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Mechanical Properties of Nanocrystalline Tetragonal Zirconia Stabilized with CaO, MgO and Y_2O_3

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The citrate gel method, similar to the polymerized complex method, was used to synthesize homogeneous tetragonal zirconia at 1000 °C. Nanocrystalline tetragonal phase has been fully stabilized at wide temperature range with 10 mol.% CaO, MgO, and Y_2O_3 addition. Scanning electron microscopy, X-ray diffraction, and microhardness tests are used to characterize synthesized materials. The grain size and dislocation density were calculated from X-ray diffraction data. The examined material exhibits indentation size effect behavior. Results revealed that the Vickers and Knoop microhardness are dependent on indentation test load. Geometrically necessary dislocation model and modified proportional resistance model are used to analyze the load dependence of the microhardness. The highest hardness values were obtained for the samples with CaO addition; however the lowest values were acquired for sample stabilized with Y_2O_3 by using both Knoop and Vickers techniques. This situation might be explained using the Hall–Petch relation.

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1. Introduction

Tetragonal zirconia (t-ZrO_2) stabilized by aliovalent oxides (MgO, CaO, Y_2O_3, CeO_2, etc.) at low temperature is used for broad industrial applications such as structural ceramics, refractory materials, biomaterials, catalysts, in oxygen sensor and fuel cells [1]. This material exhibits the excellent strength, fracture toughness, thermal stability and ionic conductivity at high temperature [2–4]. Tetragonal phase can be typically synthesized by solid-state reaction, coprecipitation, pyrolysis of organic precursors, metal alkoxides hydrolysis, hydrothermal, combustion route and polymer complex methods [5, 6]. These methods frequently result in the crystallization of metastable phases at relatively lower temperatures where no phase separation occurs [7].

Microindentations have been extensively applied at the microstructural level to measure hardness of materials, which is not only a routinely measured mechanical characteristic, but also a microstructural investigation method in terms of structure-property relations. Moreover, the microhardness is sensitive to structural parameters as well as to mechanical characterization parameters (such as yield stress, modulus of elasticity) [5, 6]. It is well known that the apparent microhardness of solids depends on the applied indentation test load. This phenomenon, known as the indentation size effect (ISE), usually involves a decrease in the apparent microhardness with increasing applied test load, i.e. with increasing indentation size. The apparent hardness is a function of the applied load at low indentation test loads, where there is no constant value for the hardness (H_{LD}; load-dependent hardness). At high indentation test loads, the hardness is constant with respect to the indentation test load and a single, well defined hardness value exists (H_{LI}; load-independent hardness). H_{LI} has also been referred to as the "true" hardness in some of the literature.

2. Experimental procedure

Zirconia powders doped with 10 mol.% of Y_2O_3, MgO and CaO were prepared by the citric acid sol–gel method. $ZrOCl_2{\cdot}8H_2O$ (Fluka, 99%), $MgCO_3$ (Sigma, 99%), YCl_3 (Fluka, 99%) and $Ca(NO_3)_2$ (Fluka, 99%) were used as starting materials. Citric acid (Fluka, 99.5%) and distilled water were used for gelation agent and solvent, respectively. The synthesis method was described in previous publication [8]. Heat treatment for gel precursors was carried out at 1000 °C for 2 h. The powders were pressed into disc pellets using a pressure of 200 MPa in a uniaxial single-action press and then sintered at 1500 °C for 4 h. The phase contents of the powders were identified by X-ray diffractometer (Rigaku, Miniflex) using Cu K_α radiation over the range of 20–80° at a rate of 2°/min. The relative density of the sintered ceramics was measured using the Archimedes method. Hardness measurements were made ranging from at 0.098 to 9.8 N load where a loading time of 15 s was used to measure the diagonals of the indentations. The indentation diagonal lengths were measured by Nikon MA 100 inverted metal microscope using Clemex Professional microscopy image analysis software. 50× and 20× objective lenses were used on the Nikon MA 100 instrument. In view of the

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scatter of the microhardness data, the hardness value was a mean of at least six measurements under the same condition. The hardness values (H_V) from the length of the two diagonals of the square-shaped Vickers indents were calculated with the equation $H_V = 1.854(P/d^2)$ where P is the applied test load in N, d is the average of two indentation diagonal lengths in μm, and 1.8544 is a geometrical constant of the diamond pyramid.

3. Results and discussion

Synthesized zirconia powders have mostly tetragonal phase before sintering. After sintering, high temperature treatment leading to grain growth of structure changed phase types and content. Figure 1 illustrates X-ray diffraction (XRD) pattern of stabilized zirconia samples that have mixture of tetragonal and monoclinic phases. Figure 2 shows microstructure of stabilized zirconia with various oxides. It is stated that grain size and porosity as well as types of phase affect structural properties of ceramic. Fine grain size and less porosity in the microstructure are critical issue to get better mechanical properties for the materials.

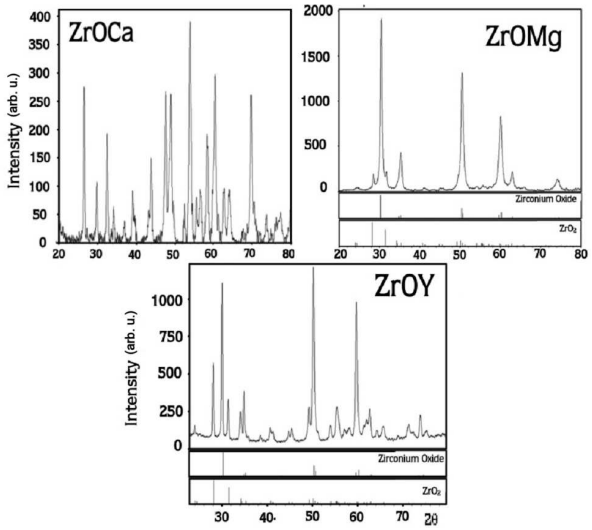

Fig. 1. XRD pattern of ZrOCa, ZrOMg, and ZrOY ceramics.

Figure 3 shows the variation of H_V and H_K as a function of applied test loads ranging from 0.098 to 9.8 N for all specimens. The variation of microhardness with applied indentation test load for each specimen indicates that the H_V and the H_K decrease with increasing applied indentation test load, and then reach saturation at about 4.9 N. The entire hardness profile consists of two regimes: load-dependent and load-independent.

The behaviour of hardness in both regimes could qualitatively be explained by considering the nature of the indented surface. At small loads, the indenter may penetrate only the region nearest to the surface. A sharp fall of the hardness value occurs in the low load region

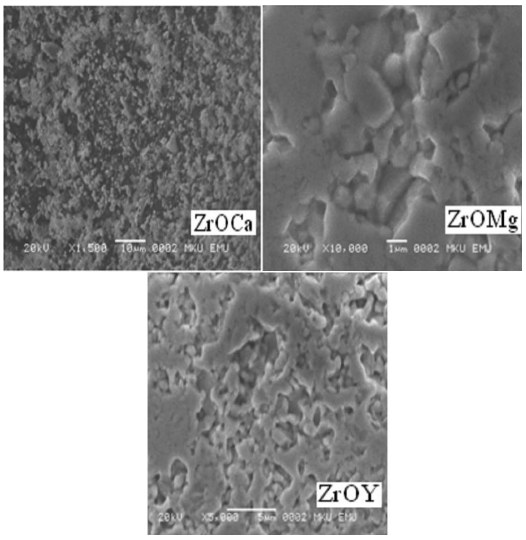

Fig. 2. SEM image of ZrOCa, ZrOMg and ZrOY.

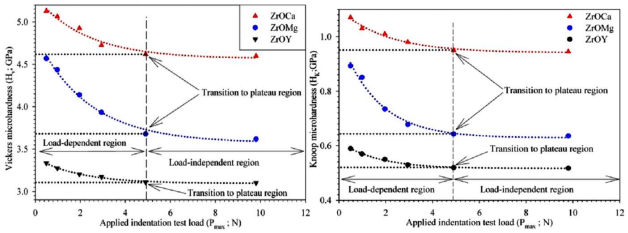

Fig. 3. Vickers and Knoop microhardness variation as a function of applied indentation test load.

depending on the strain distribution of the near surface layers. Further than a certain limit, the indenter penetrates beyond the surface and the bulk density of the inner zone may be different from the surface density. Accordingly, the presence of chemical contamination on the surface layer may cause deformation characteristics different from those of the inner layers. The effect of the inner layers becomes more prominent at high loads, and ultimately no change is observed in the hardness with the variation of the load. This dependence of microhardness on the applied load at low test loads is known as the ISE.

In order to explain the Vickers microhardness variation as a function of applied indentation test load, the geometrically necessary dislocations model (GNDs) was used. According to GNDs

$$\frac{H}{H_0} = \sqrt{1 + \frac{h^*}{h}},$$

H is the nominal hardness for a given depth; h^* and h are characteristic depths which depend on the shape of the indenter and the material. Finally, H_0 can be defined as the hardness that would arise from the statistically stored dislocations alone, or equivalently the hardness obtained in the limit for an infinite depth (size independent hardness).

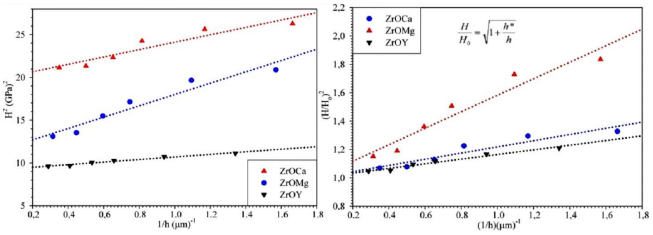

Fig. 4. The relationship between H^2 and $1/h$ (left) and application of Nix and Gao model to the zirconia ceramics (right).

In Fig. 4a, the square of the dynamic hardness value obtained in the indentation tests is plotted as a function of the reciprocal of the indentation depth. There is a linear relationship between H^2 and $1/h$, in agreement with equation

$$\frac{H}{H_0} = \sqrt{1 + \frac{h^*}{h}}.$$

This means that the microhardness decreases due to the indentation size effect. The values of H_0 and h^* can easily be determined from the intersection point and the slope of the curve, respectively. Then the relationship between $(H/H_0)^2$ and $1/h$ is shown in Fig. 4b. It is almost linear and also consistent well with Ref. [9].

The GNDs model can be used to determine the load--independent Vickers microhardness values, H_{GNG}, of the zirconia ceramics. The obtained values were 4.450, 3.373, and 3.032 GPa for ZrOCa, ZrOMg, and ZrOY, respectively. These values are very close to the plateau region in Fig. 3a.

In order to explain the Knoop microhardness variation as a function of applied indentation test load, the modified proportional resistance (MPSR) model was used. According to MPSR model Gong and coworkers suggest that $P_{\max}$ and indentation test size related as below

$$P_{\max} = a_0 + a_1 d + a_2 d^2, \tag{1}$$

where a_0 is constant related to the surface residual stresses associated with the surface machining and polishing and the parameters a_1 and a_2 are constants for a given material. The values a_1 and a_2 may be calculated by plotting the experimental $P(d)$ data as $P_{\max}$ versus d plot. Typical examples of the plots of $P_{\max}$ versus d with the $r^2 = 0.999$ are shown in Fig. 5.

H_{MPSR} can be calculated by

$$H_{\mathrm{MPSR}} = \alpha \frac{P_{\mathrm{eff}}}{d^2} = \alpha \left(\frac{P_{\max} - a_0 - a_1 d}{d^2} \right) = \alpha a_2, \tag{2}$$

where α is a constant depending only on the indenter geometry. For a Vickers indenter, $\alpha = 1.8544$. The MPSR model was used to determine the load--independent Knoop microhardness values, H_{MPSR}, of the zirconia ceramics. The obtained values were 0.907, 0.593, and 0.478 GPa for ZrOCa, ZrOMg, and ZrOY, respectively. These values are very close to the plateau region in Fig. 3b. The highest hardness values were obtained for the samples with CaO addition; however the lowest values were acquired for sample stabilized with Y_2O_3 by using both Knoop and Vickers techniques [10].

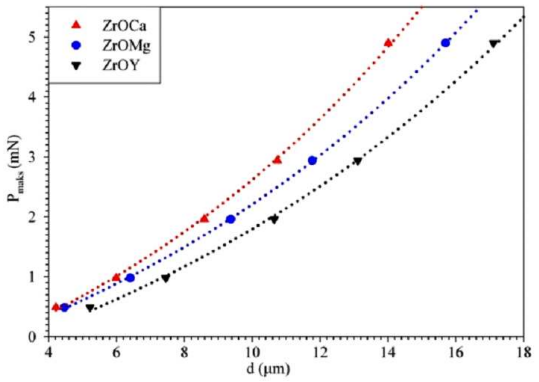

Fig. 5. Plots of $P_{\max}$ versus d according to MPSR model.

It is well known that any defect in the regular crystal structure or grain boundaries obstructs the dislocation, which makes plastic deformation more difficult. This requires extra force to achieve the dislocation, or to strengthen the material. So, one can say that the greater the crystal defects or grain boundary density are, the greater are the hardness values.

Acknowledgments

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