Improving the reliability of technological equipment in the production of thermoelectric elements

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Abstract. The article is devoted to increasing the service life of the bearing of the mixing assembly in the installation for the synthesis of bismuth telluride. Comparative tribological experiments were carried out. It is shown that the implementation of a bearing bush from a nanostructured crystal of partially stabilized zirconium dioxide can increase by 4 times the reliability and service life of the installation.

1. Introduction

The quality of high-performance thermoelectric modules based on nanostructured highly stable crystals of bismuth telluride is largely determined by the reliability of the synthesis plants designed to obtain non-oriented thermoelectric material from the initial components. Blocks of semiconductor material in the installation are created from the melt by a given thermal cycle of heating and holding the melt in a neutral medium (helium) in the installation shown in figure 1.

Figure 1. Structural functional diagram of the installation for the synthesis of bismuth telluride.
The least reliable and durable unit of synthesis plants is a mixing device, which is an original unit, the service life of which is limited by the wear of supporting elements made of graphite and operating under conditions of friction without lubrication, high temperatures (500 °C) and in helium medium.

The production of nanostructured crystals is carried out in a continuous technological cycle. According to technical requirements, it is necessary to ensure, within 6 months (4320 hours), trouble-free operation of technological equipment with the reliability function \( P(t) = 0.95 \). The existing design of the mixing unit does not satisfy these requirements. An extremely aggressive environment forces the entire installation to be made of graphite. The limiting unit limiting the service life of the plant are the sliding bearings of the stirring unit, the wear resistance of which is low.

The appearance of new ceramic composite ceramics [1–4] and nanostructured crystals of partially stabilized zirconium dioxide (PSZ crystals) [5–8] opens up the possibility of increasing the service life of the mixing device.

The purpose of the work is to increase the resource and reliability of the sliding supports in the melt mixing device by installing bushings made of materials based on compounds of refractory elements (ceramics or crystals), working in tandem with tool steel Y10A. The choice of this pair is due to the requirements of ensuring high wear resistance, viscosity, temperature resistance.

2. Materials and equipment

The objects of study were: samples of nanostructured \( \text{ZrO}_2 + 3.7 \text{ mol.\% Y}_2\text{O}_3 \) crystal, the amount of stabilizing additive was substantiated in [9]; sintered zirconia ceramic materials with additions of cerium oxides and lanthanum corundum hexaaluminate nanoceramic composite obtained by the sol-gel technology. Samples were made in the form of fingers with a square cross section of \( 5 \times 5 \times 10^{-3} \text{ m} \) and a length of \( 7.5 \times 10^{-3} \text{ m} \). The end working surfaces of finger samples are flat with a roughness of \( \text{Ra} = 0.8 \). The counterbody is made in the form of a disk with a diameter of \( 12 \times 10^{-2} \text{ m} \), made of hardened tool steel Y10A, HRC 49–52.

Tribological studies were carried out on the universal friction machine YMT-1 according to the method [9] with a change in average contact pressures in the range of \( 2.5 < \text{p} < 25 \text{ MPa} \) and sliding speed of \( 0.2 < \text{v} < 2 \text{ m/sec} \). The model friction unit was made according to the “disk-finger” scheme. Finger ceramic samples were made in the form of rods with a diameter of 8 mm, the counterbody – disks with a diameter of 120 mm were made of tool steel Y10A.

3. Results and discussion

The choice of materials for sleeve bearings is due to the high corrosion resistance of materials and strength properties. Table 1 shows a comparison of the mechanical characteristics of ceramic materials that are promising and have found application in friction units. The absence of grain boundaries in PSZ crystals leads to higher mechanical characteristics as compared with ceramics.

| Material | Elasticity module (GPa) | Hardness (GPa) | Fracture toughness (MPa*\( \text{m}^{1/2} \)) | Compression strength (MPa) | Bending strength (MPa) |
|----------|------------------------|----------------|---------------------------------|--------------------------|-----------------------|
| \(\text{ZrO}_2 + 3\text{mol.}\text{Y}_2\text{O}_3\) | 353 | 15 | 10 | 2700 | 924 |
| SiC | 430 | 29 | 4 | – | – |
| Si\(_3\)N\(_4\) | 300–320 | 15 | 5–8 | 3500 | 800 |
| Al\(_2\)O\(_3\) | 380–390 | 22 | 2.3–3.5 | 4000 | 450–700 |

To test the corrosion resistance of the PSZ crystals, the samples were kept in a chamber in an aggressive environment under working conditions for 1 month. As a result of the experiment, no traces of corrosion were found. PSZ crystals retain their performance in the temperature range from – 140°C
to +1400°C (melting point ~ 2800°C), have the highest crack resistance compared with other ceramics, and hence a higher wear resistance and antifriction. These properties determine the competitive advantages of nanostructured PSZ crystals over the tested samples of technical ceramics due to the unique combination of strength and tribological properties. The sizes of the PSZ crystal domains were estimated on the basis of measurements and analysis of the broadening of diffraction reflexes caused by violations of the periodicity of the three-dimensional crystal lattice. The main types of violations are: limited size of the region of the crystal lattice that scatters radiation coherently (the size of the region of coherent scattering – RCS, corresponding to the characteristic size of the domains), and disturbance of interplanar distances in the lattice – microstrain. The data for calculating the regions of coherent scattering (D) and microstrains (ε) in synthesized PSZ crystals that are promising for tribological applications are given in table 2. A standard (not broadened) profile was obtained by recording the standard of polycrystalline silicon with the same shooting parameters.

| No. | Structure          | D, nm | ε, 10^{-3} |
|-----|--------------------|-------|------------|
| 1   | ZrO₂–2.5 mol.% Y₂O₃ | 38    | 4.7        |
| 2   | ZrO₂–3 mol.% Y₂O₃  | 115   | 2.7        |
| 3   | ZrO₂–3.5 mol.% Y₂O₃| 64    | 1.8        |
| 4   | ZrO₂–4 mol.% Y₂O₃  | 63    | 1.5        |

The wear rate and friction coefficients of PSZ crystals + 3 %Y₂O₃ annealed in vacuum are close to the most wear-resistant samples, have a high stability during reproduction, namely, the standard deviation is 0.030, which is 36% less than that of non-annealed samples. A distinctive feature of these crystals is the practical absence of chips during testing, which makes them attractive for use in friction units.

The sliding speed of the samples in the conducted tests for friction and wear was selected from the condition of the onset of luminescence of the samples, which corresponded to a temperature of about 500°C. With an increase in the sliding speed, the friction coefficient decreased (figure 2): at P = 500 H – by 1.53 times from f_{υc} = 0.52 m/sec to f_{υc} = 0.34 m/sec.

In the course of the experiment, the friction heating of the friction unit occurred and at v = υc, the crystal sample began to glow. The critical velocity υc = 1.41 m/sec corresponded to the load P = 500 H (p = 10MPa); load P = 936 H (p = 18.6 MPa) – υc = 0.23 m/sec. For friction regimes, the densities of heat fluxes are as follows:

\[ P = 500 \text{ H (p = 10 MPa)}, f = 0.52, \nu = 1.41 \text{ m/sec} \rightarrow q = fpv = 7.33 \cdot 10^6 \text{ W/m}^2 \]
\[ P = 936 \text{ H (p = 18.6 MPa)}, f = 0.63, \nu = 0.23 \text{ m/sec} \rightarrow q = fpv = 2.69 \cdot 10^6 \text{ W/m}^2 \]
The falling character of the dependence $v = \phi(v)$ can be explained by the influence of the temperature factor. As the sliding speed in the contact of conjugated bodies increases, the frictional heating of the samples occurs, the mechanical strength of the surface layers decreases and, as a consequence, the strength of adhesion bonds decreases in the areas of actual contact of the conjugated bodies.

The tribotechnical characteristics of the crystals depend on the contact pressure. Test conditions: contact pressure $p$ varies in the range of $p = 5-80$ MPa; counterbody – steel U10A, friction without lubrication. The sliding speed at each pressure $p$ was chosen from the condition that the bulk temperature of the ceramic sample did not exceed 400°C, which was controlled by the glow of the sample. The test results are presented in figure 3.

![Figure 3](image)

**Figure 3.** The dependence of the friction coefficient of the PSZ crystal on the load.

Comparative wear resistance tests were carried out under friction mode without lubrication at a specific load of 6 MPa and a sliding speed of $v = 0.2$ m/sec. The choice of load and sliding speed is based on the results of the strength and tribological calculation of the node mixing node according to the methods of [10]. The crystals of partially stabilized zirconium dioxide (PSZ crystals) are distinguished by better antifriction and wear resistance (table 3). To a greater extent, these benefits relate to crystals annealed after growing.

**Table 3.** The results of comparative tribological tests.

| No. | Material | Basic structure, atom. % | $f$ | $I*10$ |
|-----|----------|--------------------------|-----|--------|
| 1   | Original crystal ZrO$_2$ + 3 mol.% Y$_2$O$_3$ | Zr-83.1 Y-10.1 | 0.35 | 2.5 |
| 2   | Same crystal annealed in vacuum | Zr-36.5 Ce-50 | 0.30 | 1.8 |
| 3   | Ceramics ZrO$_2$ + 17mol.% CeO$_2$. | Zr-70.1 Y-17.3 | 0.52 | 2.9 |
| 4   | Nanocomposite based on corundum | Mg- non-determ. Al - base | 0.56 | 3.2 |

The wear rate and friction coefficients of PSZ crystals + 3 %Y$_2$O$_3$ annealed in vacuum are close to the most wear-resistant samples, have a high stability during reproduction, namely, the standard deviation is 0.03, which is 36% less than that of non-annealed samples. A distinctive feature of these crystals is the practical absence of chips during testing, which makes them attractive for use in friction units.
Let us look at a dry friction bearing. The case, as well as the shaft with working blades, is made of graphite and constructively form two slide bearings. The shaft is driven by a flexible coupling from the electric motor. Sliding bearings are loaded with a radial force from the tension of a flexible connection (belt). Workload fluctuations are minor. The shaft rotates, the sleeve is not movable. Technical requirements for materials of a friction pair are formulated on the basis of the requirements for reliability and service life of process equipment. The mixing device in the unit for the synthesis of the blocks works for 1 hour during the day, therefore during the calculation period, with a duration of 4320 hours, 180 hours are in operation. Based on the required level of equipment reliability \( P(t) = 0.95 \), we determine the required safety factor (m) based on the wear rate of materials of a friction pair (m = 1.7).

Let us determine the contact parameters of the sliding bearing by calculation methods [11, 12]: the average pressure at the contact area \( \rho_c = 1.31 \) MPa (with a load factor \( \beta = 0.016 \) half the contact angle \( \phi_0 = 14^\circ \), sliding speed \( V = 0.256 \) (m/sec). Wear rate [4] for graphite material according to the criterion of Archard is equal to \( I/p = 2*10^{-9} \), the limit gap \( \Delta_{lim} = 100 \) microns.

The service life of the bearing was determined as the number of revolutions of the shaft and its adequate operation time, at which the total wear of the bodies in frictionlessness will reach the value of the maximum permissible wear. The accuracy of the calculations is determined by the accuracy of the determination of the elemental law of wear \( J(p) \), which includes the main parameters and the degree of their influence on the wear of materials. The method is universal, can be applied to various typical friction units. The service life of the support device mixing in graphite performance is equal to

\[
T = \frac{\Delta_{lim}}{m(I/p)pV} = 24.3 \text{ (hrs)}
\]  

(1)

The result of the calculation and the practice of operating the synthesis plants indicate that the mixing unit is not very wear-resistant and that it must be replaced regularly.

Tribotechnical characteristics of materials are defined in [7, 9, 13] and the life of the support calculated by the formula (1) is given in table 4. The wear rate and friction coefficients of PSZ + 3 %\( \text{Y}_2\text{O}_3 \) crystals annealed in vacuum are close to the most wear-resistant samples, have high stability during reproduction, namely the value of the standard deviation is equal to 0.030, which is 36% less than that of non-annealed samples. A distinctive feature of these crystals is the practical absence of chips during testing, which makes them attractive for use in friction units.

**Table 4.** Tribological properties of the slewing with sleeves of promising structural ceramics and crystals.

| No. | Base material | Additives, % | Friction coeff. f | Wear coeff. \( I/p \) (MPa)\(^{1}\) | Estimated life of the support (hrs.) at \( P(t) = 0.95 \) |
|-----|---------------|--------------|-------------------|----------------------------------------|----------------------------------|
|     | \( \text{ZrO}_2 + +3\% \text{Y}_2\text{O}_3 \) | original     | 0.30              | \(5.0*10^{-10}\)                            | 100                             |
| 1   | orient. (001) | annealed     | 0.27              | \(4.5*10^{-10}\)                            | 111                             |
| 2   | \( \text{ZrO}_2 + +3\% \text{Y}_2\text{O}_3 \) | \( \text{CeO}_2+\text{Er}_2\text{O}_3 \) | 0.12              | \(2.4*10^{-10}\)                            | 208                             |
| 3   | \( \text{Si}_3\text{N}_4 \) (NC-132) | –            | 0.48              | \(1.0*10^{-9}\)                            | 86                              |
| 4   | Nanocompos.   | + La, + Y    | 0.56              | \(6.4*10^{-10}\)                            | 50                              |
| 5   | \( \text{Al}_2\text{O}_3 + \text{ZrO}_2 + +m \text{ mol\%} \) | 17% \( \text{CeO}_2 \) | 0.52              | \(5.8*10^{-10}\)                            | 92                              |

The study of surface morphology showed that there is a partial change from the initial state associated with the appearance of films of secondary structures. Figure 4a and figure 4b present a general view of the secondary structures of the friction surfaces under study in samples of PSZ crystals. Films (light areas) are present on rubbing surfaces, and the overall pattern of film distribution over the surface, the
level of film continuity, and the area of individual film sections are different for samples with different concentrations of stabilizing Y2O3.

![Figure 4. Friction surface at magnification: 2a) – (x100); 2b) – (x300).](image)

Analysis of the morphology of the surface secondary structures allows us to conclude that the destruction of the surface layers of the samples occurs mainly by local destruction and peeling of the surface films. In this case, the process of destruction is localized in the layer of secondary structures.

4. Conclusion

On the basis of the obtained data on the wear resistance of the samples, the expected life of the slide bearings of the mixing device was calculated with the probability of failure-free operation (reliability function) equal to P(t) = 0.95. The calculation data show that the only way to ensure a given level of reliability is the installation of micro-doped cerium nanostructured PSZ in sliding bearings. The manufacture of bushings from any other material among those tested will lead to a decrease in the level of reliability.

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