



## Study of the Structure and Mechanical Properties of PSZ (Partially Stabilized Zirconia) after Heat Treatment at 1600 °C

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The phase composition and twin structure of PSZ crystals after heat treatment at 1600 °C have been studied in relation to the content of the stabilizing impurity (Y<sub>2</sub>O<sub>3</sub>) by X-ray diffraction and transmission electron microscopy. The measurement of both hardness and fracture toughness by microindentation has been carried out. Studies have shown that crystals of PSZ obtained by directional solidification of the melt consist of two tetragonal phases (t and t'), with varying degrees of tetragonality. The yttrium-enriched phase t' is "untransformable" in contrast to the t phase, with a lower content of yttrium, which, under the influence of mechanical stress, undergoes a martensitic transition to the monoclinic form. Increasing the stabilizing impurity concentration leads to an increase in the volume fraction of the "untransformable" phase. Increasing the concentration of Y<sub>2</sub>O<sub>3</sub> also affects the form and dispersion of the twin domains. In this work it is shown that the quantity of hardening (fracture toughness) is proportional to the content of the transformable t phase. This work was supported by grants from the company "OPTEC"

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### 1. INTRODUCTION

Zirconia based materials have a variety of unique physicochemical, electrical and mechanical properties including high strength, hardness, impact toughness, wear resistance, low coefficient of friction, high melting point, chemical inertness, low heat conductivity and biocompatibility. These properties account for the wide range of applications, from wear resistant ceramic bearings to medical and surgical instruments [1-2]. Such materials can be used to produce components for devices functioning under extreme conditions: at high mechanical loadings, in aggressive media, at elevated temperatures, without lubrication, etc. This material, with its high fracture toughness due to the inherent phase transition similar to martensitic transformations in steels, has received the name 'ceramic steel' [3].

Such properties of PSZ crystals are related to features of their phase composition, structure and presence of nano and micro twin structure [4]. Changing the growth conditions and process annealing PSZ crystals affects the phase composition and structure, and thus the mechanical characteristics of the material.

The heat treatment is carried out in the temperature range 1400-1600°C to investigate the structural stability of the solid solutions, which depends on the nature and concentration of the stabilizing oxide, method for producing the material. The outcome will depend on the temperature and duration of destabilizing annealing. In work [5] it is shown that the high mechanical properties of PSZ crystals remain at the annealing temperature 1400°C, with their smaller degradation as compared to ceramics. Inasmuch as this annealing correspond operating temperatures of the

material. Therefore the study of the influence of thermal annealing on the structural stability of the solid solutions at these temperatures is extremely important for practical applications of the material.

### 2. EXPERIMENTAL

Yttrium oxide stabilized (concentration range 2.8 – 4.0 mol. %) PSZ crystals were grown using directional melt crystallization in a cold crucible at a 10 mm/h crystallization rate. The phase composition and structure of the PSZ were studied using X-ray diffraction on a Bruker D8 instrument and transmission electron microscopy (TEM) on a JEM-2100 microscope at a 200 kV accelerating voltage. The specimens for the electron microscopy study were prepared as follows. Wafers were cut from the crystals so that the plane of the wafer was oriented either orthogonally to the <100> crystal axes. The specimens were ground to a 200 μm thickness. 3 mm diameter discs were cut out of the source material by ultrasonic cutting, followed by the dimpling the center of the discs, and finally the specimens were thinned by ion beam etching. Hardness and fracture toughness were measured by microhardness indentation. Then, the plates ZrO<sub>2</sub>, stabilized from 2.8 to 4.0 mol. % Y<sub>2</sub>O<sub>3</sub>, annealed in air at 1600°C. Conditions of heat treatment are – 6 hours heating, 14 hours ageing, 6 hours cooling.

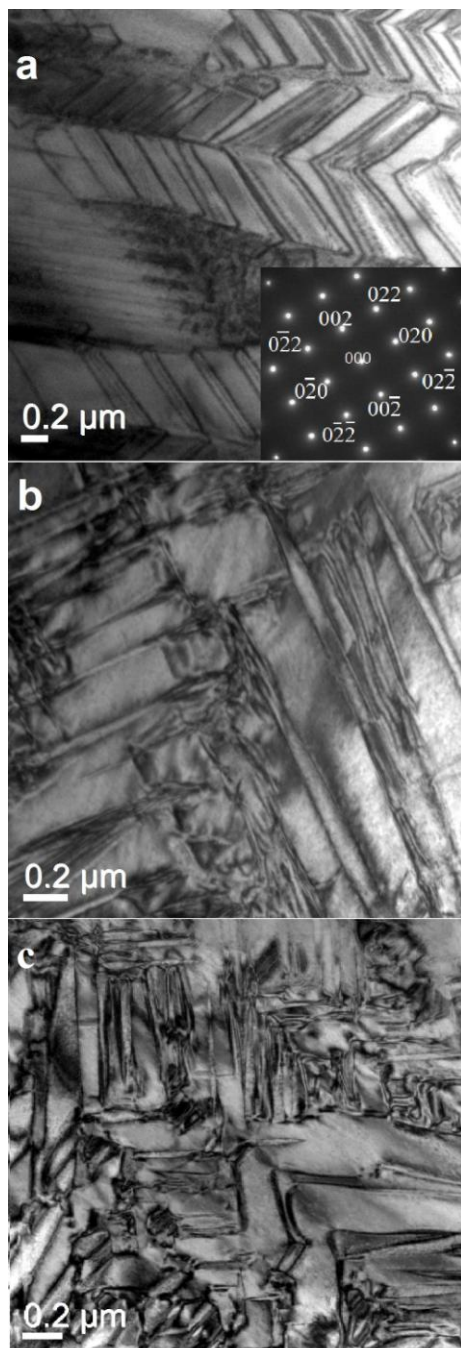
### 3. RESULTS AND DISCUSSION

#### 3.1 Research of the structure PSZ crystals by transmission electron microscopy

All the specimens had a well developed twin domain structure. Fig. 1 (a, b, c) shows a typical example of the

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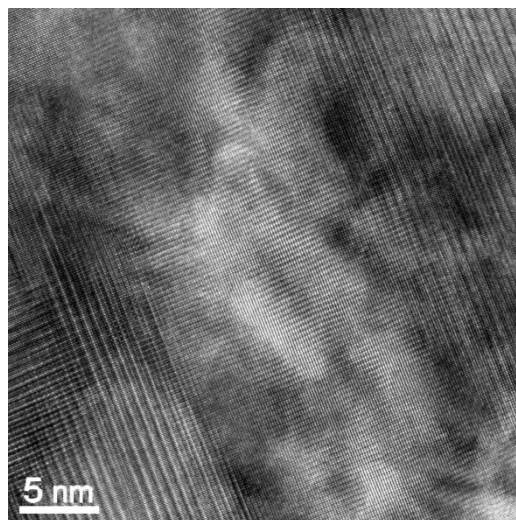
twined structure for samples of compositions: 2.8, 3.0 and 3.2 mol. %  $Y_2O_3$ . It is seen that the dispersion and morphology of the structure does not change significantly with an increase in the concentration of stabilizing impurities to 3.2 mol. %  $Y_2O_3$ . TEM study of the PSZ crystals showed that, according to the electron diffraction patterns, all the specimens are single crystals. Fig. 1a (bottom right) shows the diffraction pattern of the samples cut perpendicular to the axis of the crystal  $\langle 100 \rangle$ .



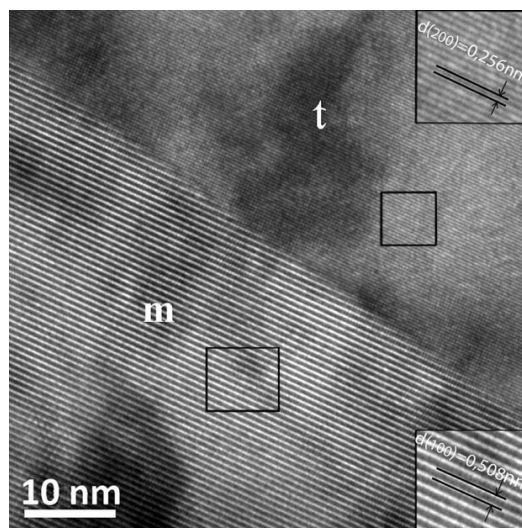
**Fig. 1** – TEM images of the twin structure typical for sample with the concentration of the stabilizing impurity (a) - 2.8 mol. %  $Y_2O_3$ , (b) - 3.0 mol. %  $Y_2O_3$ , (c) - 3.2 mol. %  $Y_2O_3$

A more detailed high resolution TEM study showed that large domains consist of smaller twinned domains.

Fig. 2 shows a TEM image of 10–15 nm sized twins. Also, high resolution TEM identified coherent monoclinic phase inclusions in the structure (Fig. 4). After annealing at 1600 °C in samples with  $Y_2O_3$  to 3.2 mol. % formed regions of the monoclinic phase in the form of a domain, width ~ 20 nm, which is coherent with the conjugate phase of the tetragonal domains (Fig. 3).



**Fig. 2** – High-resolution image of twin domains in the  $ZrO_2$  2.8 mol.%  $Y_2O_3$  sample.

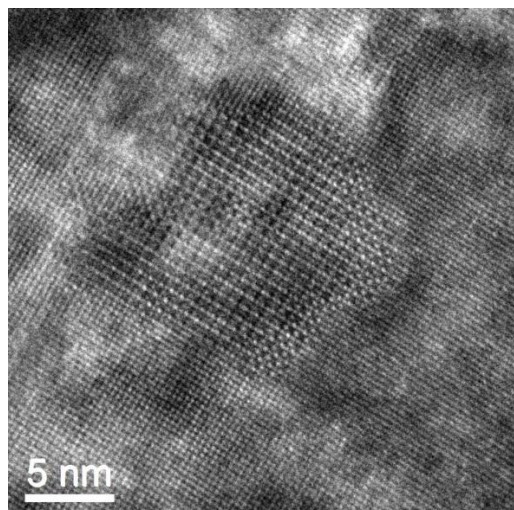


**Fig. 3** – High-resolution TEM image of a coherent boundary between tetragonal (*t*) and monoclinic (*m*) phase of the sample after annealing at 1600°C

Unlike to the crystals after growth, where there was a small inclusion monoclinic phase dimensions of about 10 nm with indistinct boundaries (Fig. 4). The occurrence of coherent monoclinic phase inclusions in these specimens can be caused by the low concentration of the stabilizing impurity and its local fluctuations during crystallization. These inclusions may serve as nuclei for the formation of the monoclinic phase regions during subsequent heat treatment of crystals at a temperature corresponding to the two-phase region in the phase diagram. The morphology and relative position of twin domains in samples of 3.7 - 4.0 mol. %  $Y_2O_3$ , was

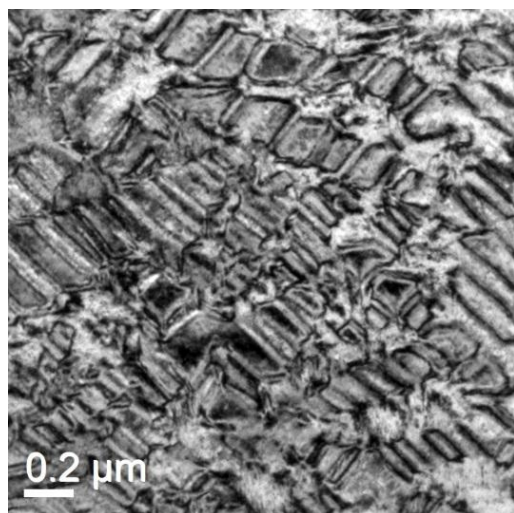


different from the crystals with lower concentrations of 2.8 - 3.2 mol. %  $Y_2O_3$ . The twin structure becomes more homogeneous and dispersed (Fig. 5). At higher stabilizing impurity concentrations (3.7–4 mol. %  $Y_2O_3$ ), no twinning hierarchy was observed, atomic plane traces inside twin domains were not broken, and minimum twin domain sizes could be identified in diffraction contrast images.



**Fig. 4** – High-resolution image of inclusion monoclinic phase in the  $ZrO_2$  2.8 mol.%  $Y_2O_3$  sample after growth

This suggests that twinning occurs simultaneously and is localized within small volumes. In samples with a stabilizing concentration of impurities 2.8 to 3.2 mol. %  $Y_2O_3$  twinning first goes to the larger domains, which also twinning.

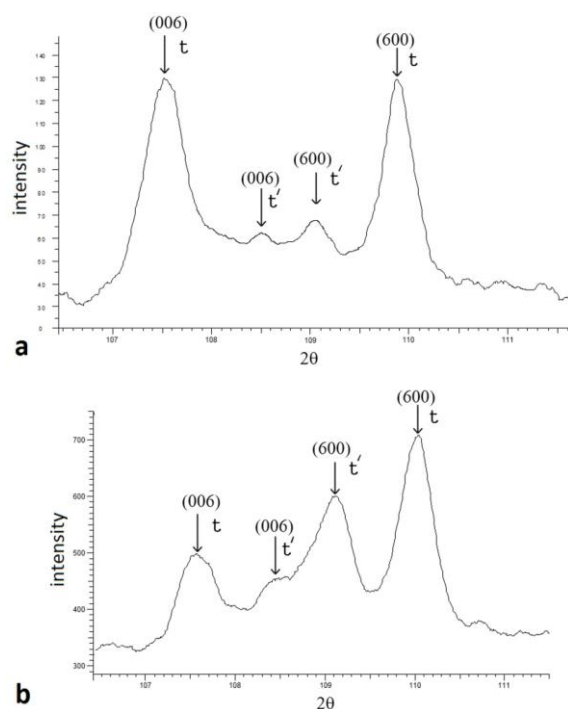


**Fig. 5** – TEM images of the twin structure typical for sample  $ZrO_2$  4.0 mol. %  $Y_2O_3$

### 3.2 Phase analysis

In accordance with the  $ZrO_2$ - $Y_2O_3$  phase diagram, PSZ crystals growing during melt synthesis initially have a cubic structure, and a phase transformations occur during cooling in the solid state. As the temperature decreases, the cubic phase becomes unstable and transforms to a tetragonal modification. The slight atomic

shifts, mainly affecting the oxygen ions, distort the symmetry of the initial structure. The oxygen ions shift relative to the perfect fluorite lattice positions (1/4, 1/4, 1/4). Generally, the tetragonal phase lattice is slightly elongated along the  $c$  axis as compared to the cubic phase lattice. X-ray diffraction from the PSZ phase showed that the material has two tetragonal phases of the  $P42/mnc$  space symmetry group. The simultaneous occurrence of the (006) and (600) reflections in the diffraction pattern is accounted for by twinning as will be shown below in the discussion of the transmission electron microscopy results. Analysis of the diffraction profile was hindered by the superimposition of the split reflections due to the presence of the tetragonal lattice and  $R\alpha$ -doublet splitting; therefore we conducted an additional experiment with  $R\beta$  radiation which allowed us to definitely confirm that the splitting is due to the presence of the two tetragonal phases (Fig. 5a).



**Fig. 5a** – X-ray diffraction patterns of the YSZ 2.8 mol. %  $Y_2O_3$ , **5b** – X-ray diffraction patterns of the YSZ 4.0 mol.%  $Y_2O_3$

Phase constituent study of zirconia doped to different  $Y_2O_3$  concentrations (2.8–4.0 mol. %) showed that all the specimens, regardless of the stabilizing impurity content, have two tetragonal zirconia modification phases with varying degrees of tetragonality. Both phases have a slightly distorted fluorite structure and differ in the ratio of their lattice parameters. For one tetragonal phase –  $t$ , the  $c/a$  ratio was 1.014–1.015, and for the other tetragonal phase –  $t'$ , the  $c/a$  ratio was close to 1, i.e. 1.004–1.005 [6]. The yttrium rich  $t'$  phase is not transformable unlike the lower yttrium content  $t$  phase which undergoes a martensitic transformation to the monoclinic state under mechanical stress [7]: this transformation may suppress the sources of stress concentration and increase the fracture toughness of the material. There is data [8] on a wide range of tetragonal phase modifications depending on the degree of tetragonality. The  $c/a$

ratio may vary over a wide range from 1.005 (for the so-called  $t'$  phase, which does not transform under mechanical stress) to  $c/a = 1.035$  for the readily transformable to monoclinic phase. For example, if the  $t'$  phase forms during the cubic to tetragonal phase transition, it will not transform to the phase even under intense grinding of the specimen. The phase with the higher  $c/a$  ratio will transform easier in an elastic stress field. Thus, the specimens contain two tetragonal phases with  $c/a = 1.004$ – $1.005$  and  $c/a = 1.014$ – $1.015$  [9]. The intensity of the diffraction peaks suggests that the higher tetragonal degree phase dominates in the crystals with a 2.8 mol. %  $Y_2O_3$  stabilizing impurity concentration. However, as the stabilizing impurity concentration is increased, the volume fraction of the untransformable  $t'$  phase increases gradually, and the volume fraction of the  $t$  phase decreases (Fig. 5a, b).

Analysis of broadening of the diffraction peaks has shown that after annealing at 1600°C diffraction line width is reduced compared to the crystals after growth.

On the width of the diffraction peaks can affect microstress and dispersion of coherent domains in domain-twinned structure. Comparison of the domain size on TEM images before and after annealing 1600 °C showed that a significant change in the dispersion did not happen. It can be assumed that the width of the diffraction peaks are not changed due to increased dispersion of the domain, but due to the removal of microstrain in the PSZ crystals after annealing. The microstresses may be partially removed by the formation of a more ordered domain structure.

### 3.3 Mechanical properties Conclusion

Microhardness measurements were carried out at a load of 500 g. The table shows that the microhardness not dependent on the concentration  $Y_2O_3$ . Also, a significant change was not found when compared microhardness PSZ crystals before and after annealing. To obtain the dependence of fracture toughness from the content of  $Y_2O_3$ , chose the load at which a crack formed on the crystals of all compositions. A sample with the lowest impurity concentration of the stabilizing 2.8 mol. %  $Y_2O_3$ , was the most resistant to cracking. This result can be explained by the high content in it (2.8 mol. %  $Y_2O_3$ )  $t$  tetragonal phase, which provides a transformational mechanism of hardening of the material. Compared with the crystal growth PSZ after annealing at 1600°C resulted in a slight improvement of fracture toughness values for the crystal with an impurity concentration of the stabilizing 2.8 mol. % - 3.2 mol. %  $Y_2O_3$ . This may be due to the relaxation of microstress in the PSZ crystals after annealing.

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### 4. CONCLUSION

Studies of the structure, phase composition, microhardness and fracture toughness of PSZ crystals after annealing at a temperature of 1600 °C were carried out. TEM studies have shown that crystals of all compositions have complex twinned structure. Upon cooling, the crystal phase transformation with different specific volumes ( $F \rightarrow t$ ) leads to the formation of elastic stress relaxation which occurs by twinning. A more thorough study TEM high resolution revealed that major domains consist from small twin domains. It can be assumed that the process of twinning occurs as long as in the sample remain elastic stresses are sufficient for twinning. At the same time dislocation are not detected in the samples.

Upon cooling, the crystal transition from the cubic single-phase to two-phase region, according to the state diagram, goes at a lower temperature with increasing concentration of yttrium, which affects on the character the twin structure. In samples of all compositions was found the presence of two tetragonal phases with different degrees of tetragonal ( $t$  and  $t'$ ). Moreover, the volume fraction of «transformed» ( $t$ ) phase decreases with increasing concentration of the stabilizing impurity. Reduction of  $t$  phase affects on the "transformational" hardening when advancing microcrack induces  $t - m$  martensitic transition which absorbs energy stress and blocks the advancing microcrack eventually stopping it. Measurement of the mechanical properties shows that the microhardness of crystals does not change for different compositions. But a noticeable decrease in the fracture toughness with increasing doping concentration was discovered. We believe that this is due to the decrease in the volume fraction of transformable tetragonal phase.

**Table 1** – Dependence of microhardness and fracture toughness PSZ crystals before and after annealing from the  $Y_2O_3$  concentration

Compositions $Y_2O_3$ , %				
2,8	3,0	3,2	3,7	4,0
The values of microhardness, HV (300 g)				
1410±40	1420±30	1400±20	1420±25	1450±40
The values fracture toughness for PSZ, $MPa \cdot m^{-1/2}$ (10 kg)				
10±0,6	9±0,6	7±0,6	6±0,6	5±0,6
The values fracture toughness for PSZ after annealing, $MPa \cdot m^{-1/2}$ (10 kg)				
11±0,6	10±0,6	8±0,6	7±0,6	6±0,6