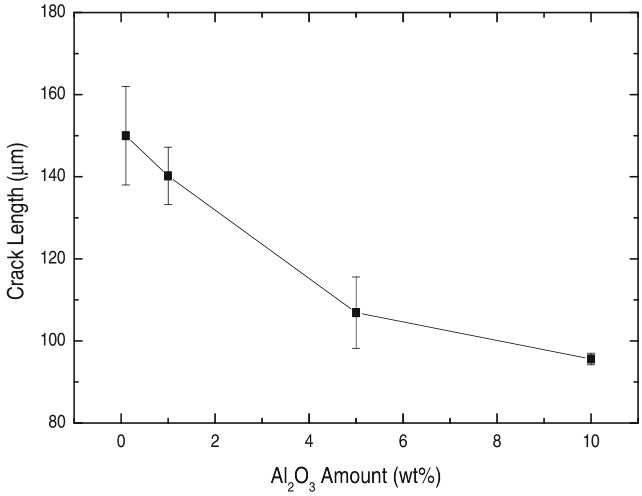

Fig. 5 The change of indentation-crack length as a function of Al_2O_3 content

segregated at grain boundaries of the c-ZrO_2. The comparison of the grain size of the specimens at the same heat treatment indicated that grains were larger in the undoped c-ZrO_2 than in the Al_2O_3-doped c-ZrO_2 specimens. Also, the grain size of the Al_2O_3-doped c-ZrO_2 decreased with increasing Al_2O_3 content.

The result of the Vickers hardness carried out on the various amount of Al_2O_3-doped c-ZrO_2 specimens is shown in Fig. 3. It was seen that the addition of Al_2O_3 resulted in an enhancement of Vickers hardness and also, the hardness values increased with increasing Al_2O_3 content. This increase in hardness can be attributed to smaller grain size of the Al_2O_3-doped c-ZrO_2 specimens. Plastic deformation of the c-ZrO_2 matrix with up to 10 wt.% Al_2O_3 can be much harder than that of the monolithic c-ZrO_2 because grain boundaries work as an obstacle for plastic deformation. The increase in hardness with increasing Al_2O_3 content can also be explained by the increased hard Al_2O_3 grains in the c-ZrO_2 matrix.

The relation between fracture toughness and Al_2O_3 content is also shown in Fig. 3. It was observed that fracture toughness values increased as the Al_2O_3 content increased. For example, undoped c-ZrO_2 had a fracture toughness of 1.5±0.03 $MPa/m^{1/2}$, whereas c-ZrO_2 specimen containing 10 wt.% Al_2O_3 had a fracture toughness of 2.41±0.02 $MPa/m^{1/2}$. Figure 4 shows SEM microstructures of the cracks generated by the indentation load of 20 kg. Note that cracks emanate from the corners of the indents, and crack lengths were different depending on the Al_2O_3 content. For the undoped c-ZrO_2, the indents with long

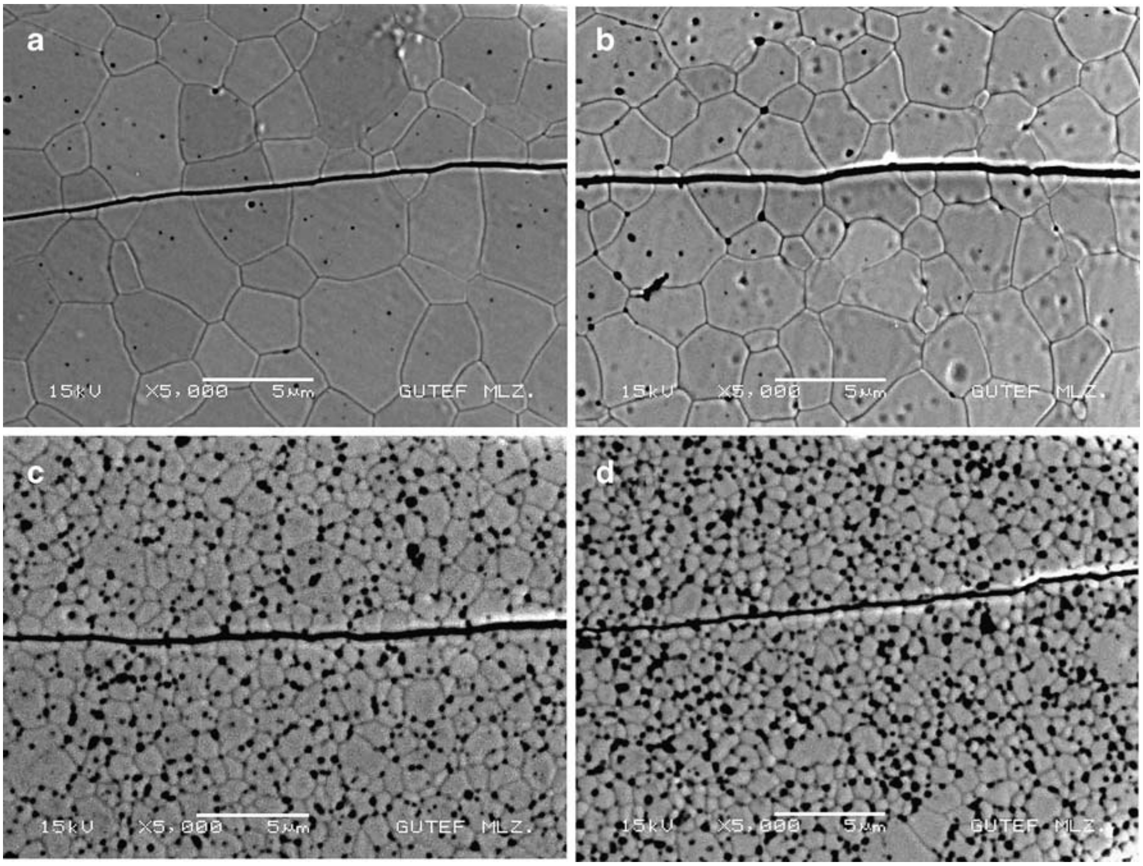

Fig. 6 Crack propagation paths in the c-ZrO_2 specimens doped with various amounts of Al_2O_3 **a** undoped, **b** 1 wt.% Al_2O_3, **c** 5 wt.% Al_2O_3 and **d** 10 wt.% Al_2O_3

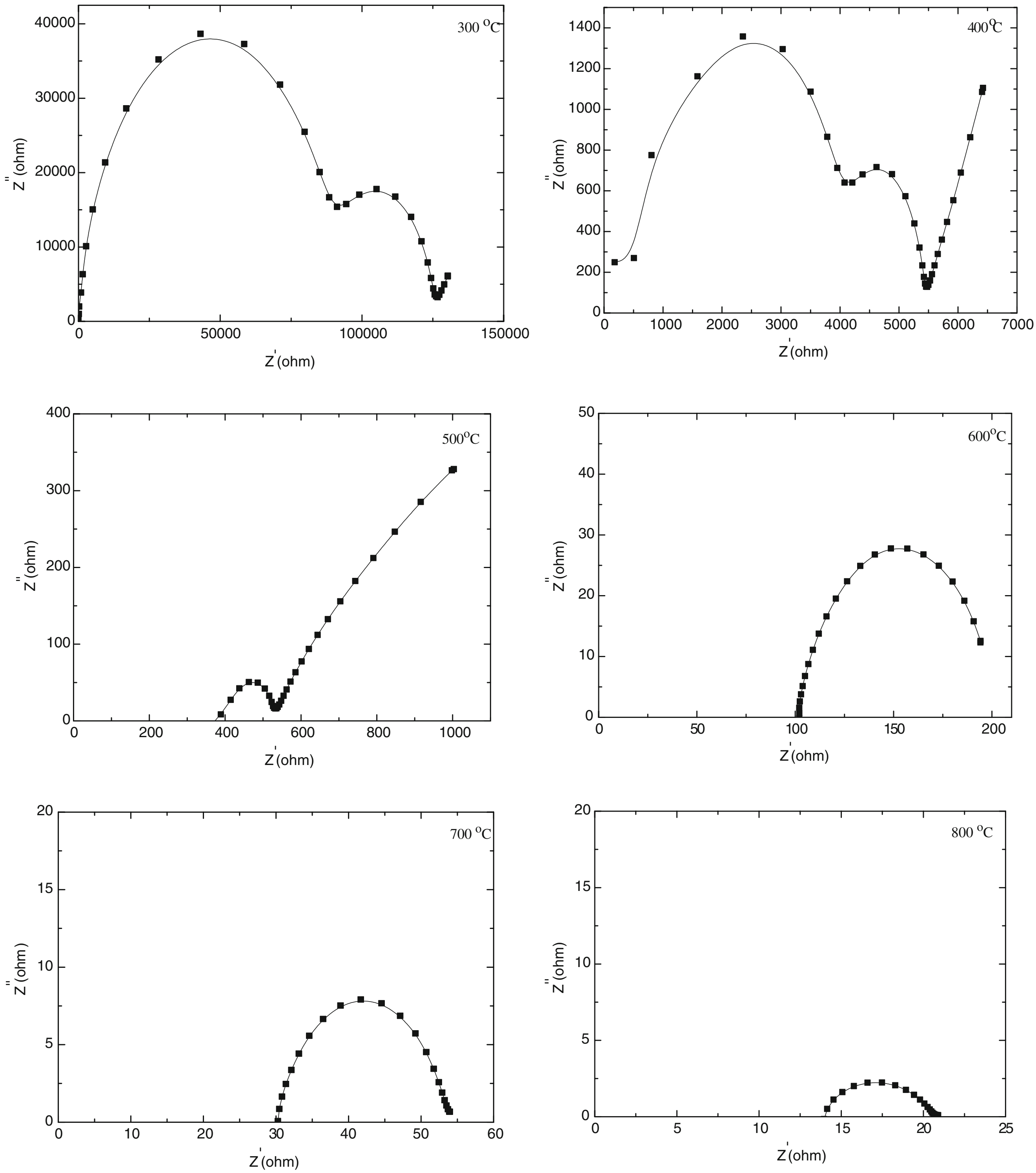

Fig. 7 The ac impedance spectroscopes of 5 wt.% Al_2O_3-doped c-ZrO_2 specimens tested at different temperatures

crack lengths were observed. On the contrary, with increasing Al_2O_3 amount, the crack lengths decreased (Fig. 5). The increase in the fracture toughness and the decrease in the crack length in the specimens with higher amount of Al_2O_3 could be attributed to increment of Al_2O_3 content and thus smaller grain size. In general, smaller grain size shows higher fracture toughness. When a crack propagates, it follows either grain boundaries or around grains. The new surfaces are generated with the refinement of grains. This results in greater surface energy and higher value of fracture toughness. Thus, by controlling the grain size, fracture toughness can be controlled. SEM investigations of the indentation cracks on thermally etched surfaces showed that cracks propagated through the c-ZrO_2 grains, c-ZrO_2 grain boundaries, the interface between the c-ZrO_2 and the Al_2O_3 grains depending on the Al_2O_3 content (Fig. 6). The cracks propagated straight through the c-ZrO_2 grains, i.e. transgranular fracture mode for the undoped c-ZrO_2 (Fig. 6a), while it was deflected by Al_2O_3 particles in the Al_2O_3-doped c-ZrO_2 specimens in which reinforcing particles were dispersed finely and uniformly to achieve an effective toughening of the c-ZrO_2 matrix. Therefore, crack deflection was the reason for fracture toughness improvement. The deflection was caused as a result of the residual stresses associated with differential Young's modulus and the coefficients of the thermal expansion between c-ZrO_2 (10.5×10^{-6} K^{-1}) and Al_2O_3 (8.8×10^{-6} K^{-1}) grains [8]. In the c-ZrO_2 matrix, tensile and compressive stresses are developed. On the other hand, the Al_2O_3 grains and c-ZrO_2/Al_2O_3 interface are in compression. When a crack propagates through Al_2O_3-doped c-ZrO_2 specimen, residual stress field in the matrix attracts the crack towards the Al_2O_3 particles, and the crack either passes through the Al_2O_3 particles or propagates along the particle/matrix interface. In either case, crack deflection and fracture energy of Al_2O_3 particles and/or c-ZrO_2/Al_2O_3 interface lead to an improvement in fracture toughness [8].

Generally, the ac impedance of an ionic conductor contains the contributions from grain interior, grain boundary and electrode–electrolyte interface, which can be reflected in a complex plane by three successive arcs [9]. In a practical case, however, not all these arcs can be observed, depending on the nature of the specimens and testing conditions. In the present study, the electrical measurements were carried out on undoped and Al_2O_3-doped c-ZrO_2 specimens sintered at 1,450 °C. As an example, the ac impedance spectroscopes of 5 wt.% Al_2O_3-doped c-ZrO_2 specimens tested at different temperatures are shown in Fig. 7. Three arcs can be identified clearly at temperatures of 300 and 400 °C. Whereas when the temperature was higher than 400 °C, the grain boundary arc disappeared as the activation energy for the grain boundary conductivity is higher than that for the grains. It was also seen that the resistances of the grain and grain boundaries decreased significantly with increasing temperature. This decrease was mainly due to thermally-activated character of ionic motion.

Figure 8 shows the effect of Al_2O_3 content on the grain conductivity of c-ZrO_2 at 400 °C. The grain conductivity at all temperatures increased slightly with increasing Al_2O_3 content up to 1 wt.%. The increased conductivity was mainly a result of the increased grain size and the consequent reduction in the grain boundary area. It is well known that silica has a marked negative influence on the conductivity. The increase in the conductivity may also result from the well-known 'silica scavenging' effect of Al_2O_3. The presence of minor silica impurities may lead to the formation of Y–Si–O phases at the grain boundaries and to the depletion of the grain surface layer with yttria. Thus, minor alumina additions may scavenge silica, suppressing this depletion. In the case of the c-ZrO_2 with higher than 1 wt.% Al_2O_3, the grain conductivity decreased with increasing Al_2O_3 content. The decrease in the conductivity could be due to the grain refinement. As mentioned above, the addition of Al_2O_3 inhibited the grain growth by grain boundary pinning. Consequently, the grain size of the Al_2O_3-doped c-ZrO_2 is smaller than non-Al_2O_3-containing c-ZrO_2. The tendency for this effect was to decrease the conductivity. The decrease in conductivity above 1 wt % Al_2O_3 can also be attributed to the decrease in the volume fraction of the conducting phase in the specimens.

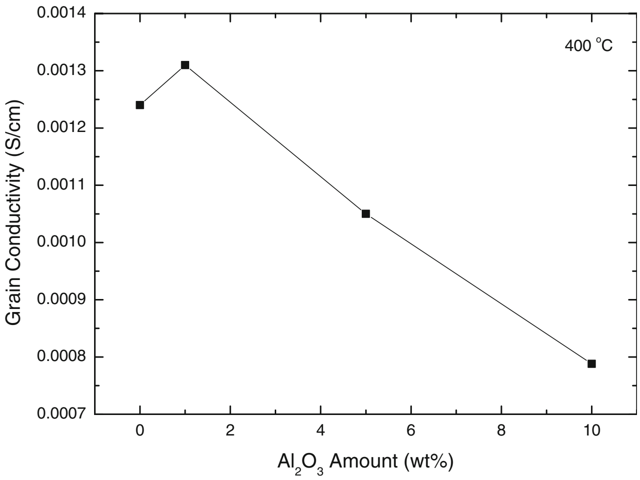

Fig. 8 The effect of Al_2O_3 content on the grain conductivity of c-ZrO_2 at 400 °C

Conclusion

The c-ZrO_2 specimen doped up to 0.3 wt.% Al_2O_3 reveals no Al_2O_3 peaks, indicating that Al_2O_3 was completely solubilised in the c-ZrO_2 matrix. However, when >0.3 wt.% Al_2O_3 was added, Al_2O_3 peaks started to appear, showing that overdoped Al_2O_3 was not solubilised in the c-ZrO_2 matrix.

The results of the Vickers hardness showed that the hardness of the Al_2O_3-doped c-ZrO_2 specimens increased with increasing Al_2O_3 content, and this increase was due to the decreased grain size. The fracture toughness also increased with increasing Al_2O_3 content. The increase of fracture toughness can be attributed to smaller grain size, the increment of Young's modulus of Al_2O_3-doped c-ZrO_2 specimens and different expansion coefficients of c-ZrO_2 and Al_2O_3 grains.

The grain conductivity increased slightly with increasing Al_2O_3 content up to 1 wt.%. The increased conductivity is mainly a result of the increased grain size and the consequent reduction in the grain boundary area. Also, the Al_2O_3 in cubic zirconia acts as a scavenger for SiO_2. In the case of cubic zirconia with higher than 1 wt.% Al_2O_3, the grain conductivity decreased with increasing Al_2O_3 content. The decrease of the conductivity could be due to the grain refinement.

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