Comparison of mechanical properties of zirconia crystals partially stabilized with yttria and gadolinia

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Abstract. (ZrO2)0.97(Y2O3)0.03 and (ZrO2)0.97(Gd2O3)0.03 solid solution crystals have been grown using directional melt crystallization in cold container. The structure and phase composition of the crystals have been studied using X -ray diffraction and transmission electron microscopy. The mechanical properties of the crystals e.g. microhardness and fracture toughness have been studied with microindentation. We show that the main hardening mechanism in the 3GdSZ and 3YSZ crystals is transformation hardening. No microhardness anisotropy has been observed in the crystals. The highest fracture toughness among the crystals has been obtained for the 3GdSZ crystals in the {100} plane.

1. Introduction

Partially stabilized zirconia (PSZ) base crystalline materials have promising properties for multiple applications and are of great interest from research and practical viewpoints. The importance of these materials is determined by the prospects of their use as high strength and high wear resistance nonmetallic structural materials, thermal barriers and protective coatings as well as biologically inert materials for medical applications [1–3].

PSZ base materials have high fracture toughness (2–10 MPa·m1/2) [4] which is mainly accounted for by stresses induced by the tetragonal-monoclinic phase transition which impede crack propagation in the material. This phenomenon is known as transformation hardening and was discussed earlier [5-8]. Unlike ceramics an important feature of single crystals is a clear anisotropy of the mechanical properties.

The aim of this work was to compare structure and properties of gadolinia and yttria stabilized PSZ crystals.
2. Experimental

Solid solution single crystals were grown using directional melt crystallization in cold container in a Kristall-407 growth chamber, the cold container diameter being 130 mm and the growth rate being 10 mm/h. The charge was produced from zirconia, yttria and gadolinia powders with at least a 99.99% purity.

The phase composition of the specimens was analyzed using X-ray diffraction on a BrukerD8 diffractometer in CuKα radiation. The structure of the crystals was characterized using transmission electron microscopy under a JEM 2100 microscope at a 200 kV acceleration voltage. The specimen was thinned by ion beam etching on a PIPSII instrument.

The density of the crystals was determined using hydrostatic weighing. The microhardness and impact toughness of the crystals were studied using the indentation method. The microhardness was measured on a DM 8 B AUTO driven microhardness tester with a diamond tetrahedral Vickers pyramid at 20 N loads. The impact toughness was determined with a WolpertHardnessTester 930 at a minimum load of 50 N.

3. Results and Discussion

ZrO₂ crystals partially stabilized with 3 mol.% Y₂O₃ and 3 mol.% Gd₂O₃ (hereinafter 3YSZ and 3GdSZ) were grown using directional melt crystallization in cold container. The gadolinia stabilized crystals had generally the same shape, color and size as the yttria stabilized crystals. All the crystals had pillar shapes that are typical of this growth technique. The crystals were white and nontransparent.

| Specimen | Phase composition | Phase content, vol.% | c, Å   | a, Å   | c/√2a  |
|----------|------------------|----------------------|--------|--------|--------|
| 3YSZ     | t phase          | 85                   | 5.172(1)| 3.605(1)| 1.014  |
|          | t’ phase         | 15                   | 5.152(2)| 3.625(1)| 1.005  |
| 3GdSZ    | t phase          | 90                   | 5.182(1)| 3.607(1)| 1.016  |
|          | t’ phase         | 10                   | 5.160(2)| 3.635(1)| 1.004  |

Under mechanical stresses the tetragonal phase (t) with the tetragonality degree c/√2a = 1.014-1.016 may undergo a tetragonal-monoclinic transition e.g. transformation hardening: a propagating microcrack induces a martensitic tetragonal-monoclinic transition which absorbs the stress energy and stops the propagating microcrack. The second tetragonal phase (t’) with the tetragonality degree c/√2a 1.003–1.006 is non-transformable, i.e., it does not transform to the monoclinic phase even during intense grinding. An increase in the tetragonality degree of the transformable phase and a decrease in the tetragonality degree of the non-transformable phase in the 3GdSZ crystals can be associated with a lower content of the stabilizing oxide in the transformable phase and a higher content of the stabilizing oxide in the non-transformable one.

Transmission electron microscopy study of the crystal structure showed that all the crystals contained twins. The structure of the test crystals had no twin-free regions. The shapes and sizes of the twins in the 3YSZ and 3GdSZ crystals were almost the same (figure 1).

Figure 1. TEM images of 3YSZ (a) and 3GdSZ (b) crystal structure.
Twinning occurs during crystal cooling upon the transition from the single-phase cubic region to the two-phase region in accordance with the phase diagram, favoring stress relief during the cubic-tetragonal phase transition. The twin structure formation completes at ~1400 °C when diffusion cation mobility is suppressed.

Table 2 shows the microhardness and impact toughness of the 3YSZ and 3GdSZ crystals for wafers cut out perpendicular to the <100>, <110> and <111> directions.

**Table 2.** Microhardness and fracture toughness of 3YSZ and 3GdSZ crystals.

| Specimen | {100} | {110} | {111} |
|----------|-------|-------|-------|
|          | HV, GPa | K<sub>IC</sub>, MPa·m<sup>1/2</sup> | HV, GPa | K<sub>IC</sub>, MPa·m<sup>1/2</sup> | HV, GPa | K<sub>IC</sub>, MPa·m<sup>1/2</sup> |
| 3YSZ     | 13.0 ± 0.4 | 10.5 ± 0.3 | 13.5 ± 0.4 | 8.5 ± 0.3 | 13.3 ± 0.4 | 10.0 ± 0.3 |
| 3GdSZ    | 12.6 ± 0.4 | 12.0 ± 0.3 | 12.3 ± 0.4 | 9.5 ± 0.3 | 12.5 ± 0.4 | 11.5 ± 0.3 |

The microhardness figures of the 3YSZ and 3GdSZ crystals are close, the fracture toughness being higher for the 3GdSZ crystals. The microhardness depends but slightly on plane crystallographic orientation whereas fracture toughness differs for different crystal planes. The fracture toughness values for the {100} and {111} planes are higher than those for the {110} plane. The fracture toughness anisotropy is more pronounced in the 3GdSZ crystal than in the 3YSZ one.

The monoclinic phase distribution around indentations was studied as a function of the stabilizing oxide type and concentration by analyzing the Raman spectra taken in the vicinity of indentations for the same loads (20 N) using the method described earlier [9, 10].

Figure 2 shows comparison between the monoclinic phase distribution around indentations for the 3YSZ and 3GdSZ crystal specimens with (100) orientation for a 20 N load and indentation diagonals oriented along the <010> direction. Local Raman spectrum analysis was carried out along the indentation diagonals and perpendicular to the indentation sides.

**Figure 2.** Monoclinic phase formation intensity around indentations in 3YSZ and 3GdSZ specimens at 20 N load on the (100) plane with indentation diagonals oriented along the <100> direction: (a and b): along indentation diagonals; (c and d): perpendicular to indentation sides.
It can be seen from figure 2 that the monoclinic phase precipitation intensity around indentations is higher for the 3GdSZ crystals than for the 3YSZ ones.

4. Conclusions
Comparison of the structure and properties of the gadolinia and yttria stabilized PSZ crystals showed that the higher transformable phase content in the Gd$_2$O$_3$ stabilized PSZ crystals than in the Y$_2$O$_3$ stabilized PSZ crystals and the lower stabilizing oxide concentration in the former crystals lead to the higher fracture toughness of the former crystals, the microhardness figures of the two crystals being close. The main hardening mechanism in the 3GdSZ and 3YSZ crystals is transformation hardening. No microhardness anisotropy was observed in the crystals. The highest fracture toughness among the crystals was obtained for the 3GdSZ crystals in the \{100\} plane.

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