

Effect of Sintering Temperature on Crack Growth Resistance Characteristics of Yttria-Stabilized Zirconia

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Zirconium oxide (zirconia) ZrO_2 is widely used for applications in high-temperature structural materials. In this work, yttria-stabilized zirconia has been studied. Series of specimens of ZrO_2 ceramics stabilized with 6, 7, and 8 mol% Y_2O_3 were prepared using the conventional sintering technique. Four sintering temperatures (1450, 1500, 1550, and 1600°C) were used for the 6% yttria-stabilized zirconia series, and two sintering temperatures (1550 and 1600°C) were used for the 7% and 8% yttria-stabilized ZrO_2 series. The tests of microhardness and fracture toughness of the materials were performed by the indentation method. It was found that both the yttria percentage and the sintering temperature affect the mechanical behaviour of the ceramics. The maximum transformation toughening effect during indentation was revealed for the ceramic ZrO_2 -6 mol% Y_2O_3 . Using the phase balance analysis, it was found that such toughening of ceramics is related to corresponding levels of fracture toughness.

topics: YSZ ceramics, microstructure, phase balance, microhardness, fracture toughness

1. Introduction

Precision products are often manufactured of advanced ceramic materials to ensure a long life cycle, thus solving the issues of extreme operating conditions such as high pressure, high temperature, corrosion, abrasion etc. The products may be manufactured of aluminum oxide, zirconia, sintered silicon carbide or other ceramics [1–3].

The structural integrity and lifetime of products made of yttria-stabilized zirconia (YSZ) ceramics need to be improved taking into account the above-mentioned extreme conditions [4, 5]. Therefore, the substantiation of the chemical composition and the modes of material production are the crucial issues affecting the resulting phase balance and the mechanical properties of the manufactured material [3, 6, 7].

In a number of scientific works [8–10] the correlations between chemical composition, in particular the content of Y_2O_3 and Fe_2O_3 additives [8], sintering modes [9, 10], and mechanical properties

of the microstructure and translucency of YSZ ceramics were evaluated. The content of Y_2O_3 varied from 2 to 10 mol% and sintering temperatures varied from 1475 to 1600°C. The microstructure, phase composition and set of physical properties were analyzed [8, 10]. In particular, in the 3YSZ ceramics, only the tetragonal ZrO_2 phase was revealed, while in the 5YSZ ceramics the cubic ZrO_2 phase was detected after sintering at 1600°C. In this sintering mode, an increase in grain size from 0.8 to 2.3 μm was found with an increase in the Y_2O_3 content from 3 to 5%. Besides, the effect of the Y_2O_3 content on the strength of the material was revealed.

The authors of a series of works studied the phase evolution in plasma-sprayed [11] and EB-PVD coatings [12] based on YSZ. It was revealed using neutron scattering studies and XRD analysis [11] that the tetragonal ZrO_2 phase decomposes into monoclinic and cubic phases, with decreasing yttria content in the tetragonal phase. In the EB-PVD coatings [12, 13] it was found that the metastable

tetragonal ZrO_2 phase transforms into a tetragonal phase with low yttria content and a cubic or tetragonal phase with high yttria content in the temperature range of 1300 to 1400°C. After heat treatment of studied EB-PVD coatings at temperatures in the range of 1100 to 1500°C [13], the tetragonal ZrO_2 (t- ZrO_2) phase decomposed into a tetragonal phase with low Y_2O_3 percentage and both tetragonal and cubic phases with high Y_2O_3 percentage. Using computer simulations, it was found that the domain boundaries have a cubic-like structure containing a relatively high number of yttrium ions [14].

YSZ ceramics of various chemical compositions as materials for monolithic restorations in dentistry were studied in [15–17]. It was found that low-temperature degradation could occur when the t- ZrO_2 phase is transformed to the monoclinic ZrO_2 (m- ZrO_2) phase during aging at temperature in a range of 100–300°C. This transformation was accelerated when material was exposed to a humid environment. As a result, its mechanical properties were degraded. Correlations between the degree of t-m phase transformation and the level of retaining the residual compressive stresses on the surface were found in [15]. The lattice distortion after the t-m phase transformation was also estimated [16].

Traditionally, the bearing capacity of ceramic products is estimated using the strength and wear resistance characteristics of the materials of which these products are made [1, 15]. However, to avoid the interaction of the materials with the operating environments [6, 18–20], it is necessary to obtain a material with an appropriate microstructure resistant to degradation in operation conditions [18, 21, 22]. Therefore, more structurally sensitive methods should be used for the diagnostic of the load-bearing capacity of such materials and products. One of them is indentation test as the most common mechanical method [23, 24]. To evaluate the material sensitivity to crack initiation and growth, fracture toughness tests with different loading schemes and specimen shapes are used in the fracture mechanics [19, 24–26]. Therefore, the relationship between the microstructure parameters and the crack growth resistance characteristics of the YSZ ceramic material sintered in different modes should be investigated to find an appropriate way of creation of a ceramic material with high crack growth resistance.

2. Material and methods

In this work, we have studied yttria-stabilized zirconia (YSZ) ceramics sintered from commercial starting powders. The powders were manufactured in the Vol'nogorskii Mining and Smelting Plant, Ukraine. The initial particle sizes of starting powders of ZrO_2 and Y_2O_3 were in the range of 100–150 nm and 10–30 nm, respectively. A series of YSZ ceramic beam specimens $4.2 \times 4.2 \times 50 \text{ mm}^3$ in size, stabilized with 6, 7, and 8 mol% Y_2O_3

(hereinafter: 6YSZ, 7YSZ, and 8YSZ, respectively) were sintered in a furnace for 2 h in argon. Four sintering temperatures (1450, 1500, 1550, and 1600°C) were used for the 6YSZ series and two sintering temperatures (1550 and 1600°C) were used for the 7YSZ and 8YSZ series. Thus, eight variants of the material were obtained. When marking these variants, we indicated the corresponding chemical composition and sintering temperature, e.g. 6YSZ-1450. The side surfaces of the specimens were polished after sintering, and the final size $3.6 \times 3.6 \times 50 \text{ mm}^3$ of each specimen was reached.

The microhardness of the material variants was measured using a NOVOTEST TC-MKB1 microhardness tester. The following set of indentation loads was used: 0.49, 0.98, 1.96, 2.94, 4.91, and 9.81 N. Conditions for the microhardness measurement are regulated by the relevant standard [23]. The optical microscope Neophot-21 was used to study the imprint and crack geometry. At least 10 indentations were made for each level of the indentation load set to determine the microhardness of each material variant.

To characterize the propensity of a material to brittle fracture due to nucleation and propagation of cracks [24, 25], we estimated the fracture toughness of the material by calculating the critical stress intensity factor (SIF), denoted as K_{Ic} . There exists a wide range of methods for evaluating the fracture toughness of materials under the Vickers pyramid indentation, along with many formulae for calculating the K_{Ic} values [24]. Recently [26], we have examined various formulae to compare the calculation results with those based on traditional methods of fracture mechanics. We concluded that the formula presented in [27] is optimal for the characterization of the ZrO_2 - Y_2O_3 ceramics. In our work, we used this formula to assess the fracture toughness of the studied material variants.

X-ray powder diffraction data were obtained by using a DRON-4.07M diffractometer with Cu K_α radiation, operated at a voltage of 40 kV and a current of 20 mA. All procedures, including indexing, structure solutions, and refinement of profile and structural parameters, were performed with the WinCSD [28] program package.

3. Results and discussion

The obtained XRD patterns of the tested material variants show, in general, a phase balance for the 6YSZ, 7YSZ, and 8YSZ ceramics (Fig. 1). Ambiguous changes in the phase balance with changes in the sintering temperature were revealed, from 1450 to 1600°C, for the 6YSZ ceramics. In particular, for this material sintered at 1550°C, the maximum percentage of t- ZrO_2 (over 56 wt%) was found along with a decrease in weight fraction in m- ZrO_2 (to 32 wt%) and cubic ZrO_2 (to 11 wt%).

Graphical representation of the Rietveld refinements of the selected specimens is shown in Fig. 2.

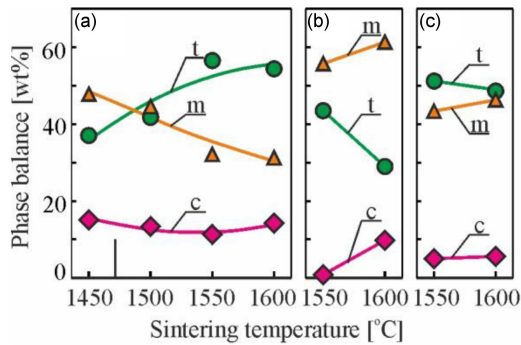


Fig. 1. Changes in zirconia phase balance of the investigated materials of variants (a) 6YSZ-1450, 6YS-1500, 6YSZ-1550, 6YSZ-1600, (b) 7YSZ-1550, 7YSZ-1600, and (c) 8YSZ-1550, 8YSZ-1600 depending on the sintering temperature. Phase marking: t — tetragonal, m — monoclinic, c — cubic.

Thus, in the 6YSZ ceramics, the sintering temperature of 1550°C allows for providing a relatively high percentage of the t-ZrO₂ phase, while the m-ZrO₂ phase weight fraction is decreased compared to the 6YSZ-1450 and 6YSZ-1500 variants. Similarly, the weight fraction of the cubic ZrO₂ (c-ZrO₂) phase reaches its minimum for the 6YSZ-1550 variant. In the 7YSZ ceramics at the sintering temperature of 1550°C, a relatively high percentage of m-ZrO₂ phase (over 55 wt%) was obtained, while the t-ZrO₂ phase weight fraction (about 43 wt%) was obtained lower than for both variants 6YSZ-1550 and 8YSZ-1550.

The general tendencies of the phase balance changes in the 6YSZ, 7YSZ, and 8YSZ ceramics can be described as follows:

- with increasing the sintering temperature, the amount of the tetragonal phase increases when the content of the stabilizing Y₂O₃ additive is quite low (6YSZ ceramics);
- the sintering temperature 1550°C is critical as in the 6YSZ, 7YSZ, and 8YSZ ceramics the percentage of the tetragonal phase decreases and the percentage of the monoclinic phase increases with the further increase of sintering temperature;
- the cubic phase is probably the balance because the amount of cubic phase is quite low, especially in the 7YSZ and 8YSZ ceramics;
- the maximum m-ZrO₂ phase percentage is reached in the variant 7YSZ-1600 due to the phase balance (i.e., decrease in the t-ZrO₂ phase weight fraction and a slight increase in the c-ZrO₂ phase weight fraction).

It was revealed that an increase of the sintering temperature from 1450 to 1500°C led to an improvement of the mechanical properties of the 6YSZ ceramics. In particular, an increase in the

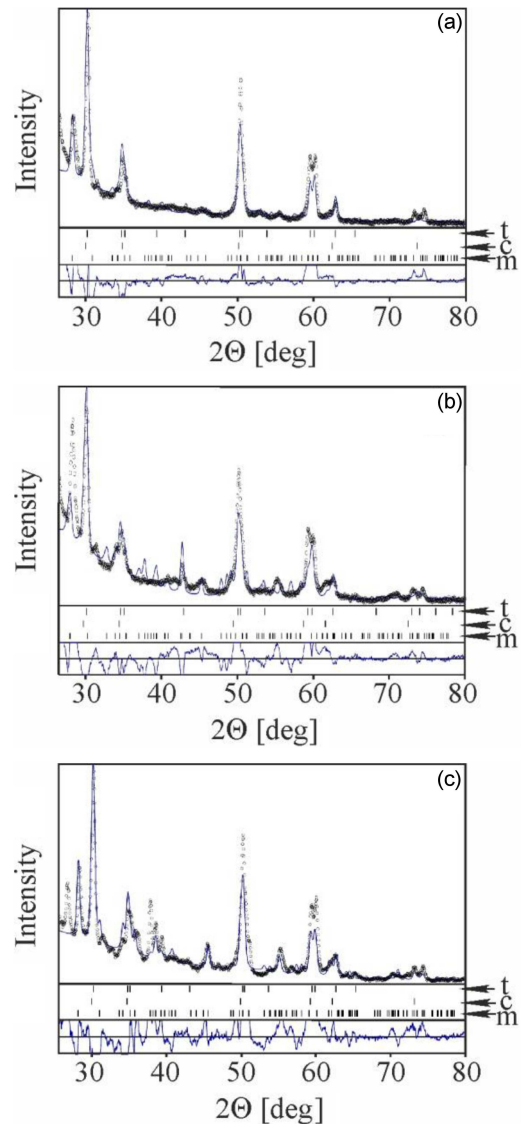


Fig. 2. XRD patterns of the investigated materials of variants (a) 6YSZ-1550, (b) 7YSZ-1550, and (c) 8YSZ-1550. Phase marking: t — tetragonal, m — monoclinic, c — cubic'.

microhardness (by 5–6%, Fig. 3a) was observed for this material and the same tendency in fracture toughness (by 3–4%, Fig. 3b) was found. The levels of these characteristics remain unchanged while increasing the sintering temperature up to 1550°C.

The increase of the sintering temperature to 1600°C leads to an intensive grain growth in the YSZ ceramics. This, in turn, leads to the suppression of the process of the metastable tetragonal to monoclinic phase transformation (t-m) of ZrO₂ [17] in the case when the average grain size of the t-ZrO₂ phase is larger than the admissible one. The latter is about 1 μm for ceramics of this type. According to [17], the microhardness of m-ZrO₂ is lower than t-ZrO₂. During indentation, the t-m transition occurs with the formation of m-ZrO₂, which reduces the microhardness.

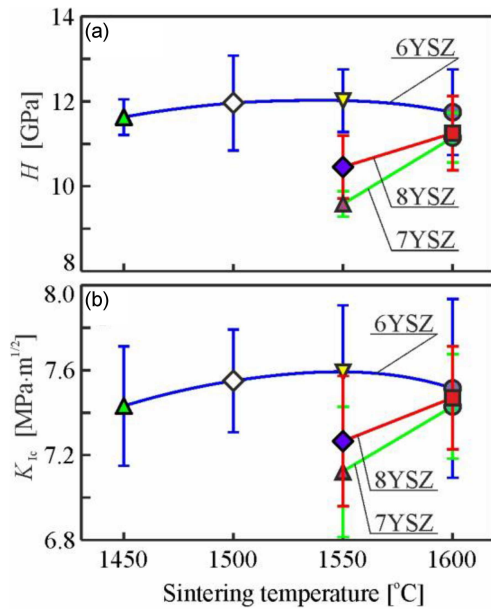


Fig. 3. Changes in (a) microhardness and (b) fracture toughness of the 6YSZ, 7YSZ, and 8YSZ ceramics depending on the sintering temperature. The microhardness was measured under the indentation load of 9.81 N.

In contrast to the 6YSZ ceramics, a substantial increase in the m-ZrO₂ weight fraction was revealed for the 7YSZ and 8YSZ ceramics while increasing the sintering temperature from 1550 to 1600°C (Fig. 1). This in turn leads to a decrease in the t-ZrO₂ or c-ZrO₂ weight fractions in these ceramics.

A common result of the two above-mentioned processes, i.e., suppression of the t-m transformation of ZrO₂ with the sintering temperature increase and the stress-induced formation of m-ZrO₂, is displayed in Fig. 3a and b. For the case of the sintering temperature of 1550°C, differences are observed between the average values of both the microhardness (Fig. 3a) and fracture toughness (Fig. 3b) for the 7YSZ and 8YSZ ceramics. The latter has an advantage over the previous one both in terms of microhardness and fracture toughness. Probably, a high percentage of m-ZrO₂ in the 7YSZ ceramics (Fig. 1b) causes a decrease in microhardness, whereas a slight effect of the t-m transformation occurs at a comparatively low percentage of t-ZrO₂. In contrast, the microhardness of 8YSZ ceramics is higher due to the lower percentage of m-ZrO₂ (Fig. 1c). On the other hand, since the percentage of t-ZrO₂ is higher in the 8YSZ ceramics (Fig. 1c), the t-m transformation significantly affects the microhardness by lowering it, and, oppositely, increases the fracture toughness of the material (Fig. 3a and b).

The pattern of calculated critical SIF K_{Ic} values (Fig. 3b) is evidence that the sintering temperature 1550°C is critical in the microstructure formation process. A pronounced t-m transition occurred in

the crack tip vicinity of a specimen of the 6YSZ ceramics indented with a Vickers pyramid. For the material sintered at 1600°C, the t-m transformation dynamics are less pronounced. In this case, mainly the t-ZrO₂ provides the desired level of crack growth resistance (Fig. 3b), which is reflected by similar values of fracture toughness of the 6YSZ, 7YSZ, and 8YSZ ceramics, and by similar microhardness values for these material variants.

Thus, for the 6YSZ, 7YSZ, and 8YSZ ceramics, phase balances were defined, at which the maximum fracture toughness is reached. The maximum value of K_{Ic} using the Vickers indentation method for the 6YSZ ceramics was obtained at the maximum content of the tetragonal phase (variant 6YSZ-1550). On the other hand, for ceramics with a higher content of the stabilizing Y₂O₃ additive (7YSZ and 8YSZ ceramics), the maximum K_{Ic} levels were reached at the maximum content of the monoclinic phase (variants 7YSZ-1600 and 8YSZ-1600, respectively).

4. Conclusion

In this work, the phase composition and mechanical properties of 6YSZ, 7YSZ, and 8YSZ ceramics depending on the sintering temperature have been studied. It was shown that the fracture toughness of YSZ ceramics depends strongly on the phase transformations occurring in the material.

The conditions for the formation of tetragonal, monoclinic, and cubic phases of zirconia in the studied YSZ ceramics were substantiated.

The highest level of fracture toughness was found in the 6YSZ ceramics sintered at 1550°C compared to other studied variants of the material.

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