Zirconia crystals for tribotechnical applications doped by rare earth elements

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Abstract. The article discusses the impact of rare-earth microadditives on the mechanical properties of nanostructured zirconia crystals stabilized with yttrium oxide as applied to the friction units of devices. The mechanical properties of the surface layers were studied by the nondestructive method of kinetic microindentation. Compressive strength was determined by the standard destructive compression test method. Comparative tribological tests were carried out with dry sliding friction of the test samples on steel according to the disk-finger scheme. The effect of the ionic radius of the alloying element on the compressive strength is investigated. It was established that the doping of zirconia crystals is ambiguous, because it can improve and worsen the tribological properties of crystals. On the basis of the study, a comparison is made of the mechanical properties of crystals and ceramics used in the supports of the axis of precision instruments and areas that are promising for the use of zirconia crystals in instrumentation are identified.

1. Introduction

Increasing the service life and reliability of the mechanical modules of devices and microelectronic mechanical systems is mainly achieved by improving the tribological and strength properties of materials for moving mates of parts due to the use of supports containing ceramics and crystals. One of the most important tasks of modern materials science is the creation of new structural non-metallic materials in which strength, wear resistance, high fracture toughness and chemical inertness are combined with high resistance in an oxidizing medium over a wide temperature range. These materials include partially stabilized zirconia dioxide (PSZ). At present, partially stabilized tribological zirconia dioxide is obtained mainly by ceramic technology [1]. Nanostructured powders are used to improve the mechanical properties of ceramics [2–4]. In the article [5], it is noted that the morphology of the starting powders is a key factor for optimizing the mechanical properties of the material. Various technologies for compacting and sintering ceramic materials are being improved: self-propagating high-temperature synthesis [6, 7], sintering in a nitrogen medium [8], gelcasting method combined with pressureless sintering, which ensured excellent mechanical properties (bending strength 890 MPa, fracture toughness 10.2 MPa • m 0.5, Vickers hardness 13.2 GPa and the lowest porosity) [9]. The low-temperature degradation and mechanical properties of zirconium ceramic synthesized by a solid-state reaction are studied [10]. The prospects of using partially stabilized zirconia dioxide crystals (PSZ crystals) obtained from a melt by crystallization in a cold container for friction nodes have been established [11]. Materials based on zirconium dioxide obtained in practice are single or
multiphase solid solutions of zirconium oxide with one or more oxides of alkaline earth, rare earth and some other elements. As a rule, such materials are metastable at room temperature, but nevertheless, under certain conditions, they have a fairly high degree of stability and do not undergo phase transformations for a long time under repeated temperature influences. When synthesized from a melt, a growing PSZ single crystal has an initial cubic structure, and phase transformations occur in it during cooling in the solid phase. The transition of the cubic phase to the tetragonal phase is accompanied by the formation of a domain structure in crystals with sizes of 10–100 nm. PSZ crystals have a unique combination of mechanical properties [12], however, they have significant anisotropy along the crystal axes [13]. There is a search for ways to improve the tribological and strength properties of crystals [14]. The structure and transport properties of PSC crystals [15, 16], spectral-luminescent properties [17, 18] are studied. Doping with rare-earth elements has spread to improve the various properties of PSC crystals [15–18], however, the mechanical properties of doped PSC crystals have been studied very little. With respect to tribological applications, interest is mainly in hardness, fracture toughness, elastic modulus, and compressive strength [1]. The mechanical treatment of the surfaces of the samples during their manufacture leads to a change in surface properties. The most reliable information on the mechanical properties of the surface layer of the material, namely, plasticity and elasticity, can be obtained by the method of testing for kinetic microhardness.

The purpose of this work is to study the influence of rare earth microadditives on the tribological and strength properties of nanostructured partially stabilized zirconia crystals (PSZ crystals).

Materials and equipment. Samples from PSZ crystals of the composition ZrO$_2$-3 mol% Y$_2$O$_3$ with impurities of transition and rare earth elements were made in the form of rectangular fingers measuring 5x5x8 mm. Typical crystal sizes were 10–20 mm in cross section and 40–60 mm in length at growth rates of 15 mm/h. The crystals were colored depending on the type of impurity used. Crystal faces are predominantly shiny; a dull surface was present in the form of small sections on separate faces. A quantitative chemical electronic microanalysis was carried out at the facility «CAMEBAX SX-50» for an adequate interpretation of the results of studies of samples from PSZ crystals.

Tests to determine the mechanical properties of PSZ crystals were performed on a MNT Z AE_000 kinetic microhardness meter manufactured by CSM Instruments (Switzerland) in accordance with the ISO/DIS 14577 standard with a Vickers tetrahedral indenter according to the method [19]. Tribological tests were performed on the installation of UMT-1 according to the disk-finger scheme according to the method [20].

2. Results and Discussion

Samples were selected with the same content of a stabilizing additive of yttrium oxide for testing. A typical surface morphology of the growth faces of crystals of various chemical composition is shown in figure 1.

![Figure 1](image_url)

**Figure 1.** The growth surface of the crystal PSZ with the following composition: a) 97.2 mol % ZrO$_2$+1.0 mol % Y$_2$O$_3$+1.8 mol % CeO$_2$; b) 97.2 mol % ZrO$_2$+2.0 mol % Y$_2$O$_3$+0.8 mol % CeO$_2$.  

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**Note:** The intended content was cut off in the middle, so the full context is not available. The text appears to be a scientific document discussing the properties and synthesis of partially stabilized zirconia (PSZ) crystals, with a focus on the influence of rare earth elements on their mechanical and tribological properties. The methods used for analysis and testing are described, along with results and discussion of properties such as hardness, fracture toughness, and mechanical treatment.
The presence of a monoclinic phase in samples with a concentration of 1 mol% Y$_2$O$_3$ + 1.8 mol% CeO$_2$ (Nd$_2$O$_3$) is accompanied by the formation of microcracks on the surface of PSZZ crystals (figure 1a). With an increase in the concentration of yttrium oxide, there are no microcracks, and the surface morphology has the form of a “parquet” microstructure typical of the tetragonal phase composition of PSZ crystals (figure 1b); therefore, samples with a stabilizing additive content of 3 mol% were chosen for experiments Y$_2$O$_3$.

The most important characteristics of the mechanical properties of the surface layers of rubbing parts are hardness, modulus of elasticity and the coefficient of irreversible energy loss, taking into account the energy costs of plastic deformation and cracking. The irreversible loss coefficient $K_p$ is determined by the formula:

$$K_p = \eta_{IT} = \frac{W_{plast}}{W_{gen}}$$

where $\eta_{IT}$ – elastic component of the indentation work;

$$\eta_{IT} = \frac{W_{elast}}{W_{gen}} \times 100,$$

where $W_{elast}$ – is reverse work with elastic deformation of indentation (energy of elastic restoration of the indent after unloading), N·m; $W_{plast}$ – work during plastic deformation of indentation (energy absorbed in the loading – unloading cycle, N·m; $W_{gen}$ – general (full) mechanical work of indentation, Н·м; $W_{gen} = W_{elast} + W_{plast}$.

In fact, the coefficient $K_p$ reflects the irreversible energy loss during indenter indentation, which consists of the actual energy losses due to plastic deformations and the energy losses spent on brittle fracture (crack formation). Samples were tested to determine the strength characteristics of PSZ crystals of the composition ZrO$_2$ – 3 mol% Y$_2$O$_3$ with impurities of transition and rare earth elements. Fingerprints were deposited on the surface of samples of PSZ crystals of arbitrary crystallographic orientation. The number of prints (number of diagrams) for each surface is from 3 to 10 for different samples. These figures are not always sufficient for a correct statistical analysis because of the possible variation in the shape of the deformation diagrams for a particular sample, especially for friction surfaces. Such a spread should lead to an ambiguity in the values of microhardness over the surface of the sample. In this regard, in some experiments there was a need to increase the number of prints on the surface of the test material. Table 1 shows the data on the composition of the crystals of PSZ and test results.

| №  | Composition                              | HV, GPa | E, GPa | W$_{gen}$, $\mu$m J | W$_{plast}$, $\mu$m J | $K_p$ |
|----|-----------------------------------------|---------|--------|---------------------|----------------------|------|
| 1  | ZrO$_2$-2.8 mol %Y$_2$O$_3$              | 16.74   | 213    | 0.71                | 0.38                 | 0.535|
| 2  | ZrO$_2$-3.7 mol %Y$_2$O$_3$              | 17.17   | 217    | 0.73                | 0.37                 | 0.506|
| 3  | ZrO$_2$-2.8 mol %Y$_2$O$_3$ +0.1 weight %CeO$_2$ | 17.07   | 171    | 0.81                | 0.39                 | 0.479|
| 4  | ZrO$_2$-3.7 mol %Y$_2$O$_3$ +0.1 weight %CeO$_2$ | 17.95   | 204    | 0.72                | 0.36                 | 0.499|
| 5  | ZrO$_2$-2.8 mol %Y$_2$O$_3$ +0.6 weight %CeO$_2$ | 16.67   | 209    | 0.71                | 0.37                 | 0.521|
| 6  | ZrO$_2$-3.7 mol %Y$_2$O$_3$ +0.6 weight %CeO$_2$ | 17.16   | 204    | 0.73                | 0.37                 | 0.506|
| 7  | ZrO$_2$-2.8 mol %Y$_2$O$_3$ +1 weight %CeO$_2$ | 17.29   | 207    | 0.73                | 0.38                 | 0.516|
| 8  | ZrO$_2$-3.7 mol %Y$_2$O$_3$ +1 weight %CeO$_2$ | 17.80   | 200    | 0.73                | 0.36                 | 0.492|
| 9  | ZrO$_2$-2.8 mol %Y$_2$O$_3$ +0.1 weight %Nd$_2$O$_3$ | 16.66   | 196    | 0.73                | 0.37                 | 0.508|
We use the radial type of cracks formed in the vicinity of the indentation to assess the crack resistance. During the test, a force of the order of 8 N is applied to the Vickers indenter, kept under a load of 15 seconds, then the average length of the half-diagonals of the microprint $a_{av}$ and the average length of cracks in the corners of the imprint of $l_{av}$, measured no later than 2 minutes after unloading.

The value of the critical stress intensity factor $K_c$ was determined by the formula with a calibration coefficient (Table 2):

$$K_c = 0.015 \times \left(\frac{a}{l}\right)^{1/2} \times \left(\frac{E}{H_T}\right)^{2/3} \times \left(\frac{F}{c^{3/2}}\right),$$  \hspace{1cm} (4)

where $F$ is the maximum load, N; $a$ is the length of the semi-diagonal microprint, microns; $l$ is the length of the radial crack, microns; $c$ is the length of the crack counted from the center of the indent, microns; $E$ is the modulus of elasticity, GPa; $H_T$ is the hardness, GPa.

$$a_{av} = (a_1 + a_2)/2 = (d_1 + d_2)/4,$$

where $a_1$ and $a_2$ are the lengths of the half-diagonal microprint, microns; $d_1$ and $d_2$ are the lengths of the diagonals of the print, microns; $c = a_{av} + l_{av}$, microns.

All surfaces have roughness. The characteristic of a single roughness is the angle between the tangent to the roughness surface at the base and the surface plane. For the roughest machining surfaces, this angle does not exceed 2–3 degrees, i.e. unevenness is compressed in the contact; the ultimate compressive strength of crystals according to [13] is given in the table 2.

Table 2. Fracture and compression strength test results.

| Additional supplement | Weight, % | Color of amples | Ionic radius, nm | Strength $\sigma$, MPa | $K_c$, MPa·m$^{0.5}$ |
|-----------------------|-----------|-----------------|------------------|------------------------|---------------------|
| Cu                    | 0.3       | greenish blue   | 0.096            | 2535                  | 11.1                |
| Mn                    | 0.3       | dark grey      | 0.091            | 2340                  | 8.5                 |
| Co                    | 0.3       | violet         | 0.082            | 2531                  | 8.2                 |
| Er                    | 0.3       | pink           | 0.104            | 2461                  | 7.7                 |
| Nd                    | 0.5       | lilac          | 0.115            | 1752                  | 7.5                 |
| Pr                    | 0.5       | yellow         | 0.1             | 2094                  | 6.5                 |
| Ce                    | 0.6       | orange red     | 0.118            | 1702                  | 9.9                 |

10 ZrO$_2$-3.7 mol %Y$_2$O$_3$ +0.1 weight %
11 ZrO$_2$-3.7 mol %Y$_2$O$_3$ +0.6 weight %
12 ZrO$_2$-3.7 mol %Y$_2$O$_3$ +0.9 weight %
13 ZrO$_2$-2.8 mol %Y$_2$O$_3$ +0.6 weight %
14 ZrO$_2$-2.8 mol %Y$_2$O$_3$ +0.9 weight %
15 ZrO$_2$-2.8 mol %Y$_2$O$_3$ +0.1 weight %
16 ZrO$_2$-2.8 mol %Y$_2$O$_3$ +0.5 weight %
17 ZrO$_2$-3.7 mol %Y$_2$O$_3$ +0.1 weight %
Since the deformation of the crystal lattice is most strongly affected by the ionic radius of the implanted element, it is of interest to determine the dependence of the compressive strength on the ionic radius (figure 2). It is shown that alloying with rare-earth elements with a higher ionic radius leads to a decrease in the compressive strength of the crystal. Thus, it can be considered that alloying with additional impurities can both improve the mechanical characteristics and worsen. The stability of zirconia doped with microimpurities is based on the local strengthening of the Zr-O chemical bond as a result of the redistribution of the electron density near the impurity atom ion. The role of oxygen vacancies, the interaction of defects, the electronic structure of impurity ions and their valency, which affect the adhesion strength of molecular bonds in the areas of actual contact during external friction is confirmed in [21].

The results of tribological tests showed (table 3) a significant effect of microalloying on the coefficient of friction (f) and the wear rate (I) of the PSZ crystals.

![Figure 2. Dependence of the compressive strength of a PSZ crystal on the ionic radius of an alloying element.](image)

**Table 3.** Tribological properties of PSZ crystals with microadditives of rare earth elements.

| № crystal | Alloying elements | f    | I      | note                  |
|-----------|-------------------|------|--------|-----------------------|
| 1         | CeO$_2$+Nd$_2$O$_3$ | 0.19 | 2.25·10$^{-8}$ |                        |
| 2         | 3.3% mol Y$_2$O$_3$ | 0.23 | 2.52·10$^{-9}$ | Annealing, 2000°C°    |
| 5         | CeO$_2$+Er$_2$O$_3$ | 0.12 | 1.22·10$^{-9}$ |                        |
| 6         | Er$_2$O$_3$       | 0.25 | 1.92·10$^{-9}$ |                        |
| 7         | CeO$_2$+Er$_2$O$_3$ | 0.21 | 1.17·10$^{-9}$ |                        |
| 8         | CeO$_2$           | 0.21 | 1.39·10$^{-9}$ |                        |
| 9         | Pr                | 0.20 | 1.29·10$^{-9}$ |                        |

The results indicate that the microalloying of PSZ crystals with rare-earth elements is an effective technological method for increasing the wear resistance of PSZ crystals. By introducing the CeO$_2$ + Er$_2$O$_3$ microadditive, it is possible to increase the wear resistance by about two times, namely, the wear rate of PSZ crystals after annealing in vacuum 3.12·10$^{-9}$ decreases to 1.17·10$^{-9}$. Table 4 shows a comparison of the mechanical characteristics of ceramic materials that are promising for use in...
mechanical friction units of mechanical modules of devices and microelectronic mechanical systems (MEMS).

**Table 4.** Characteristic characteristics of the mechanical properties of ceramic materials used in precision instruments.

| Material                  | E, GPa | Strength, GPa | K<sub>IC</sub>, MPa m<sup>1/2</sup> | Cross-breaking strength, MPa |
|----------------------------|--------|---------------|-----------------------------------|----------------------------|
| ZrO<sub>2</sub> + 3molY<sub>2</sub>O<sub>3</sub> | 353    | 15            | 10                                | 924                        |
| SiC                       | 430    | 29            | 4                                 | 100–440                    |
| Si<sub>3</sub>N<sub>4</sub> | 300    | 15            | 5–8                               | 800                        |
| Al<sub>2</sub>O<sub>3</sub> | 380    | 22            | 2.3–3.5                           | 450–700                    |

3. Conclusion

It has been experimentally established that nanostructured zirconia crystals are promising for solving microtribology problems, especially in microelectronics and mechanical modules of devices (axle supports “on stones”). Improving the characteristics of microelectronic mechanical systems (MEMS) of the future is largely determined by higher values of the characteristics of the mechanical and tribological properties of the new structural material. The experiments suggest that the only alternative to silicon crystals are nanostructured PSZ crystals. A comparison of the properties of silicon crystals with PSZ crystals shows that:

a) The elastic modulus of silicon (190 GPa) is close to steel, nickel and is much higher than that of quartz, as well as many alkaline borosilicate lead-containing glasses, but it is almost two times less than the elastic modulus of ChSc crystals (350–400 GPa).

b) The microhardness of silicon (8.5 GPa) is close to quartz and significantly higher than glass (5.3 GPa), but is almost 1.5 times inferior to the microhardness of a PSZ crystal (10–15 GPa).

c) The characteristics of viscosity and elasticity of crystals of PSZ are significantly higher than that of any other ceramic materials, as well as silicon crystals, which are brittle material. Due to the fragility of crystals in MEMS manufacturing technology, it is necessary that all mechanical processes, such as cutting, turning and polishing, be minimized or eliminated. The machining results in brittle edges and surface defects that can lead to chips and/or create internal stresses with subsequent consequences for breakage.

d) Silicon crystals do not withstand bending tests, and PSZ crystals have the greatest bending strength of ceramic materials.

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