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Investigation of the Microstructure and Nanostructure of Partially Stabilized Zirconia Crystals

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Abstract—This paper reports on the results of investigations into the dependence of the structure of partially stabilized zirconia crystals on the composition and technological conditions used for their growth. The zirconia crystals containing from 0 to 4 mol % Y_2O_3 are grown by directional crystallization in a cold container with the use of direct high-frequency heating. The microstructure and nanostructure of the grown crystals are examined using transmission and scanning electron microscopy. It is established that the formation of the structure depends directly on the composition of the crystals and the conditions of their growth.

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INTRODUCTION

At present, the design and production of new materials with good mechanical and tribological characteristics have been an important problem in many branches of industry. For these purposes, composite and ceramic materials are finding ever-widening application. However, apart from good strength properties, ceramic materials exhibit low cracking resistance and poor antifriction characteristics due primarily to the presence of grain boundaries in the ceramic products. Moreover, the disturbance of the boundary lubricating film can result in local heating and subsequent fracture of the ceramic part; hence, potentially high strength properties of ceramic materials remain unrealized. In addition, the cost of ceramic materials with a density closest to the theoretical value is rather high.

Solving the problem of the production of low-cost superstrength materials is associated primarily with the synthesis of nanostructured partially stabilized zirconia single crystals (solid solutions of yttria in zirconia). Partially stabilized zirconia crystals have been grown by directional crystallization in a cold container with the use of direct high-frequency heating (the skull-melting technique) [1].

The absence of grain boundaries in partially stabilized zirconia crystals and the presence of a domain nanostructure, which is formed upon the phase transition from the cubic structure to the tetragonal structure during cooling of the crystal, are responsible for the high strength properties of the material [2]. Partially stabilized zirconia crystals retain their performance characteristics over a wide temperature range from –140 to 1400°C (the melting temperature is ~2800°C) and possess the highest fracture toughness and, consequently, a high wear resistance as compared to other ceramic materials. Owing to these properties, partially stabilized zirconia crystals have competitive advantages over the world's best specimens of technical ceramic materials and crystals.

The purpose of this study was to determine the dependence of the structure of partially stabilized zirconia crystals on their composition and growth conditions.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

For our investigations, we grew a series of crystals of the composition ZrO_2–(0–4 mol %)Y_2O_3. The crystals were grown according to the skull-melting technique on a Kristall-407 growth apparatus equipped with a cold container 130 mm in diameter. The growth rate was varied from 3 to 40 mm/h. This growth technique is almost wasteless (because crystalline wastes can be remelted); furthermore, it does not impose requirements on the granulometric composition of the initial materials. This reduces the cost of the material as compared to the corresponding ceramics and makes it possible to produce pore-free materials.

The nanostructure of partially stabilized zirconia crystals was examined using high-resolution transmission electron microscopy on a Philips EM430ST electron microscope operating at an accelerating voltage of 200 kV, as well as X-ray diffraction on DRON-2.0 and URD-63 diffractometers. The X-ray diffraction data on the broadening of the diffraction reflections were used to estimate the sizes of coherent scattering regions.

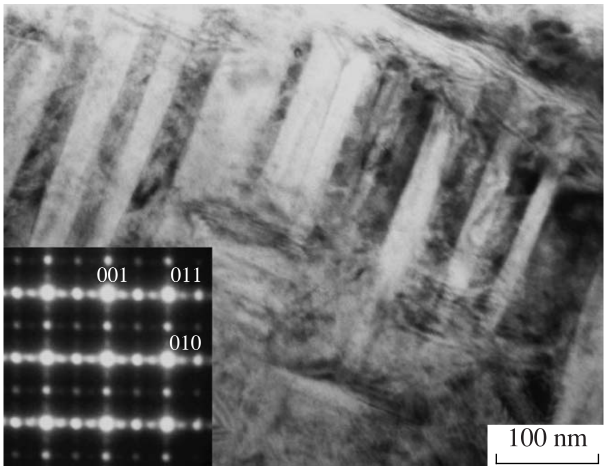

Fig. 1. Structure and diffraction pattern (taken along the ⟨100⟩ zone axis) of the ZrO_2–3 mol % Y_2O_3 sample grown at a rate of 10 mm/h.

The microstructure of the crystals was investigated using scanning electron microscopy with a JEOL-5900 electron microscope.

RESULTS AND DISCUSSION

The examination of the ZrO_2–3 mol % Y_2O_3 crystal by transmission electron microscopy has revealed that the sample contains domain assemblies 30–100 nm wide and 400–800 nm long, which form a tiling structure. The presence of domain assemblies in the crystal is confirmed by the diffraction pattern taken along the ⟨100⟩ zone axis and shown in Fig. 1. In turn, each structural unit of the assembly exhibits a band contrast with a period of approximately 10 nm. This indicates the existence of a fine domain substructure in the structural units forming assemblies. The sizes of units of this fine structure are estimated to be (0.1–0.5) × (10–20) nm. According to the X-ray diffraction data, the sizes of coherent scattering regions fall in the range from 87 to 310 nm, which is in good agreement with the aforementioned sizes of the assemblies. The investigation of the nanostructure of the ZrO_2–2.5 mol % Y_2O_3 crystals has demonstrated that the formation of a domain structure begins at an yttria concentration of 2.5 mol % (more specifically, a system of parallel domains appears there with elements of a tweed structure) (Fig. 2). It should be noted that, in the ZrO_2–4 mol % Y_2O_3 crystals, we revealed only individual regions with a weakly pronounced domain structure (Fig. 3).

According to the estimates obtained from examining the microstructure of the growth surface of the crystal with the use of the scanning electron microscope (magnification, ×25000), the smallest structural units have a width of 70 to 300 nm and a length of 300 to 900 nm, which are close to the estimated sizes of the assemblies observed with the transmission electron microscope. This observation allows us to draw the conclusion that the microstructure of the growth surface of the crystals reflects their internal structure (i.e., the structure of domain assemblies).

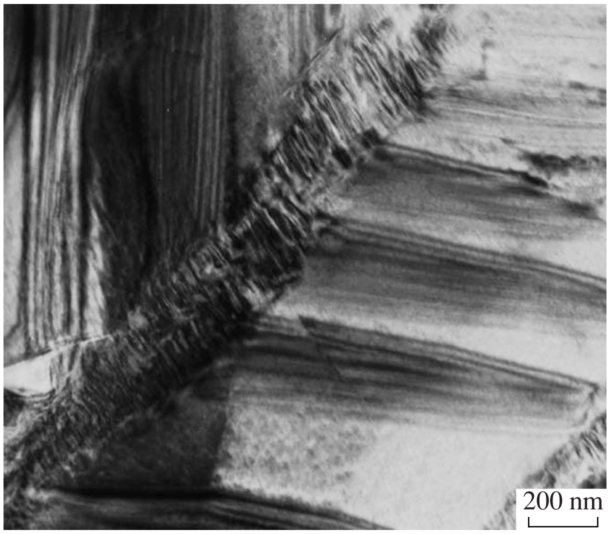

Fig. 2. Structure of the ZrO_2–2.5 mol % Y_2O_3 sample grown at a rate of 10 mm/h.

Further investigation of the microstructure of the grown crystals was performed with a lower resolution. It was revealed that the microstructure of the crystals

Fig. 3. Structure of the ZrO_2–4 mol % Y_2O_3 sample grown at a rate of 10 mm/h.

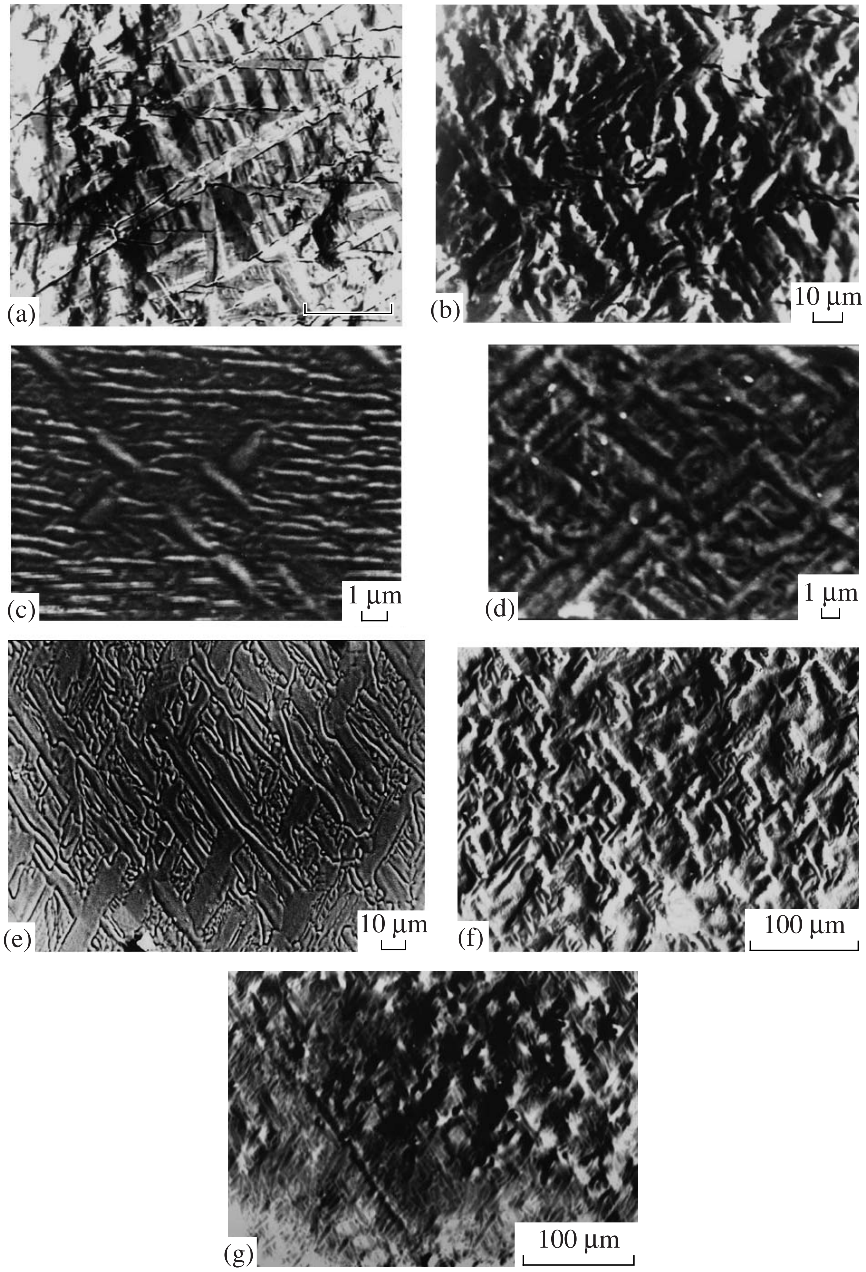

Fig. 4. Surface microstructure of the facets of the ZrO_2–*x* mol % Y_2O_3 crystals grown at a rate of 10 mm/h for *x* = (a) 0, (b) 2.0, (c, d) 2.5, and (e–g) 3.0.

depends on their initial composition and the crystallization conditions.

The micrographs of the growth surface of the crystals grown at a rate of 10 mm/h with different contents of the stabilizing Y_2O_3 oxide are displayed in Fig. 4. The surface of the growth facets of the undoped ZrO_2 samples is characterized by a relief typical of crystals that underwent a phase transition from the tetragonal structure to the monoclinic structure (Fig. 4a). This transition was accompanied by a substantial change in the volume (as large as 5 vol %) and brought about cracking. A regular network of microcracks is clearly seen in Fig. 4a. Moreover, it is seen that systems of parallel cracks intersect at an angle close to 30°.

It is worth noting that microcracks are also seen on the growth surface of the ZrO_2–2 mol % Y_2O_3 samples (Fig. 4b); however, these microcracks are considerably shorter and many of them are bent. The growth surface contains structural fragments similar to those described above and structural units of a new type, the so-called tweed structure, which is typical of materials with a higher Y_2O_3 concentration. For these types of structures, the characteristic angles of the intersection of structural units are close to 80°–90°.

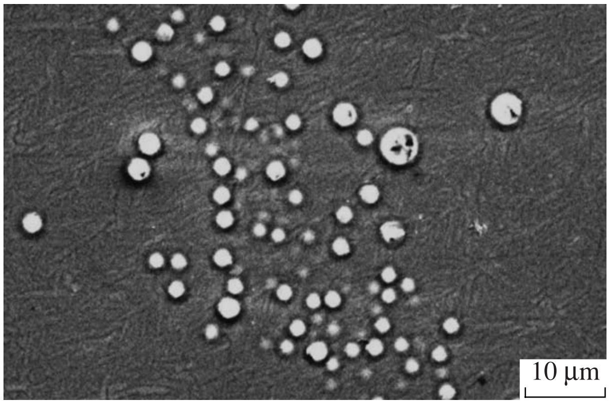

Fig. 5. Surface microstructure of the facets of the ZrO_2–3 mol % Y_2O_3 crystals with impurity inclusions. The grown rate of the crystal is 3 mm/h.

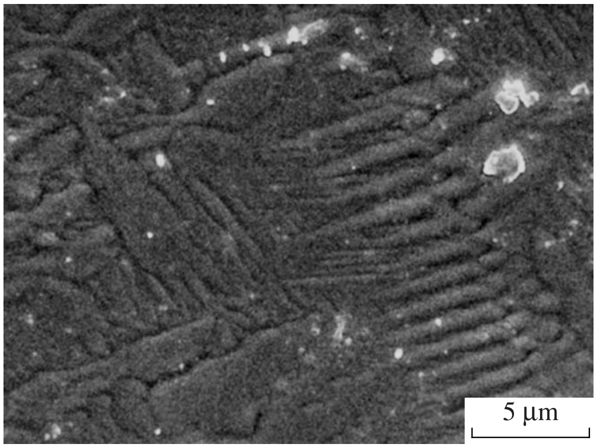

Fig. 6. Surface microstructure of the facets of the ZrO_2–3.5 mol % Y_2O_3 crystals grown at a rate of 10 mm/h.

In the crystals with an yttria concentration of 2.5 mol % (Figs. 4c, 4d), cracks are almost completely absent and units of the tweed structure, which occupy the larger part of the crystal surface, are more pronounced (Fig. 4c). However, in some regions of the crystal surface, there are only individual units of the tweed structure (Fig. 4d).

In the ZrO_2–3.0 mol % Y_2O_3 crystals (Figs. 4e–4g), we revealed two characteristic types of growth surface structures, namely, “smooth” facets of the first type (Fig. 4e) and “dull” facets of the second type (Fig. 4f). The boundary between the smooth and dull surface regions is shown in Fig. 4g. The surface of any one of these types can be characteristic of either all facets of a crystal block, or some of them, or even a part of one of the facets. The first type of surface is represented by a fairly regular structure that is similar in character to a tweed structure. This structure consists of small-sized elongated tetragonal prisms (1–10 μm in length and 0.5–3.0 μm in width), which are aligned parallel to each other and arranged in groups. The groups themselves are oriented with respect to each other at angles close to 80°–90°. The second type of surfaces has a more pronounced relief and consists of larger sized (as compared to the former case) parallel prisms (up to 50 μm in length and more than 5 μm in width). Owing to this structural relief, the facet has a dull appearance.

Surfaces of the second type are observed in the central and lower parts of the crystal ingot, and their formation depends on the volume of the melt and the length of the crystal. It is worth noting that, in this case, single-crystal blocks frequently grow together throughout these surfaces and cannot always be separated from each other without damage to the crystals themselves. Most likely, this process is affected by the thermal annealing that is performed in the course of crystal growth and determines the phase composition and the microstructure of the crystals. It should also be noted that, at a growth rate of 3 mm/h, dull facets on the crystal surface are absent. Large crystals in the grown block almost never grow together. Their number in the crystal block is relatively small, and thermomechanical stresses are relived predominantly over the boundaries of the blocks and partially in their bulk. The latter process results in cracking of the crystals.

Surfaces of the second type are also observed in the case where the initial melt contains impurities with a distribution coefficient significantly smaller than unity. However, unlike the aforementioned surfaces, these surfaces are covered with a characteristic deposit of rejected impurities, which is clearly visible under an electron microscope and can be easily determined using the X-ray spectral method (Fig. 5).

An increase in the yttria concentration to 4 mol % leads to a decrease in the size of structural units from (1.5–3.5) × (15–20) to (0.1–0.2) × (1–2) μm. The microstructure of the material changes from a typical tweed structure in the concentration range 2.5–3.0 mol % Y_2O_3 to a smooth structure with individual fragments of

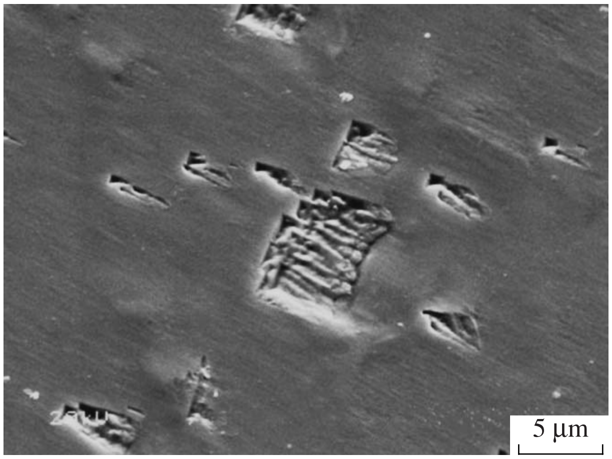

Fig. 7. Surface microstructure of the facets of the ZrO_2–4 mol % Y_2O_3 crystals grown at a rate of 10 mm/h.

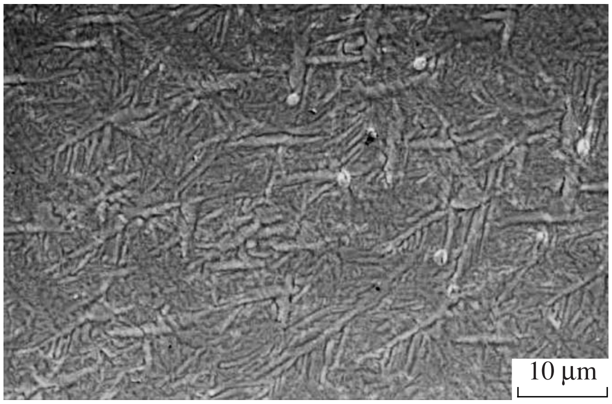

Fig. 8. Surface of the facets of the ZrO_2–3 mol % Y_2O_3 crystals grown at a rate of 3 mm/h.

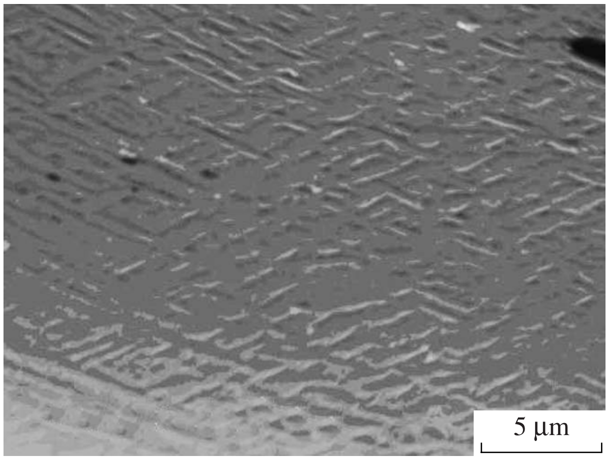

Fig. 9. Surface microstructure of the facets of the ZrO_2–4 mol % Y_2O_3 crystals grown at a rate of 3 mm/h.

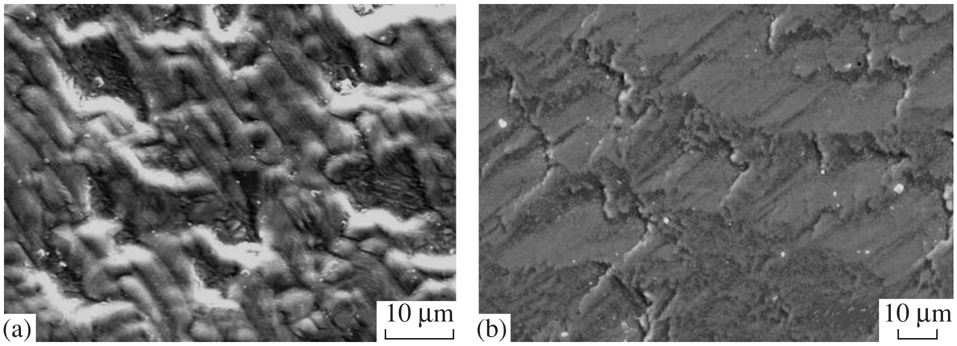

Fig. 10. Dull surface of the facets of the (a) ZrO_2–2.5 mol % Y_2O_3 and (b) ZrO_2–4 mol % Y_2O_3 crystals grown at a rate of 40 mm/h.

structural units at concentrations ranging from 3.5 to 4.0 mol % Y_2O_3. For example, in the ZrO_2–3.5 mol % Y_2O_3 crystal, islands consisting of parallel structural units without perpendicular intersections are observed against the background of the tweed structure (Fig. 6). The ZrO_2–4 mol % Y_2O_3 crystal has a smooth structureless surface that contains very rarely occurring islands with a pronounced microstructure (Fig. 7). The appearance of the island structure can indicate that the phase transformations occurring in the crystal during cooling are not complete. Consequently, at temperatures that correspond to the two-phase region in the phase diagram of the ZrO_2–Y_2O_3 system [3, 4], yttria is differently redistributed between two tetragonal phases. It seems likely that the phases with different yttria contents can have different microstructures.

For crystals of the same composition, the type and sizes of structural units change with a variation in the growth rate. For the crystals containing 2.5–3.0 mol % Y_2O_3, a decrease in the growth rate from 10 to 3 mm/h results in a decrease in the size of the structural units forming the tweed structure that is characteristic of the entire crystal surface (Fig. 8). For example, in the case of the ZrO_2–3 mol % Y_2O_3 crystals, the sizes of structural units decrease from (1.5–3.0) × (15–20) to (0.1–0.5) × (1–10) µm. Surfaces of the second type are very rarely observed and also have a tweed structure. In the upper part of the ZrO_2–2.5 mol % Y_2O_3 crystal, there are microcrack-containing regions with a structural relief that is characteristic of tetragonal–monoclinic phase transitions. This martensitic transition occurs as a result of the decrease in the Y_2O_3 concentration toward the end of the crystal growth (below 2.5 mol %), because the effective distribution coefficient of yttria is larger than unity [5]. The formation of the monoclinic phase in individual regions toward the end of the growth of the ZrO_2–2.5 mol % Y_2O_3 crystal is confirmed by the results obtained from Raman spectroscopic investigations of the crystal structure [6]. In the ZrO_2–4 mol % Y_2O_3 crystal grown at a rate of 3 mm/h, dull regions are almost absent and the surface of the crystal facets is smooth, contains no regions with a pronounced microstructure, and is characterized only by the growth morphology (layers, steps, growth hillocks) typical of single crystals (Fig. 9). An increase in the growth rate to 20 mm/h leads to an increase in the fraction of the crystal surface with a microstructure different from the tweed structure; i.e., this is favorable, to a greater extent, for the quenching process and time-limited diffusion processes that occur during cooling of the crystals and affect the formation of the microstructure. A further increase in the growth rate to 40 mm/h has a more profound effect on the morphology of the growth surface of single crystals as compared to that observed at lower growth rates. The surfaces of the crystal facets become dull as a result of the formation of large growth steps, hillocks, overgrowths, etc.; consequently, they almost completely mask the microstructure of the material. In the ZrO_2–(2.5–3.0) mol % Y_2O_3 crystals, the tweed microstructure is clearly distinguishable in the facets with surfaces of the second type (Fig. 10a). However, in the ZrO_2–(3.5–4.0) mol % Y_2O_3 crystals, overgrowths and growth steps (Fig. 10b) almost completely mask the microstructure.

CONCLUSIONS

Thus, the results of the above investigations have demonstrated that the partially stabilized zirconia crystals grown in our experiments have a nanocrystalline structure, which is formed upon the phase transition from the cubic structure to the tetragonal structure during controlled cooling of the crystals. The examination of the partially stabilized zirconia crystals with the use of a transmission electron microscope revealed that this structure is formed beginning with an yttria concentration of 2.5 mol % and observed only in isolated regions when the yttria concentration reaches 4.0 mol %. The size of the fine structural units in the ZrO_2–3 mol % Y_2O_3 crystal was estimated to be (0.1–0.5) × (10–20) nm.

The morphology of the growth surface of the partially stabilized zirconia crystals reflects the microstructure of the material fairly well. The microstructure of the crystals depends on their initial composition and the crystallization conditions. An increase in the concentration of the stabilizing oxide leads to a decrease in the size of structural units, whereas the microstructure of the material changes from a typical tweed structure in the concentration range 2.5–3.0 mol % Y_2O_3 to a smooth structure at 4.0 mol % Y_2O_3. As the growth rate increases from 10 to 40 mm/h, the surface of the crystals becomes duller, predominantly due to the formation of various growth defects. A decrease in the growth rate to 3 mm/h results in a decrease in the size of structural units, and the surface of the crystals becomes smoother than the surface of crystals that have the same composition but were grown at higher rates.

A comparison of the results obtained using scanning and transmission electron microscopy has shown that the microstructure of the growth surface of the crystals reflects their internal structure (i.e., the structure of domain assemblies).

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