Effect of heat treatment on the structure and mechanical properties of partially gadolinia-stabilized zirconia crystals

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1. Introduction

Zirconia-based solid solutions have high melting points (~3000°C), are chemically and biologically inert, and have good mechanical properties [1–3]. Ceramics based on partially stabilized zirconia are widely used as components in device building, medical tools, and high-temperature electrochemistry [1–3]. These materials also find wide application in the fabrication of thermal barrier coatings [4–9]. Components made of zirconia-based materials can be operated in corrosive media and at high temperatures. However, cubic and tetragonal zirconia-based solid solutions are thermodynamically metastable; if operated at high temperatures or at high humidity, these solid solutions may undergo structural transformations that lead to a significant degradation in their performance [10,11]. It was shown [12–14] that if ZrO2-based thermal barrier coatings stabilized with 6–8 mol.% YO1.5 were operated at high temperatures, and then the tetragonal t’ phase decomposed into two phases, i.e. the Yttria-depleted tetragonal t phase and the yttria-enriched cubic c phase. Changes in the phase composition and microstructure of the material may reduce its strength, e.g. decrease its fracture toughness [15,16].

The structures and properties of zirconia-based single crystals with the same composition as ceramic materials are of interest to researchers [17–19]. It was shown [20] that the mechanical properties of ceramics and single crystals of partially stabilized zirconia degrade at high temperatures (~1400°C). However, the degradation of the mechanical properties of the crystals is less dramatic than that of the ceramics. Unlike ceramics with the same composition, crystals exhibit little, if any, low-temperature degradation [18]. Decreasing the temperature to ~140°C increases the ultimate strength of zirconia-based crystals by 30% [21].

Yttria-stabilized zirconia-based materials have been studied the most widely so far. However, there are quite a few works dealing with the effect of heat treatment on the structure and properties of zirconia-based materials stabilized with other oxides [15,16,22]. On the other hand, gadolinia-stabilized materials that can be used for the fabrication of thermal barrier coatings due to their low heat conductivity have been increasingly studied. Comparing the mechanical properties of gadolinia- and yttria-stabilized zirconia-based polycrystalline materials shows that gadolinia-stabilized specimens exhibit higher fracture toughness than yttria-stabilized specimens after long-term annealing at 1150°C [15]. Studying the effect of...
thermal annealing on the high-temperature structural stability of solid solutions is of utmost importance for practical applications of the material because this annealing temperature is close to the operating temperatures of the material.

We studied the phase composition and mechanical characteristics of \((\text{ZrO}_2)_{x} \cdot (\text{Gd}_2\text{O}_3)_{1-x}\) (x = 0.02–0.04) crystals grown by directional melt crystallization in our previous work [23]. We show that an increase in the \(\text{Gd}_2\text{O}_3\) concentration in the crystals from 2.8 to 4.0 mol. % decreases the content of the transformable tetragonal \(t\) phase, tetragonality degree and intensity of the indentation-induced tetragonal to the monoclinic phase transition. These factors are known to eventually decrease the fracture toughness of crystals that have an increased \(\text{Gd}_2\text{O}_3\) concentration.

This work aims to study the effect of high-temperature air and vacuum annealing on the phase composition, structure, and mechanical properties of partially \(\text{Gd}_2\text{O}_3\)-stabilized \(\text{ZrO}_2\)-based crystals.

2. Experimental

\((\text{ZrO}_2)_{x} \cdot (\text{Gd}_2\text{O}_3)_{1-x}\) crystals (x = 0.028–0.04) were melt grown using direct RF heating [23] in a 100 mm diameter cold skull. The as-crystallized melt ingot was 4–5 kg. The cooling of the crystalline ingot was controlled by measuring the temperature on the surface of the top heat screen with a Gulton 900–1999 radiation pyrometer (above 1000°C) and a Pt/Pt-Rh thermocouple (from 1000°C to 500°C). The ingot cooling rate from the melt temperature to 1000°C was ~200°C/min, and from 1000°C to 500°C, the ingot cooling rate was ~30°C/min.

The as-grown crystals were heat-treated at 1600°C in the air in an HT 04/16.2 high-temperature furnace or in a \(1.33 \cdot 10^{-2}\) Pa vacuum in an SShV 1.25/25 furnace with molybdenum heaters.

The phase composition of the crystals was studied using X-ray diffraction with a Bruker D8 instrument using the standard method for single crystals. The as-grown crystals had no predominant crystallographic orientation. Therefore, each crystal was preliminarily oriented along with specific crystallographic directions in the diffractometer. Then, the crystals were cut into plates on a diamond disc cutting machine. The phase composition of the crystals was studied for plates cut from the crystals perpendicular to the \(<100>\) direction. The \(\{100\}\) planes of the crystals that had a multiphase composition exhibited simultaneous reflections on a single cut that were produced by different phases; these reflections split at large 2θ values of ~130 arc degrees. The phase fractions were determined from the diffraction peak intensities normalized to the integral reflection coefficients of the different phases.

Local phase analysis in the vicinity of indentations was carried out using Raman spectroscopy in the wavenumber range of 50–1400 cm\(^{-1}\) on a Renishaw inVia Raman confocal microscope. A laser with a radiation wavelength of 532 nm was used as an excitation source. The laser focus point was chosen using a built-in optical microscope (>20). The focused beam diameter on the sample was ~1 μm. To record the Raman spectra, the laser radiation power was set equal to 100 mW, and the signal accumulation time was 5 s.

The structure of the crystals was studied with transmission electron microscopy (TEM) with a JEOL 2100 microscope at a 200 kV accelerating voltage. The specimens for TEM were made from plates perpendicularly cut from the crystal in regard to the \(<111>\) and \(<100>\) axes. An ultrasonic disc cutter was used to cut samples into discs 3 mm in diameter, which were then polished to a thickness of ~100 μm. The discs were further dimpled to a thickness of ~25 μm in a dimple grinder and then ion-milled in a precision ion polishing system (Gatan, PIPS II).

The density of the crystals was measured by hydrostatic weighing. The microhardness of the crystals was studied by microindentation on a DM 88 AUTO with a Vickers indenter at a 20 N load. The fracture toughness of the crystals was evaluated with a Wolpert hardness tester 930 instrument at a 200 N load. The fracture toughness \((K_{1c})\) was calculated using the Niihara equation for the Palmqvist crack system [24]

\[
K_{1c} = 0.035(L/a)^{-1/2}((C/E)/H)^{2/5}H_a^{1/2}C^{-1}
\]

where \(K_{1c}\) is the stress intensity factor (MPa·m\(^{1/2}\)); \(L\) is the radial crack length (m); \(a\) is the indentation half-width (m); \(C\) is the constraint factor (=3); \(E\) is the Young modulus (Pa); and \(H\) is the microhardness (Pa). \(K_{1c}\) was calculated for the radial cracks around the indentation, the length of which met the criterion 0.25 ≤ \(l/a\) ≤ 2.5 for Palmqvist cracks.

3. Results and discussion

(Table 1) summarizes the compositions, notations, and densities of the as-annealed crystals. The data obtained on the grown crystals are presented for comparison [23].

All the crystals had columnar shapes that are typical of this growth method. The crystals are white and nontransparent. The crystal bulk has no cracks. The cross-sections of single-unit crystals are 20 mm, and their heights are ~40 mm.

The densities of the crystals increase with the concentration of stabilizing gadolinia in the zirconia-based solid solutions. The densities of the crystals do not change after air annealing within the measurement.
error and slightly decrease after vacuum annealing. This decrease in the densities of the crystals after vacuum annealing may originate from the formation of nonstoichiometric vacancies.

Vacuum annealing changes the color of the crystals to black due to the formation of an intense and wide absorption band peaking near 0.5 μm [25]. The effect of heat treatment on the absorption spectra of the ZrO$_2$-Gd$_2$O$_3$ crystals is caused by a change in the charge state of the defects as a result of the crystal composition deviating from the stoichiometric composition. The deviation from the stoichiometric composition that occurs during vacuum annealing is caused by oxygen depletion. Each oxygen atom lost by the crystal leaves an anion vacancy and two electrons that are redistributed between the defects. This redistribution is controlled by the temperature, defect concentration, and electron bond energy at the defects. The deviation from the stoichiometric composition increases with an increase in temperature and a decrease in the oxygen partial pressure in the atmosphere; therefore, vacuum annealing increases the concentration of excess electrons and color centers [26,27].

Figure 1 shows an image of the as-grown [23], vacuum-annealed, and air-annealed 4.0GdSZ crystals. The as-grown crystals are white and nontransparent. Vacuum annealing changes the crystal color to gray. Similar color changes are observed after vacuum annealing the other compositions of ZrO$_2$-Gd$_2$O$_3$ crystals. Air annealing does not change the crystal color.

Phase composition analysis of the crystals shows that all the test crystals, as-grown and as-annealed contain two tetragonal phases (t and t’) with different tetragonality degrees. Annealing the crystals does not lead to a change in the qualitative phase composition but leads to a change in the crystal lattice parameters of the tetragonal phases and a slight change in the widths of the diffraction lines.

In accordance with the equilibrium phase diagram of the ZrO$_2$-Gd$_2$O$_3$ system [28], crystal cooling to the subsolidus region causes a transition from the high-temperature single-phase cubic region (c) to the two-phase region (c + t). If the crystals are cooled in this two-phase region under conditions close to equilibrium, the cubic solid solution will decompose into two equilibrium phases, i.e. the tetragonal phase (t) and the cubic phase (c). Under our experimental conditions of crystal growth, the cooled crystals decrease quite rapidly (~100°C/min), and as a result, the decomposition of the cubic solid solution is incomplete and frozen at an intermediate stage. The diffusion of cations stops almost completely at ~1200-1400°C [29,30]. As a result, the crystals contain two metastable tetragonal phases, the compositions of which are within the two-phase region near the equilibrium boundaries.

Figure 2 shows the change in the a and c lattice parameters for the t and t’ phases of the as-grown and as-annealed crystals as a function of the Gd$_2$O$_3$ concentration. One can trace a common tendency of the change in the lattice parameters for the t and t’ tetragonal phases as a function of the Gd$_2$O$_3$ concentration. An increase in the Gd$_2$O$_3$ concentration increases the a lattice parameter and reduces the c lattice parameter of both phases.

Vacuum annealing of the crystals reduces the a and c lattice parameters in comparison with those of the as-grown crystals. This change can be caused by the formation of nonstoichiometric vacancies after vacuum annealing that reduce the volume of the crystal lattice [31].

Air annealing of the crystals reduces the a lattice parameter and increases the c lattice parameter of the t phase. Moreover, the a lattice parameter of the t’ phase increases considerably, and the c lattice parameter of the t’ phase slightly decreases. Thus, air annealing the crystals oppositely changes the lattice parameters of the t and t’ phases in opposite directions.

Table 1. Compositions, notations, and densities of crystals.

| Composition | Notation | As-Grown | Air Annealed | Vacuum Annealed |
|-------------|----------|----------|--------------|-----------------|
| ZrO$_2$O$_{3.5}$Gd$_2$O$_3$O$_{0.02}$ | 2.8GdSZ | 6.235(2) | 6.234(2) | 6.231(2) |
| ZrO$_2$O$_{3.5}$Gd$_2$O$_3$O$_{0.03}$ | 3.2GdSZ | 6.261(2) | 6.259(2) | 6.249(2) |
| ZrO$_2$O$_{3.5}$Gd$_2$O$_3$O$_{0.03}$ | 3.7GdSZ | 6.269(2) | 6.269(2) | 6.262(2) |
| ZrO$_2$O$_{3.5}$Gd$_2$O$_3$O$_{0.04}$ | 4.0GdSZ | 6.272(2) | 6.276(2) | 6.273(2) |
the growth crystals are provided in (Table 2) for comparison [23].

Several formulas for calculating the stabilizing oxide concentration from zirconia-based solid solution lattice parameters have been reported [32–37]. A study of molten ZrO₂–RO₁.₅ specimens (R is a rare earth element) [34] in the 4–10 mol.% RO₁.₅ concentration range shows that the tetragonality degree c/√2a does not depend on the stabilizing oxide type but only on the stabilizing oxide concentration.

Therefore, we calculated the Gd₂O₃ concentration in the tetragonal phases using the reported formula [35] for ceramic specimens of partially stabilized zirconia:

\[
\text{RO}_{1.5}\text{ mol}\% = \frac{1.0223 - \frac{c}{\sqrt{2}a}}{0.001319}
\]

where c and a are the tetragonal phase lattice parameters.

The data presented in (Table 2) suggest that the ratio of the two tetragonal phases depends on the Gd₂O₃ concentration. As the Gd₂O₃ concentration is increased from 2.8 to 4.0 mol.%, the quantity of the tetragonal phase in the as-grown crystals decreases from 90 to 70 wt.%. Air or vacuum annealing of the crystals slightly changes the ratio of the phases.

The typical tetragonality degrees of the t and t’ phases are in the 1.015–1.016 and 1.004–1.006 ranges, respectively. As the Gd₂O₃ concentration is increased, the tetragonality degree of the crystals decreases, i.e., an increase in the Gd₂O₃ stabilizing oxide concentration decreases the tetragonal distortions in the crystaline structure.
Air or vacuum annealing of all the test crystals increases the tetragonality degree of the \( t \) phase and decreases the tetragonality degree of the \( t' \) phase in comparison with the as-grown crystals. However, air annealing produces larger changes in the tetragonality degrees of these phases. The smaller degree of tetragonality change upon vacuum annealing probably originates from an increase in the quantity of oxygen vacancies that have an additional stabilizing effect on the transformable tetragonal phase [38].

The calculated data on the solute \( \text{Gd}_2\text{O}_3 \) concentration in the \( t \) and \( t' \) phases of the crystals show that the \( \text{Gd}_2\text{O}_3 \) concentration in the \( t' \) phase is almost 3 times that in the \( t \) phase. Air or vacuum annealing of the crystals increases the \( \text{Gd}_2\text{O}_3 \) content in the \( t' \) phase, thereby decreasing its content in the \( t \) phase.

Thus, air or vacuum annealing at 1600°C causes some redistribution of the stabilizing oxide between the tetragonal phases, i.e. the \( t \) phase is depleted of gadolinia while the \( t' \) phase becomes gadolinia enriched. This result clearly stems from the fact that additional annealing causes greater phase segregation, thus bringing the system closer to an equilibrium state. The experimentally observed slight dependence on the lattice parameters and the tetragonality degree of the phases on the annealing atmosphere is likely to indicate that the role of the annealing temperature is predominant.

A detailed structural study of the \( \text{ZrO}_2\text{-Gd}_2\text{O}_3 \) crystals was carried out using transmission electron microscopy. Multiple twins are found in all the as-grown and as-annealed crystals. The crystals do not contain twin-free regions. Twinning occurs during the cooling of a single crystal due to the relaxation of elastic stresses developed in the structure during the phase transition of the high-temperature cubic phase to the low-temperature tetragonal phase. The pattern and sizes of the twins vary depending on the \( \text{Gd}_2\text{O}_3 \) concentration in the crystals. The 2.8GdSZ and 3.2GdSZ crystals contain regions with large elongated twins, the sizes of which reach ~200-400 nm in one of the directions. Regions containing large twins in these crystals are often at the boundaries of fine twins sized up to 50 nm. The 3.7GdSZ and 4.0GdSZ crystals retain the twin structure with variable twin sizes. However, the sizes of the largest twins are mainly within 200 nm, and the number of regions containing fine twins increases. Air and vacuum annealing of the crystals does not produce any visible changes in the sizes of the twins. Figure 3 shows TEM images of twins in the structures of the as-grown, air-annealed, and vacuum-annealed 2.8GdSZ and 4.0GdSZ crystals.

The electron diffraction patterns taken in different regions of the crystals always show results typical of a single-crystal structure. Crystals of all compositions only contain low-angle boundaries, and the grain

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**Figure 3.** TEM images of twins in the (a) as-grown, (b) air-annealed and (c) vacuum-annealed 2.8GdSZ crystal and (d) as-grown, (e) air-annealed and (f) vacuum-annealed 4.0GdSZ crystal.
misorientation angles are within 2 arc degrees. The positions of the reflections in the electron diffraction patterns indicate the presence of a tetragonal zirconia modification. Figure 4(a,b) shows images of twins for different sections of the 2.8GdSZ crystal. The electron diffraction pattern for the <111> axis (Figure 4(a)) shows weak 110 and 112 reflections in the tetragonal ZrO₂ modification. The close interplanar distances do not allow us to separate the t and t’ phases in the electron diffraction patterns. However, according to the energy-dispersion spectroscopy (EDX) data, the Gd₂O₃ concentration in the fine twin regions is higher than that in the large twin regions (Figure 4(c,d)) shows a more magnified image of the twin structure of the selected areas, which shows where the EDX spectra are taken (Figure 4(e,f)). The Gd₂O₃ concentration in the fine twin structure regions is in good agreement with the Gd₂O₃ concentration in the t’ phase calculated from the lattice parameters of the solid solution. The Gd₂O₃ concentration in the large twin regions is lower.
and similar to the Gd₂O₃ concentration calculated for the t phase. The observed differences in the size and morphology of the t and t’ phase twins are probably related to the conditions of their formation during the directional crystallization of the melt. As noted earlier, when a cubic solid solution is cooled from a high-temperature single-phase cubic region (c) to the two-phase (c + t) region, nuclei of the t phase depleted of gadolinia are formed in it, and the c phase is enriched in Gd₂O₃. The t phase regions depleted by Gd₂O₃ are formed in it, and the c phase becomes gadolinia enriched. The relaxation of elastic stresses during the cubic-tetragonal phase transition leads to the formation of large twins in the t phase. The tetragonal t phase is retained to room temperature, and the c phase is transformed into the gadolinia-rich tetragonal t’ phase upon further cooling [39]. The c→t’ transition is accompanied by the formation of smaller twins in comparison with the twins of the t phase. This difference may be due to the fact that the formation of the twin structure of the t and t’ phases occurs during cooling at different temperatures.

Thus, the t’ phase regions are mainly located at the boundaries of the t phase regions. Large twins in the primary twinning plane are typical of the t phase. Twins in the t’ phase have a twinning hierarchy: first-order twins contain second- and third-order twins. Most likely, the Gd₂O₃-rich t’ phase is more susceptible to twinning than the t phase with a lower Gd₂O₃ concentration. Elastic stress relaxation in the t’ phase may occur by multistage twinning; therefore, twins in the t’ phase are smaller than the twins in the t phase.

Unlike ceramics, crystals exhibit anisotropic mechanical properties [17,40], which should be taken into account if the material is practically applied. With regard to earlier results [23] on the mechanical properties of ZrO₂-Gd₂O₃ solid solutions in regard to the different crystallographic faces of the crystals, we studied the effect of annealing on the microhardness and fracture toughness of specimens cut from crystals perpendicular to the <100> direction in regard to different indenter diagonal orientations in the specimen plane.

(Table 3) summarizes the microhardness data for the as-grown and as-annealed ZrO₂-Gd₂O₃ crystals. With an increase in the Gd₂O₃ concentration from 2.8 to 4.0 mol.%, the microhardness of the crystals change slightly. No anisotropy in the microhardness of the specimen plane is found. The microhardness values of the samples heat-treated in air and in vacuum are comparable and are within the measurement error. However, a slight decrease in the microhardness of the as-grown crystals is observed after annealing. We believe that such a change in the microhardness of crystals after annealing is due to a decrease in microtresses, which is confirmed by a decrease in the width of the diffraction lines.

Figure 5 shows diagrams of the anisotropic fracture toughness of the as-annealed ZrO₂-Gd₂O₃ crystals. The values of the fracture toughness of the crystals before annealing are provided for comparison [23]. The fracture toughness of the crystals is measured in the (100) plane by rotating the specimens in their planes from 0 to 360 arc degrees. Since the specimens are cut perpendicular to the fourth-order axis of the crystals, anisotropy diagrams are shown for the 0 to 90 arc degree range. The diagonal orientation of the indenter along the <100> direction corresponds to 0 arc degrees.

As shown in Figure 5, the as-grown and as-annealed crystals exhibit a decrease in the fracture toughness with an increase in the Gd₂O₃ concentration. The study of the fracture toughness anisotropy in the specimen plane shows the lowest fracture toughness for the diagonal orientation of the indenter in the <110> direction. It should be noted that for crystals with a high fracture toughness, the KIC anisotropy in the specimen plane is larger. Annealing the crystals increases their fracture toughness, and the fracture toughness of all the air-annealed crystals is higher than that of the vacuum-annealed crystals. The higher the Gd₂O₃ concentration in the crystals is, the greater the effect of annealing on the fracture toughness. The fracture toughness of the air-annealed 2.8GdSZ crystal increases by 15–25%; regarding 3.2GdSZ, the increase in the fracture toughness is approximately 40%, and for the 3.7GdSZ and 4.0GdSZ specimens, air annealing increases the fracture toughness almost twofold. The KIC value of the vacuum-annealed crystals is in between the fracture toughness of the as-grown and air-annealed crystals.

The increase in the fracture toughness of the crystals as a result of the 1600°C heat treatment may originate from the redistribution of Gd₂O₃ between the t and t’ tetragonal phases. The gadolinia-depleted tetragonal t phase may undergo a phase transition to a stable monoclinic phase under external loads. The tetragonal to monoclinic transformation at the crack tip causes energy absorption and hinders further crack propagation. The gadolinia-rich tetragonal t’ phase cannot undergo the tetragonal to monoclinic transition under external loads. The contribution of transformation hardening to the mechanical properties of the crystals depends on the quantity of the transformable phase and its capability of the phase transition to the monoclinic phase. The probability of the tetragonal to monoclinic transition under external loads increases.

| Table 3. Microhardness of as-grown, air annealed, and vacuum annealed ZrO₂-Gd₂O₃ crystals. |
|-----------------------------------------------|
| Specimen | As-grown [23] | Vacuum Annealing | Air Annealing |
|----------------|----------------|-----------------|---------------|
| 2.8GdSZ      | 12.6 ± 0.4     | 11.7 ± 0.4      | 11.7 ± 0.4    |
| 3.2GdSZ      | 12.5 ± 0.4     | 12.3 ± 0.4      | 12.3 ± 0.4    |
| 3.7GdSZ      | 12.8 ± 0.4     | 12.3 ± 0.4      | 12.6 ± 0.4    |
| 4.0GdSZ      | 13.4 ± 0.4     | 12.5 ± 0.4      | 12.6 ± 0.4    |
with a decrease in the stabilizing oxide concentration in the t phase. Therefore, a decrease in the Gd₂O₃ content in the transformable t phase as a result of annealing increases the efficiency of transformation hardening, thereby increasing the fracture toughness of the material.

The formation of nonstoichiometric vacancies after vacuum annealing the crystals may have an additional stabilizing effect on the tetragonal phases [38]; therefore, the fracture toughness of the vacuum-annealed crystals is lower than that of the air-annealed crystals.

Another possible mechanism affecting the mechanical properties of zirconia-based solid solutions is ferroelastic hardening [2,41,42]. The process of ferroelastic hardening differs from the stress-induced martensitic transition in that it does not change the symmetry of the crystal structure but instead changes the predominant orientation of the twins under the action of the load. This type of hardening is found in tetragonal crystals of zirconia, partially stabilized by yttria oxide [43,44]. Details of ferroelastic hardening have been investigated by the authors of works [42,45,46]. It has been shown that the implementation of this hardening mechanism depends on many factors, including the type of applied load, the crystallographic direction along which the load is applied, and the temperature at which indentation occurs [47,48].

We believe that the effect of ferroelastic hardening originates from the presence of twins in the crystals and the possibility of elastic stress relaxation through multistage twinning, i.e., the formation of first-, second-, and third-order twins. As shown earlier [45], the indentation or other deformation of zirconia-based tetragonal solid solutions causes some nearby cells with c axes parallel to the main component of the tension field to reorient such that their c axes transform to a axes and vice versa. Since twinning in zirconia-based tetragonal crystals occurs along the (110) planes, the a- and c-axes in the first- and second-order twins will reorient in different manners.

To analyze the contributions of the transformation and ferroelastic hardening mechanisms to the mechanical properties of the crystals, we recorded Raman spectra in the vicinity of indentations. We then analyzed the local phase composition of the crystals in and around indentations to locate monoclinic phase regions formed as a result of transformation hardening. We evaluated the relative intensity of the tetragonal to the monoclinic phase transition from the intensity ratio of the tetragonal and monoclinic phase peaks in the Raman spectra using the following formula [45]:

\[
\text{Intensity Ratio} = \frac{I_{\text{tetragonal}}}{I_{\text{monoclinic}}} \]

Figure 5. Fracture toughness anisotropy in the (100) plane for different diagonal orientations of the indenter in the specimen plane for the (a) 2.8GdSZ, (b) 3.2GdSZ, (c) 3.7GdSZ and 4.0GdSZ (d) crystals.
We evaluated the contribution of the ferroelastic hardening mechanism from the intensity ratio of the tetragonal phase lines in the Raman spectra, which depended on the crystallographic orientation: 1 (146 cm\(^{-1}\))/I (260 cm\(^{-1}\)). We took Raman spectra in local areas along indentation diagonals and perpendicular to its sides with a step of ~15 \(\mu\)m.

Figure 6 shows the monoclinic phase distribution and change in the tetragonal phase line intensity along a line perpendicular to the indentation side for the as-annealed 2.8GdSZ and 4.0GdSZ crystals. The data obtained on the as-grown crystals are shown in Figure 6 for comparison [23].

As shown in Figure 6, the monoclinic phase region in the 2.8GdSZ crystal around the indentation is considerably larger than that in the 4.0GdSZ crystal. Furthermore, the formation of the monoclinic phase in the 2.8GdSZ crystal is more intense than that in the 4.0GdSZ crystal. The monoclinic phase region and the tetragonal to monoclinic phase transition intensity after air and vacuum annealing increase for both crystals, but the increase for the 2.8GdSZ crystal is greater.

The contribution of the ferroelastic hardening mechanism was estimated from the ratio of the intensities of the tetragonal phase lines 1 (146 cm\(^{-1}\))/I (260 cm\(^{-1}\)) in the Raman spectra. This estimate shows that the value of 1 (146 cm\(^{-1}\))/I (260 cm\(^{-1}\)), which depends on the crystallographic orientation, is noticeably lower for the as-grown 2.8GdSZ crystals than for the 4.0GdSZ crystals, indicating that the mechanism of ferroelastic hardening in 4.0GdSZ crystals is more pronounced. This result may be associated with both an increase in the content of the nontransformed t’ phase in the 4.0GdSZ crystals and an increase in the content of gadolinium oxide in the tetragonal phases. Annealing the 2.8GdSZ crystals does not lead to a noticeable change in the value of I(146 cm\(^{-1}\))/I (260 cm\(^{-1}\)), while the 4.0GdSZ crystals show significant changes in the intensity ratio of the lines of tetragonal phases after annealing in a vacuum and especially after annealing in air. Annealing the 4.0GdSZ crystals is not accompanied by a change in their phase composition, as shown in (Table 2). Therefore, the observed changes in the 4.0GdSZ crystals are probably associated with an increase in the concentration of the stabilizing oxide and a decrease in the degree of tetragonality of the t’ phase, which possibly facilitates the twinning process.

![Figure 6](image-url)

Figure 6. (a and b) Tetragonal to monoclinic phase transition intensity and (c and d) change in the tetragonal phase line intensity ratio for the (a and c) 2.8GdSZ and (b and d) 4.0GdSZ crystals in the local areas around indentations. The inset shows the indentation images and the points where Raman spectra were taken.
during indentation and increases the efficiency of the ferroelastic hardening mechanism.

Thus, analysis of the experimental data suggests that the improvement in the fracture toughness of the as-annealed crystals originates both from transformation and ferroelastic hardening. However, the contributions of each of the two mechanisms to the mechanical properties of the crystals depend on the gadolinia concentration in the solid solution. The transformation hardening mechanism, which provides the high fracture toughness of the crystals, plays a predominant role in the plastic deformation in the 2.8GdSZ crystals. Annealing the crystals reduces the GadO{\textsubscript{3}} content in the transformable phase, thus facilitating the tetragonal to monoclinic transition under external stresses. An increase in the stabilizing oxide concentration increases the content of the nontransformable tetragonal phase in the crystals, decreases the role of the transformation hardening mechanism, and increases the role of ferroelastic hardening.

4. Conclusions

Partially gadolinia-stabilized zirconia solid solution crystals were grown using the skull melting technique. The effect of air or vacuum annealing at 1600°C on the phase composition, structure, and mechanical properties of the crystals was studied using X-ray diffraction, Raman spectroscopy, transmission electron microscopy, and indentation.

Phase composition analysis showed that all the test crystals contained two tetragonal phases, i.e. t and t', which differed in their tetragonality degrees and gadolinia contents. Air or vacuum annealing the crystals at 1600°C slightly changed the phase quantity ratio and caused some redistribution of the stabilizing oxide between the tetragonal phases, i.e. the t phase was depleted of gadolinia while the t' phase became gadolinia enriched. Transmission electron microscopy showed that twins in the t and t' phases differed in size. The sizes of the twins in the t' phase were far smaller than those in the t phase. Air and vacuum annealing of the crystals does not produce any visible changes in the sizes of the twins.

Microhardness and fracture toughness studies of the crystals showed that annealing the crystals had little effect on their microhardness but increased their fracture toughness. The higher the GadO{\textsubscript{3}} concentration in the crystals was, the greater the effect of annealing on the fracture toughness.

The contributions of transformation and ferroelastic hardening mechanisms to the fracture toughness of the crystals are analyzed. Annealing of ZrO{\textsubscript{2}}-GdO{\textsubscript{3}} crystals increases the intensity of the tetragonal to a monoclinic phase transition during indentation and increases the role of the transformation hardening mechanism. The effect of ferroelastic hardening was larger in the crystals containing 3.7 and 4.0 mol.% GadO{\textsubscript{3}}.

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References

[1] Basu B. Toughening of yttria-stabilised tetragonal zirconia ceramic. Int Mat Rev. 2005;50(4):239–256.
[2] Hannink RHJ, Kelly PM, Muddle BC. Transformation toughening in zirconia-containing ceramics. J Am Ceram Soc. 2000;83(8):461–487.
[3] Chevalier J, Gremillard L, Virkar AV, et al. The tetragonal-monoclinic transformation in zirconia: lessons learned and future trends. J Am Ceram Soc. 2009;92(9):1901–1920.
[4] Darolia R. Thermal barrier coatings technology: critical review, progress update, remaining challenges and prospects. Int Mater Rev. 2013;58(6):315–348.
[5] Padture NP, Gell M, Jordan EA. Thermal barrier coatings for gas turbine engine applications. Sci. 2002;296(5566):280–284.
[6] Clarke DR, Levi CG. Materials design for the next generation thermal barrier coatings. Annu Rev Mater Res. 2003;33(1):383–417.
[7] Sampath S, Schulz U, Jarligo MO, et al. Processing science of advanced thermal-barrier systems. MRS Bull. 2012;37(10):903–910.
[8] Singh J, Wolfe DE. Review nano and macro-structured component fabrication by electron beam-physical vapor deposition (EB-PVD). J Mater Sci. 2005;40(1):1–26.
[9] Xie L, Ma X, Jordan EH, et al. Deposition of thermal barrier coatings using the solution precursor plasma spray process. J Mater Sci. 2004;39(5):1639–1646.
[10] Schulz U. Phase transformation in EB-PVD yttria partially stabilized zirconia thermal barrier coatings during annealing. J Am Ceram Soc. 2000;83:904–910.
[11] Gibson R, Irvine JTS. Qualitative X-ray diffraction analysis of metastable tetragonal (t') zirconia. J Am Ceram Soc. 2001;84(3):615–618.
[12] Lugi V, Clarke DR. High temperature aging of YSZ coatings and subsequent transformation at low temperature. Surf Coat Technol. 2005;20(5–6):1287–1291.
[13] Krogstad JA, Gao Y, Bai J, et al. In situ diffraction study of the high-temperature decomposition of t'-zirconia. J Am Ceram Soc. 2015;98(1):247–254.
[14] Krogstad JA, Leckie RM, Kramer S, et al. Phase evolution upon aging of air plasma sprayed t'-zirconia coatings: II—microstructure evolution. J Am Ceram Soc. 2013;96(1):299–307.
[15] Loganathan A, Gandhi AS. Toughness evolution in Gad and Y-stabilized zirconia thermal barrier materials.
upon high-temperature exposure. J Mat Sci. 2017;52 (12):7199–7206.

[16] Ponnuchamy MB, Gandhi AS. Phase and fracture toughness evolution during isothermal annealing of spark plasma sintered zirconia co-doped with Yb, Gd and Nd oxides. J Eur Ceram Soc. 2015;35(6):1879–1887.

[17] Munoz A, Garcia DG, Domnguez-Rodiguez A, et al. High temperature plastic anisotropy of Y2O3–Gd2O3 partially stabilized ZrO2 single crystals. J Eur Ceram Soc. 2002;22(14–15):2609–2613.

[18] Lee JH, Heo YW, Kim JJ, et al. The aging effect on the low temperature mechanical strength of 3YSZ single crystals manufactured by the Skull melting method. Ceram Int. 2013;39(2):2031–2036.

[19] Borik MA, Bublik VT, Kulebyakin AV, et al. Phase composition, structure and mechanical properties of PSZ (partially stabilized zirconia) crystals as a function of stabilizing impurity content. J Alloys Compd. 2014;586:231–235.

[20] Ingel RH, Levis D, Bender DF, Rice RW. Physical, Microstructural and Thermomechanical Properties of ZrO2 Single Crystals In: Claussen N, Ruhle M, Heuer AH, editors. Adv. in Ceram. V12, Science and technology of zirconia II, Am. Cer. Soc. Columbus, OH; 1984. p. 408–414.

[21] Gogotsi GA, Lomonova EE, Pejchev VG. Strength and fracture toughness of zirconia crystals. J Europ Ceram Soc. 1993;11(2):123–132.

[22] Rebollo NR, Gandhi AS, Levi CG. Phase stability issues in emerging TBC systems, high temperature corrosion and materials chemistry IV: proceedings of the international symposium. Electrochem Soc Proc. 2003;16:431–442.

[23] Kulebyakin AV, Borik MA, Chislov AS, et al. Melt grown ZrO2 single crystals partially stabilized with Gd2O3: phase composition and indentation induced transformations. J Cryst Growth. 2020;535:125546.

[24] Niihara KA. A fracture mechanics analysis of indentation-induced Palmqvist crack in ceramics. J Mater Sci Lett. 1983;2(25):2221–2223.

[25] Kuz’mínov YS, Lomonova EE, Osiko VV. Cubic zirconia and skull melting. UK: Cambridge International Science Publishing Ltd; 2009.

[26] Orera VM, Merino RI, Chen Y, et al. Intrinsic electron and hole defects in stabilized zirconia single crystals. Phys Rev B. 1990;42(16):9782–9787.

[27] Orera VM, Merino RI, Pena F. Ce3+ ↔ Ce4+ conversion in ceria-doped zirconia single crystals induced by oxido-reduction treatments. Solid State Ion. 1994;72:224–231.

[28] Wang C, Zinkevich M, Aldinger F. Phase diagrams and thermodynamics of rare-earth-doped zirconia ceramics. Pure Appl Chem. 2007;79(10):1731–1753.

[29] Kilo M, Taylor MA, Argirius C, et al. cation self-diffusion of 44Ca, 88Y and 96Zr in single crystalline calcia- and yttria-doped zirconia. J Appl Phys. 2003;94 (12):7547–7552.

[30] Chevalier J, Gremliard L. The tetragonal-monoclinic transformation in zirconia: lessons learned and future trends. J Am Ceram Soc. 2009;92(9):1901–1920.

[31] Fabris S, Paxton AT, Finnis MW. A stabilization mechanism of zirconia based on oxygen vacancies only. Acta Materialia. 2002;50(20):5171–5178.

[32] Rahaman MN, Gross JR, Dutton RE, et al. Phase stability, sintering, and thermal conductivity of plasma-sprayed ZrO2–Gd2O3 compositions for potential thermal barrier coating applications. Acta Materialia. 2006;54(6):1615–1621.

[33] Cairney JM, Rebollo NR, Rühle M, et al. Phase stability of thermal barrier oxides: a comparative study of Y and Yb additions. Int J Mater Res. 2007;98(12):1177–1187.

[34] Ilavsky J, Stalick JK, Wallace J. Thermal spray yttria-stabilized zirconia phase changes during annealing. J Therm Spray Technol. 2001;10(3):497–501.

[35] Gibson IR, Irvine JTS. Qualitative X-ray diffraction analysis of metastable tetragonal (t') zirconia. J Am Ceram Soc. 2001;84(3):615–618.

[36] Yoshimura M, Yashima M, Noma T, et al. Formation of diffusionlessly transformed tetragonal phases by rapid quenching of melts in ZrO2–RO15 systems (R = rare earths). J Mater Sci. 1990;25:2011–2016.

[37] Yamashitaw I, Synchrotron X-Ray TK. Study of the crystal structure and hydrothermal degradation of yttria-stabilized tetragonal zirconia polycrystal. J Am Ceram Soc. 2008;91(5):1634–1639.

[38] Raza FM, Cornil D, Cornil J, et al. Oxygen vacancy stabilized zirconia (OVSZ); a joint experimental and theoretical study. Scr Mater. 2016;124:26–29.

[39] Sakuma T. Microstructural aspects on the cubic-tetragonal transformation in zirconia. Key Eng Mater. 1998;153:75–96. Trans Tech Publications Ltd.

[40] Borik MA, Borichevskij VP, Bublik VT, et al. Anisotropy of the mechanical properties and features of the tetragonal to monoclinic transition in partially stabilized zirconia crystals. J Alloys Compd. 2019;792:1255–1260.

[41] Zhang N, Zaeem MA. Competing mechanisms between dislocation and phase transformation in plastic deformation of single crystalline yttria-stabilized tetragonal zirconia nanopillars. Acta Materialia. 2016;120:337–347.

[42] Virkar AV. Role of ferroelasticity in toughening of zirconia. Key Eng Mater. 1998;153:154–83–210.

[43] Ingel RP, Lewis DL, Bender BA, et al. Temperature dependence of strength and fracture toughness of ZrO2 single crystals. J Am Ceram Soc. 1982;65(9): C150–151.

[44] Michel D, Mazerolles L, Perez Y, et al. Fracture of metastable tetragonal zirconia crystals. J Mater Sci. 1983;18(9):2618–2628.

[45] Chien FR, Ubic FJ, Prakash V, et al. Stress-induced martensitic transformation and ferroelastic deformation adjacent microhardness indents in tetragonal zirconia single crystals. Acta Mater. 1998;46(6):2151–2171.

[46] Baufeld B, Baither D, Messerschmidt U, et al. Ferroelasticity of t'-zirconia: II, straining in a high-voltage electron microscope. J Am Ceram Soc. 1997;80(171):1699–1705.

[47] Amazigo JC, Steady-State Crack BB. Growth in supercritically transforming materials. Int J Solids Struct. 1988;24(7):751–755.

[48] Virkar AV, Jue JF, Smith P, et al. The role of ferroelasticity in toughening of brittle materials. Phase Trans. 1991;35(1):21–46.