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Influences of ZrO_2 nanoparticles on the microstructure and mechanical behavior of Ce-TZP/Al_2O_3 nanocomposites

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Influences of ZrO_2 nanoparticles on the mechanical properties and microstructure of hot-pressing Ce-TZP/Al_2O_3 ceramics were investigated. Meanwhile, t-ZrO_2 to m-ZrO_2 transformation toughening mechanism was investigated by X-ray diffractometry (XRD) method, and deflection of samples under applied stress were recorded too. The results show that when the percentage of ZrO_2 was 20%, the mechanical properties and microstructures of materials are optimum. Moreover, TEM observation show dislocation structures formation both in the Al_2O_3 and on the grain boundary. Because the dislocation agglomeration and fixation by ZrO_2 nanoparticles could deflect cracking or stop cracking development, a strengthening and toughening effect could be achieved.

1. Introduction

After Niihara and coworkers [1] discovered that the fracture strength of Al_2O_3 ceramics could be greatly improved by addition of small amounts of SiC nanoparticles (about 5 vol%), more and more composite ceramics with nanoparticles as the second phase, also known as nanocomposites, have been investigated. Meanwhile, the fracture behavior of nanocomposites is of interest because it has been demonstrated that they can exhibit unusually high fracture strength [2].

It is well-known that zirconia ceramics has the excellent mechanical properties including high fracture strength and high fracture toughness, so it could be added to ceramic matrix as the second phase to improve the fracture behavior of composite ceramics. By far the most commonly exploited ZrO_2-containing ceramics has been ZrO_2-toughened Al_2O_3 (ZTA) [3–5]. The earlier study results indicated positive toughening effect of ZrO_2 in the ZrO_2-Al_2O_3 composites. Maximum fracture strength and fracture toughness are achieved with 10 and 20 vol% ZrO_2 in the presence of Y_2O_3 as dopant, respectively [6]. Nevertheless, it has been found that the reports on the effects of ZrO_2 as the second phase on mechanical properties of ZrO_2 containing ceramics are different yet because of different research methods and experimental environments. Therefore, it is still necessary to further investigate the effects of ZrO_2 nanoparticles on the microstructure and mechanical properties of Ce-TZP/Al_2O_3 naocomposites.

The purpose of the present study is to prepare Ce-TZP/Al_2O_3 naocomposites by hot-pressing method and to investigate effects of ZrO_2 nanoparticles on the microstructure and mechanical properties. In addition, to the best of my knowledge, the reports about dislocation structures in ceramics are much less although some authors have ever reported on it, so the present work try to investigate the effect of the dislocation structure in Al_2O_3 matrix on mechanical properties of Ce-TZP/Al_2O_3 naocomposites.

2. Experimental procedure

2.1. Sample preparation

The self-prepared Ce-TZP nanometer powder and commercial Al_2O_3 powder were used in the present experiment. Ce-TZP nanometer powder with an average particle diameter of 40 nm was prepared from $ZrOCl_2\cdot 8H_2O$, $Ce(NO_3)_4$ and $AlCl_3\cdot 6H_2O$ by chemical co-precipitation method. Five kinds of Ce-TZP/Al_2O_3

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composite powders were prepared by mixture of Al_2O_3 powder with 10, 20, 30, 40 and 50 wt% Ce-TZP powder, respectively. Subsequently, five kinds of Ce-TZP/Al_2O_3 composite powders were hot-pressed into cylinder specimens with 50 mm in diameter and 5 mm in height at 1450°C with 20 MPa, respectively.

2.2. Measurement of mechanical properties

Samples were cut from hot-pressed cylinder specimens to be bars with size of $3 \times 4 \times 35$ mm for fracture strength and $2.5 \times 5 \times 25$ mm for fracture toughness with a diamond-impregnated saw. In accordance with 10, 20, 30, 40, and 50% Ce-TZP contents, the samples are designated as sample 1, sample 2, sample 3, sample 4 and sample 5. The fracture strength were measured by the three-point bending method with a span of 30 mm and a crosshead speed of 0.5 mm/min, whereas fracture toughness were determined by single edge notched beam (SENB) with the a span of 20 mm and a crosshead speed of 0.05 mm/min on ZPM-100KN materials tester. Meanwhile, the deflection under applied stress were recorded. Vickers hardness tests were carried out on the polished surface with a load of 9.8 N. Bulk density were measured by the Archimedes method and the relative density were calculated.

2.3. Microstructure analysis

The morphologies of fracture surfaces and polished surface of samples were observed by Quanta 200 scanning electron microscope (SEM). In order to investigate stress-induced transformation toughening of zirconia, the phase composition of the materials before and after subjected to the applied stress was determined by D8 ADVANCE X-ray diffractometer (XRD). Additionally, the microstructures of samples were also investigated by JEM-2010 transmission electron microscope (TEM).

3. Results and discussion

3.1. Effect of ZrO_2 content on mechanical properties

Fig. 1 shows that the mechanical properties of Ce-TZP/Al_2O_3 naocomposites are influenced by ZrO_2 content. It is found that relative densities of samples increase with increases of ZrO_2 content from 10 to 20%, but then declines from 20 to 50%. The relative density reaches the maximum value when the percentage of ZrO_2 is 20%. Meanwhile, fracture strength and fracture toughness take the same change tendency. When ZrO_2 content is 20%, the relative density, fracture toughness and fracture strength reach 99.3%, 9.69 MPa·m$^{1/2}$ and 1092 MPa, respectively. These results are related to the densification of materials during hot-pressing. When its percentage is less than 20%, ZrO_2 nanoparticles can be uniformly dispersed in Al_2O_3 matrix. Because the homogeneous dispersion of ZrO_2 nanoparticles in Al_2O_3 matrix can effectively restrain the abnormal growth of Al_2O_3 grains, ZrO_2 nanoparticles can accelerate densification of samples under this circumstance. A full densification can be achieved when amount of ZrO_2 is 20% (see Fig. 2a). But when its percentage is more than 20%, ZrO_2 nanoparticles can not be uniformly dispersed in Al_2O_3 matrix (see Fig. 2b). The inhomogeneous dispersion of ZrO_2 nanoparticles in Al_2O_3 matrix could cause the abnormal growth of Al_2O_3 grains (see Fig. 3), which could, in turn, lead to expansion till cracking, so the relative densities, fracture strength and fracture toughness of samples with more than 20% ZrO_2 decrease.

Additionally, the Vicker's hardness of five samples are HV13.4, HV12.33, HV12.21, HV11.62 and HV11.05, respectively. These results could be interpreted as hardness mainly related to the characteristics of materials. Because Ce-TZP/Al_2O_3 was composed of ZrO_2 and Al_2O_3, its hardness determined by percentages of ZrO_2 and Al_2O_3. ZrO_2 is softer than Al_2O_3, so the hardness of samples always decreased with increases of ZrO_2 contents.

3.2. The strengthening and toughening mechanisms

In order to help investigate toughness, the maximum deflection of five samples were recorded when fracture strength and fracture toughness were measured. These values are shown in Fig. 4. It is found that the deflec-

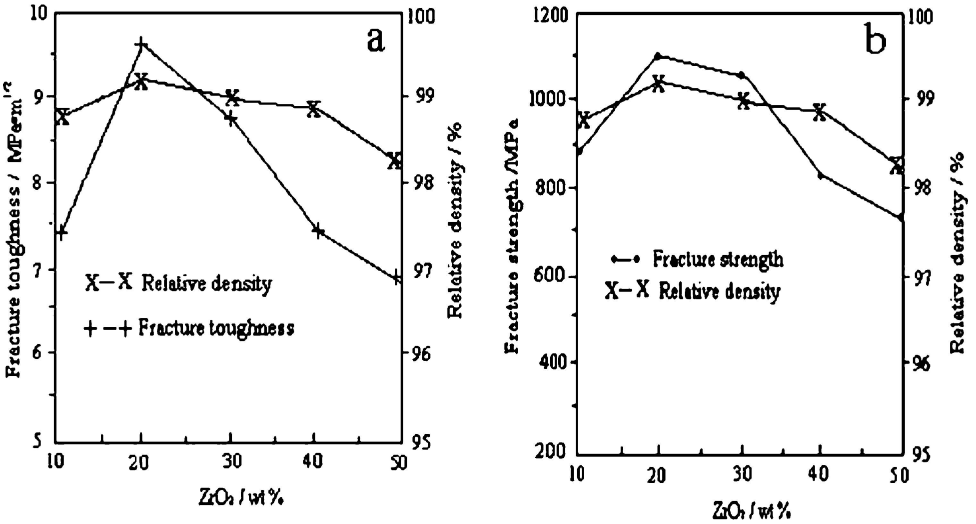

Figure 1 Effect of ZrO_2 content on fracture toughness (a), fracture strength (b) and relative density.

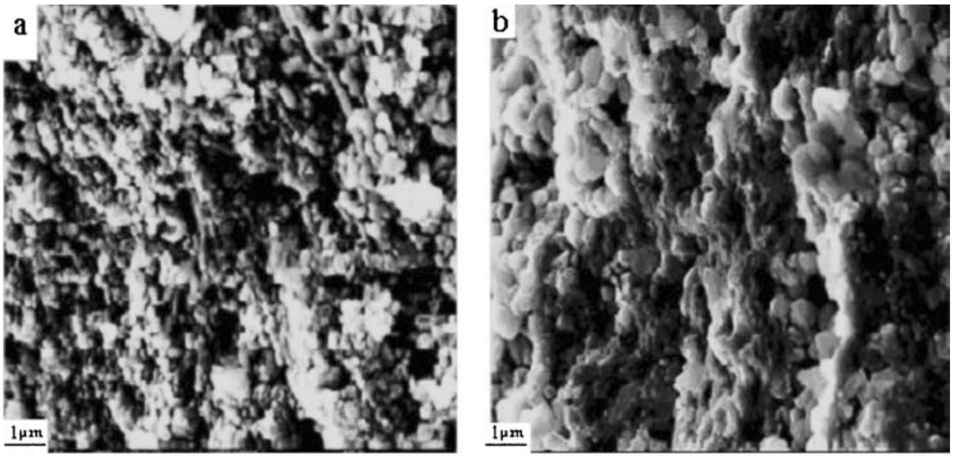

Figure 2 SEM micrographs of fracture surface (a) sample 2 and (b) sample 5.

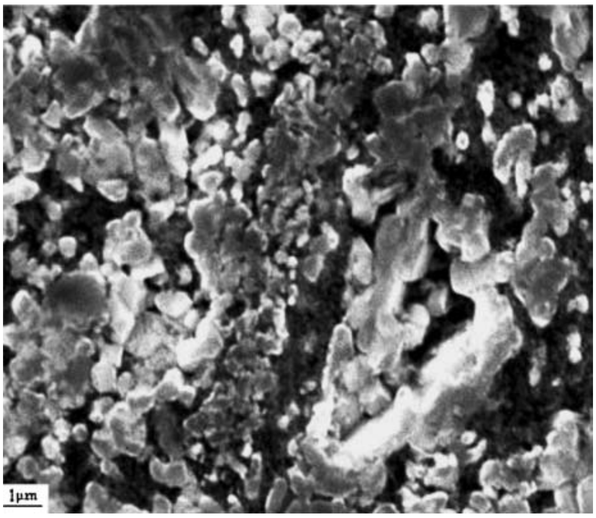

Figure 3 SEM micrographs of polished surface of sample 5.

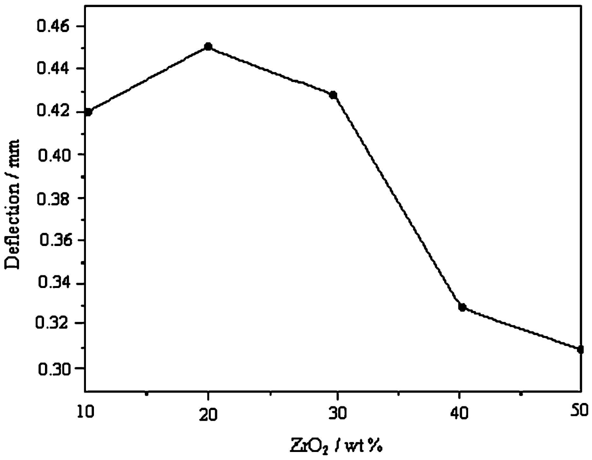

Figure 4 Influences of ZrO_2 (wt%) on deflection of samples.

tion increases with increases of ZrO_2 content firstly and reaches the maximum value at 20% ZrO_2, then decreases with increases of ZrO_2 content to the minimum value at 50% ZrO_2. This variation trend is the same as that of fracture strength, relative density and fracture toughness. This result also indicates that compared with the other samples, sample 2 has the best strengthening and toughening effects.

In Ce-TZP/Al_2O_3 nanocomposites, ZrO_2 nanoparticles distributed not only on the grain boundary but also in the grain of Al_2O_3, also known as the intergranular and intragranular ZrO_2 nanoparticles [7], respectively. The grain boundary between Al_2O_3 grains could be defined as main boundary while the grain boundary between Al_2O_3 and ZrO_2 grains as the secondary boundary. There were lots of secondary boundaries in Ce-TZP/Al_2O_3 nanocomposites. Because the thermal expansion coefficient and elastic modular of Al_2O_3 matrix is different from that of ZrO_2 nanoparticles, a residual stress existed on the secondary grain boundary. In addition, there was tensile stress around the ZrO_2 particles in Al_2O_3 matrix. This kind of tensile stress transmitted from Al_2O_3 grains to the grain boundary to form a compress stress, which could strengthen the grain boundary. Meanwhile, the residual stress could activate dislocations which are shown in Fig. 5a and b. It is found that a lot of dislocations in Fig. 5a gather at Al_2O_3 grain boundary, whereas dislocations in Fig. 5b distribute inside Al_2O_3 grains. Because the dislocation agglomeration and fixation by ZrO_2 nanoparticles could deflect cracking or stop cracking development, a strengthening and toughening effect would be achieved.

Moreover, in the ZrO_2-containing ceramics, the widely accepted toughening mechanism is transformation toughening via tetragonal-to-monoclinic transformation. Wide spread $t \rightarrow m$ transformation has been observed by XRD, TEM and neutron diffraction in zirconia subjected to applied stress [8]. In order to investigate transformation toughening of ZrO_2 in Ce-TZP/Al_2O_3 ceramics., the phase constituents of the samples before and after subjected to load were determined by X-ray diffractometry (XRD). The measurement results of all samples indicated that there were only α-Al_2O_3 and t-ZrO_2 before subjected to the applied stress, whereas the m-ZrO_2, except α-Al_2O_3 and t-ZrO_2, occurred in the samples after subjected to the applied stress. These results indicated that part of t-ZrO_2 transformed into m-ZrO_2 under the applied stress, so it could be interpreted as the stress-induced transformation toughening of zirconia. Moreover, compared with other samples, sample with 20% ZrO_2 obtained the highest percentage of m-ZrO_2 under the applied stress. Fig. 6a and b show that XRD results of sample with

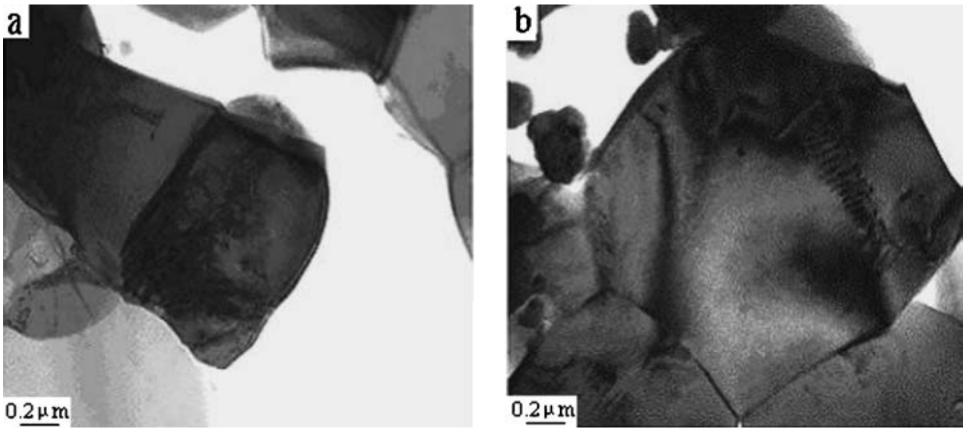

Figure 5 TEM bright field micrographs of sample 2 with 20% ZrO_2.

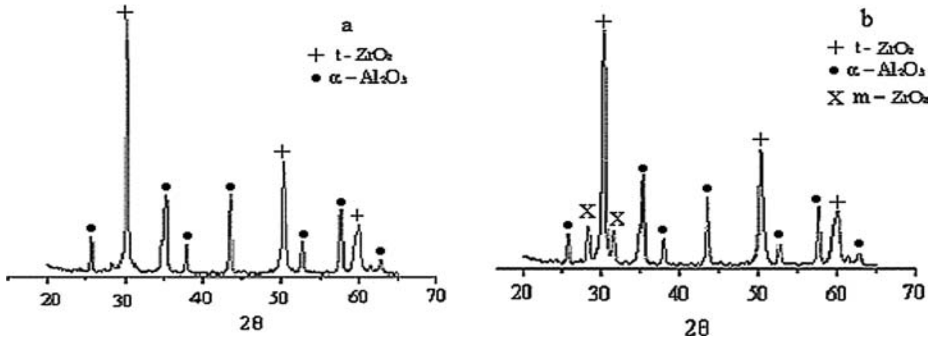

Figure 6 XRD micrograph of sample 2 with 20% ZrO_2 before (a) and after (b) subjected to the applied stress.

20% ZrO_2 before and after subjected to the applied stress, respectively.

4. Summary

The present results show that influences of ZrO_2 nanoparticles in Al_2O_3 matrix on mechanical properties and microstructures are evident. When ZrO_2 content is less than 20%, the densification is improved with increases of ZrO_2, but ZrO_2 nanparticles is disadvantageous to densification of materials when its content is more than 20%. The mechanical properties and microstructures are both optimum when ZrO_2 content is 20%. This is because homogenous distribution of less than 20% ZrO_2 in Al_2O_3 matrix could restrain abnormal growth of Al_2O_3 grains, whereas more than 20% ZrO_2 causes a negative effect. Furthermore, it is found that the deflection also reaches the maximum value when ZrO_2 content is 20%. TEM observation shows that dislocation structures formation both in the Al_2O_3 and on the grain boundary could deflect cracking or stop cracking development, so a strengthening and toughening effect would be achieved. Meanwhile, the XRD analysis of t → m transformation toughening mechanism of ZrO_2 indicated that t → m transformation occurred in all of samples under applied stress.

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