Laser frictional area treatment of zirconium crystals

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Abstract. The issues of laser treatment of nanostructured partially stabilized crystals of zirconium dioxide are studied in the article. The phenomena of formation of the topography of the surface of crystals after treatment by focused radiation of a repetitively pulsed laser at a wavelength of 1.06 μm are investigated. Structural changes in the surface layer have been studied by X-ray phase analysis. The formation of a golden film on the surface of the treated crystal and ceramic sample of the same chemical composition and the effect of reducing the coefficient of friction have been established. The tribological properties of PSZ crystals are investigated during friction without lubrication in the sliding mode.

1. Introduction

Heating a surface by exposure to laser radiation is a widespread technology used to improve the tribological properties of a surface by hardening or changing the structure of the surface layer of the material being treated. In addition to thermal effects in the interaction of a laser beam with the surface of a solid, others also take place and find application. Various types of continuous and repetitively pulsed lasers of various wavelengths are used for surface modification. Repetitively pulsed lasers are used [1] for discrete hardening of the friction surface. Laser remelting of surfaces of various materials is widely used [2, 3, 4] to change the structure in order to increase the wear resistance of friction surfaces, for example, to obtain [5] self-lubricating boride layers, for heat treatment and laser building-up of wear-resistant coatings [6, 7], to improve tribological properties [8] under conditions of friction without lubrication at high temperatures.

Alloying with boron and solid lubricant CaF₂ was used by laser infusion of the coating to create the effect of self-lubrication [9]. Laser alloying with 10% manganese was carried out to increase the wear resistance and hardness of the surface [10]. The mechanism of material removal and the formation of the surface relief under the action of a laser is described in [11, 12]. As applied to tribological problems, the use of ceramics and crystals based on zirconium dioxide is promising because these materials have a higher fracture toughness and a tendency to adhesion in comparison with most of the known ceramics and crystals. The highest mechanical characteristics are possessed by nanostructured partially stabilized crystals of zirconium dioxide (PSZ crystals) [13]. Furnace heat treatment of crystals of partially stabilized zirconium (PSZ crystals) was studied in [14]. The interaction of laser radiation with the surface of PSZ crystals is an insufficiently explored sphere.
Objectives and aims of the research. Examine the impact of high-power laser radiation on the surface layers of a promising refractory, chemically inert, high-strength, crack-resistant, nanocrystalline crystal of partially stabilized zirconium dioxide in order to increase its tribotechnical properties.

2. Materials and research methods

The object of the study were crystal samples ZrO₂ + 3 mol% Y₂O₃ and Y₂O₃ + 3.5 mol% Y₂O₃ obtained by directional controlled solidification from the melt [13]. In tribological tests, a disc made of У10А steel (chemical composition in % C 0.96 – 1.034; Si 0.17 – 0.33; Mn 0.17 – 0.28; Ni 0.2; S 0.018; P 0.025; Cr 0.2; Cu 0.2; Fe 0.07), hardness HRC 49-52 was used as a counter - body.

Laser treatment in a repetitively pulsed mode was carried out on a Kvant-12 setup with focused laser radiation at a wavelength of 1.06 μm. The focusing lens has a focal length of 100 mm and provides a change in the diameter of the light spot in the range of 0.5 - 1 mm; an elliptical spot is formed with the help of attached cylindrical lenses. The experiments were carried out with a light spot 1 mm in diameter, the duration of the radiation pulses was 4 ms, and the repetition rate of the radiation pulses from the setup was 1 Hz. The end surfaces of rod samples of PSZ crystals with a square cross section of 5x5 mm, formed in packages of 5 pieces, were treated with a laser beam by applying parallel tracks to the samples installed in a line.

The phase composition of the materials under study was determined by the method of X-ray diffractometry on a Bruker D8 setup with symmetric recording Θ - 2Θ with a scanning point detector, in the geometry of a parallel beam. Samples for phase analysis were cut from crystals perpendicular to the <100> direction. Since the intensity of reflections from single crystals is much higher than from polycrystals, on the (100) plane, in the presence of several phases in the crystal, on one cut, one can observe simultaneously reflections from different phases, which were separated at large angles 2Θ~130°. The phase fraction was determined from the intensity of the diffraction maxima, which was normalized to the integral reflection coefficient for different phases.

The study of the microstructure of the surface of the samples after laser treatment was carried out on a JEOL 5910 LV scanning electron microscopy unit and an INCA-300 OXFORD X-ray spectrum analyzer with a digital camera.

A quantitative study of the crystallographic orientation, phase composition, and texture of the resulting films after laser treatment at the microlevel was carried out using an electron microscope by electron backscatter diffraction (EBSD). The information obtained from the surface of the object was used; the penetration depth was ~ tens of nanometers.

Tribological tests were carried out on a UMT-1 friction machine on model samples according to the pin-on-disk scheme [15].

3. Results and its discussion

The studied crystals contained two tetragonal phases, transformable (t) and nontransformable (t'), differing in the degree of tetragonality (c-(2a)⁰.⁵) 1.014 and 1.005, respectively. The quantitative ratio of phases t/t' varied slightly depending on the concentration of yttrium oxide from 85 (5) / 15 (5) to 80 (5) / 20 (5).

In the experiments, the radiation energy increased stepwise from 1 to 5 J until the formation of a golden film (coating) on the surface of the PSZ crystal, the nature of which is not clear at this stage of work. The film first appeared in the center of the light spot and, with increasing power, completely covered the spot; at the same time, a crater was formed in the center of the spot due to the evaporation of material from the treated surface. To form the next deposit track, the sample was displaced perpendicular to the velocity vector by a distance equal to the diameter of the light spot. In experiments, a stable effect of the formation of a golden film is noted. The surface morphology of PSZ crystals subjected to laser modification is shown in figure 1.
Figure 1. The surface morphology of PSZ crystals of composition ZrO$_2$ –3 mol% Y$_2$O$_3$ exposed to laser radiation, obtained with an electron microscope (x 25).

It is seen that as a result of laser treatment, the crystal surface melted. In general, the modified surface is a fairly regular array of buildup, separated by parapets (bridges). A greater increase in the microscope showed that a film is formed on the surface, some areas of which contain cracks and buildup. On the surface of the PSZ crystal, holes are visible, formed due to the evaporation of the material under the influence of a laser beam. The surface is covered with a network of micro-cracks due to residual tensile stresses following structural changes. The probable mechanism of crack formation is the difference in the coefficients of linear thermal expansion of the PSZ crystal in the base and in the surface layer. Figure 2 shows cracks covering almost the entire treated surface and where the surface composition is controlled.

Figure 2. Surface morphology of PSZ crystals of composition ZrO$_2$ –3 mol% Y$_2$O$_3$ exposed to laser radiation. (Enlargement x1000)

Using Energy-dispersive X-ray spectroscopy analysis (EDXR) methods, the chemical composition of the coating formed on samples of PSZ crystals of the composition ZrO$_2$ –3 mol% Y$_2$O$_3$ subjected to laser surface modification was determined. Analysis of the chemical composition of the surface layer of the sample modified by laser treatment (figure 3) showed that the surface is represented by zirconium oxide. It should be noted that there is a deviation from stoichiometry for oxygen and a significant variation of this nonstoichiometry at different dots: from 29.12 to 48.16 for zirconium and from 51.84 to 70.44 for oxygen (data are given in atomic percentages).

The study of the obtained film was carried out after laser treatment of the sample surface by electron-backscattered diffraction (EBSD). The figure shows an image of a section of the sample
surface obtained with an electron microscope (figure 3 (a)), and the phase map corresponding to this area (figure 3 (b)).

![Figure 3. Image of the sample surface (a), and the phase map (b).](image)

The results obtained indicate that, when exposed to laser radiation, melting occurs on the surface, which leads to a significant change in the phase composition. The phase composition of the film formed after laser treatment consists of tetragonal (pink color), cubic (green), and rhombohedral (blue) phases (figure 3 (b)). A small amount of a monoclinic phase is present. The formation of the phase of metallic zirconium is practically absent; its presence can be regarded as a measurement error. Attention is drawn to the formation of a significant fraction of the orthorhombic phase.

A measure of the antifriction properties is the coefficient of friction, which was determined on model samples according to the pin-on-disk scheme. Samples (pins) are made from the same PSZ crystal. The results of comparative tests of PSZ crystals in the initial state and after laser treatment with pulses with an energy of 3 J and polycrystalline diamond at various pressures at the contact are given in table 1.

| Table 1. Coefficients of friction of surfaces during friction of PSZ crystals on steel. |
|---------------------------------|--------|--------|--------|--------|--------|
| Pressure P, MPa                 | 2.5    | 5      | 10     | 20     | 30     |
| PSZ crystal without coating     | 0.45   | 0.37   | 0.31   | 0.28   | 0.28   |
| PSZ crystal with coating        | 0.30   | 0.29   | 0.27   | 0.25   | 0.26   |
| Diamond            | -      | -      | 0.26   | 0.30   | 0.28   |

It has been experimentally established that after laser treatment of the surface of PSZ crystals, there is a noticeable (up to 1.5 times) decrease in the region of low pressures of the friction coefficient in the presence of a coating on the friction surface of PSZ crystals.

The results of tribotechnical tests of PSZ crystals after laser treatment are given in tables 2 and 3. It has been established that during friction without lubrication on Y10A steel in the contact pressure range of 2.5 - 40 MPa, the wear rate of PSZ crystals after laser treatment varies from 2.42·10⁻⁸ to 2.81·10⁻⁷. The coefficient of friction gradually decreases as the contact pressure increases from 0.32 to 0.19.
Table 2. Results of testing samples of ZrO$_2$ + 3.5 mol.% Y$_2$O$_3$ crystals after laser treatment.

| p, MPa | L, m | h, µm | f  | l     |
|--------|------|-------|----|-------|
| 2.5    | 4245 | 143   | 0.32 | 3.37·10$^{-8}$ |
| 2.5    | 6530 | 158   | 0.30 | 2.42·10$^{-8}$ |
| 5      | 1715 | 139   | 0.30 | 8.10·10$^{-8}$ |
| 5      | 5442 | 133   | 0.26 | 2.44·10$^{-8}$ |
| 10     | 1429 | 71    | 0.25 | 4.97·10$^{-8}$ |
| 10     | 2471 | 169   | 0.26 | 6.83·10$^{-8}$ |
| 20     | 1768 | 185   | 0.22 | 1.04·10$^{-7}$ |
| 20     | 1763 | 181   | 0.23 | 1.03·10$^{-7}$ |
| 40     | 605  | 170   | 0.23 | 2.81·10$^{-7}$ |
| 40     | 698  | 164   | 0.16 | 2.35·10$^{-7}$ |

Table 3. Comparative results of tribotechnical tests of samples of ZrO$_2$ + 3.5 mol% Y$_2$O$_3$ crystals after laser treatment with a pulse energy of 4 J and without treatment.

| P, MPa | Friction coefficient f | Wear intensity I |
|--------|------------------------|------------------|
|        | Without treatment      | Laser treatment  |
|        | Without treatment      | Laser treatment  |
| 2.5    | 0.46                   | 0.31             | 2.46·10$^{-9}$ | 2.89·10$^{-8}$ |
| 5      | 0.40                   | 0.28             | 2.50·10$^{-9}$ | 5.27·10$^{-8}$ |
| 10     | 0.36                   | 0.25             | 1.02·10$^{-8}$ | 5.9·10$^{-8}$  |
| 20     | 0.33                   | 0.23             | 1.06·10$^{-8}$ | 1.04·10$^{-7}$ |
| 40     | 0.29                   | 0.19             | 4.36·10$^{-8}$ | 2.58·10$^{-7}$ |

Laser treatment of PSZ crystals with high-power repetitively pulsed laser radiation in the studied range of pulses with an energy of up to 8 J and a duration of 1.5 - 2.5 ms leads to a structural modification of the surface layer, which is confirmed by previously performed microdiffraction studies. As a result of powerful thermal action, there is a significant change in the phase composition with a high content of the cubic phase (up to 14%). The results of the numerical processing of microdiffraction studies by the EBSD spectroscopy method give reason to believe that the proportion of substances formed as a result of the chemical interaction of the PSZ crystal with the plasma of the near-surface laser flare is no more than 5.8%. A gold-colored coating is formed during laser treatment, the origin of which is a consequence of either the formation of a new chemical compound, possibly zirconium nitride within an unspecified volume of 5.8%, or pure zirconium.

It was established by tribological tests that the near-surface layer formed during laser treatment, in comparison with the tribological properties of an untreated PSZ crystal, has lower values of the friction coefficient and lower wear resistance. Laser modification of the PSZ crystal reduces the coefficient of friction while maintaining the initial high bulk strength of this material. For the coating obtained as a result of laser treatment of the PSZ crystals, during friction without lubrication on Y10A steel in the range of normal pressures of 2.5 - 30 MPa, in which the experiments were carried out, the friction coefficient varies from 0.30 to 0.26. When the samples under friction without laser treatment, the friction coefficient varied from 0.45t to 0.28, i.e. the largest decrease in the coefficient of friction was 50%. At the same time, the wear rate increases by 5-10 times. However, it should be noted that in absolute terms, the rate of wear of the PSZ crystal after laser treatment remains quite high and approximately corresponds to the wear resistance of hardened Y10A tool steel Y10A ($I_{Y10A}=5·10^{-8}$).

4. Conclusion

The use of laser treatment of PSZ crystals to reduce the friction coefficient is possible with regard to the problems of microtribology, where one of the limiting factors for increasing the reliability of friction units are the antifriction properties of the material in combination with relatively high wear.
resistance, namely, in miniature friction bearings, for example, precision instruments or clock mechanisms.

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