X-Ray Diffraction Analysis of the Sintered Y–TZP–Al$_2$O$_3$ Ceramics

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Abstract. The paper discusses the wear resistance, friction coefficient, and structure of friction surfaces of fine-grained (0.2 μm) Y–TZP–Al$_2$O$_3$ composite rubbed against a steel disk counterface at a pressure of 5 MPa in a range of sliding speeds from 1 to 20 m/sec. It is shown that, starting at 2 m/sec, the fricti on surface is subdivided by a crack network into separate regions within which local spalling occurs at the maximum wear rate and a sliding speed of 5 m/sec. X-ray diffraction reveals inversion (with respect to the initial state) of the peak intensities of the tetragonal phase with random crystalline grain orientation. The degree of this inversion increases with sliding speed. These results are discussed in terms of the effects exerted by the reorientation of martensite-free deformation twins in the tetragonal phase and the formation of a quasi-liquid film on the wear resistance of fine-grained Y–TZP– Al$_2$O$_3$.

1.Introduction

Production of various friction pairs using additive technologies - modern trend of Materials. Especially promising is the synthesis of fine-grained (≤0.3 μm) ceramic products. The capability of yttria-stabilized polycrystalline tetragonal zirconia (Y-TZP) ceramics [1] to undergo phase transitions under applied stresses determines their friction behavior [1, 2]. According to [3], when Y-TZP is rubbed against steel at a speed of 1 to 47 m/sec, the dependence of the wear rate on the sliding speed is described by a curve with a peak at 4–5 m/sec. The presence of this peak is attributed to the reduction in the contribution of the transformation toughening mechanism because of the increase in the temperature in the friction area to a level at which the tetragonal phase of zirconia becomes thermodynamically stable. The subsequent decrease in the wear rate at high sliding speeds is caused, according to [3], by the quasi-liquid film on the friction surface of the ceramics, resulting from the melting and oxidation of the steel. To find out the cause of the intensive wear of Y-TZP ceramics, it appears reasonable to study materials with no martensitic transformation and mechanical properties (ultimate strength in bending and fracture toughness) sufficient for catastrophic failure not to occur during high-speed sliding on steel. Such properties are typical of Y-TZP and Y-TZP–Al$_2$O$_3$ ceramics [1] with fine-grain tetragonal phase (less than 0.3 μm) being below critical (d$_{cr}$ ~ 1 μm [1]). These ceramics do not undergo martensitic transformation during deformation and fracture [1, 4, 5].

The wear resistance of Y-TZP ceramics with submicron grains has been studied only for relatively low sliding speeds (less than 1 m/sec) [4, 5]. Our goal here is to study the dependence of the wear rate of

Y-TZP–Al_2O_3 ceramics with submicron structure on the sliding speed after dry friction with steel over a wide range of sliding speeds and to study structural changes on the friction surface.

2. Materials and experimental procedure

The samples were prepared from 80 wt.% ZrO_2 (3 mol.% Y_2O_3) + 20 wt.% Al_2O_3 powder produced by decomposing water solutions of Zr, Y, and Al salts in high-frequency plasma. X-ray diffraction revealed three phases in the starting powder: tetragonal ZrO_2, γ-Al_2O_3, and θ-Al_2O_3. After semidry compaction at a pressure of 200 MPa, the samples were nonaxially compressed with a constant true stress of 100 MPa and, in that deformed state, sintered at a temperature of 1300°C for 30 min (for more details on the sample preparation procedure, see [6]). The resulting samples of Y-TZP–Al_2O_3 composite had a density of 94% of the theoretical value, 0.2 μm mean grain size, 600 MPa bending strength, hardness HV = 12.6 GPa, and fracture toughness K_{Ic} = 8 MPa×m$^{1/2}$. After sintering, the samples contained α-Al_2O_3, while the phase composition of zirconia remained the same (tetragonal modification). Tests were conducted on a UMT-1 pin-and-disk friction machine. There was no lubrication, and the sliding speed was increased incrementally. The counterface was a disk made of martensitic cast tool steel (HRC 63–65) with excess $M_{12}C$ carbides and a minor amount of retained austenite. The ceramic samples had rectangular cross-section with a total area of 40 mm^2. The test pressure was 5 MPa, the sliding speed was varied from 1 to 20 m/sec, and the test duration was chosen so that the sliding distance was 2000 m for all speeds. Before each test, the samples were worn in at a speed of 0.1 m/sec and a pressure of 5 MPa. In each test, a computer recorded the friction coefficient at 1 s intervals. The ratio of the material volume lost by the sample during the test to the sliding distance was used as a measure of wear. The ceramic surface before and after friction was examined on a DRON-UM1 X-ray diffractometer with a CuKα-radiation source in the range of angle 2θ from 20 to 80°. Special software was used to do root-mean-square fit of Lorentzian-type profiles to the resulting X-ray patterns. The results were used together with the method described in [7] to determine the size of coherently diffracted domains (CDD). We also analyzed the intensities (I) of X-ray lines (002) and (200) of the tetragonal modification and determined the ratio $I_{(002)}/I_{(200)}$ for each friction mode. The structure of and the element concentration on the friction surfaces were analyzed with a Philips SEM-515 scanning electron microscope and an EDAX ECON IV microanalyzer.

3. Results and discussion

A feature of friction processes in the speed range of interest is release of a great amount of heat, especially at high sliding speeds. The measurement of the contact temperature between the ceramic composite and steel with an infrared pyrometer showed that, at 20 m/sec, the ceramic material heated up to 300°C, while the temperature of the steel did not exceed 200°C; the temperature in the friction areas on the ceramics (flash temperature [8]) was much higher (1600–1800°C at a speed of 10 m/sec [8]). The friction tests demonstrate that as the sliding speed is increased from 1 to 5 m/sec, the wear rate of the ceramics first increases and then (after the speed reaches 20 m/sec) decreases (Figure 1, a). The friction coefficient of the ceramics decreases from 0.8 at low speeds to 0.12 at a speed of 20 m/sec (Figure 1, b). Scanning electron microscopy has revealed grooving (typical of abrasive wear) on the surface after friction at sliding speeds to 2 m/sec. At speeds higher than 2 m/sec, the surface was covered with cracks parallel and perpendicular to the sliding direction, thus forming a network that divides the surface into separate regions. After tests at 5 m/s, the ceramic surfaces display traces of spalling, while after tests at 10 and 20 m/s, the surfaces were as smooth as after the tests at 2 m/sec.

Electron microprobe analysis has revealed that the friction surface of Y-TZP–Al_2O_3 ceramics includes not only elements of the ceramic (Zr, Y, Al), but also elements of the steel counterface (Fe, Mn, W, Ni, Cr, V, Mo). As the sliding speed is increased from 2 to 10 m/sec, the amount of the steel elements increases from 2 to 6 wt.%. Grazing-incidence X-ray diffraction examination of a 1–2 μm surface layer has discovered X-ray peaks of Fe_2O_3. This fact and [3] suggest that a quasi-liquid film was formed on the ceramic surface during friction because of the melting and oxidation of steel.
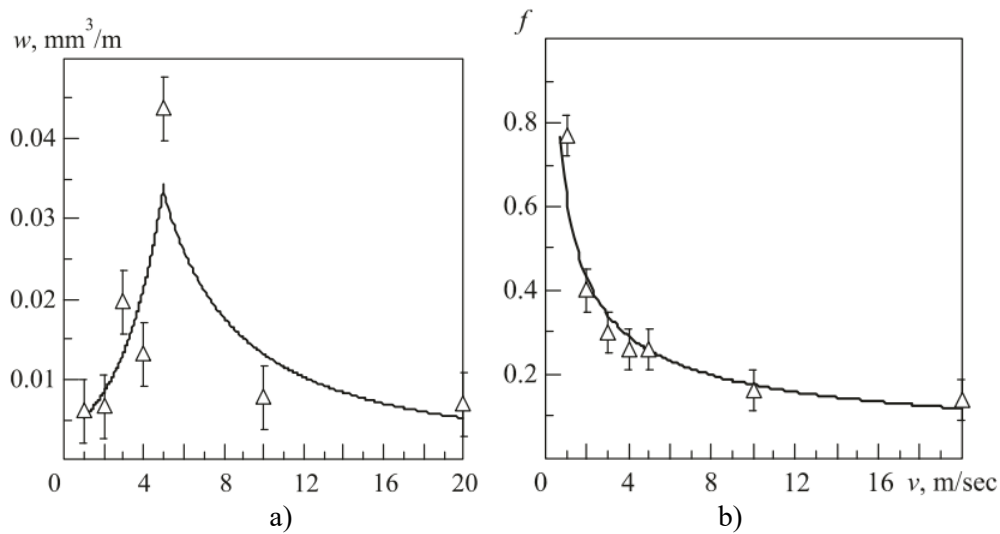
Figure 1. Dependence of wear rate (a) and friction coefficient (b) of Y-TZP–Al$_2$O$_3$ on the sliding speed on steel

An X-ray analysis of the Y-TZP–Al$_2$O$_3$ surfaces has revealed traces of tetragonal-to-monoclinic martensitic transformation neither on the fracture surface after bending test nor on the friction surfaces. The X-ray texture of the friction surface of the ceramics includes peaks (002) and (200) of tetragonal zirconia whose intensities differ from those on the initial polished surface. After friction test, the ratio I$_{(002)}$ / I$_{(200)}$ exceeds its value (0.8) for the ceramics before the test (Figure 2, a).

It is seen from Figure 2, b that the greater the ratio I$_{(002)}$ / I$_{(200)}$ of the tetragonal phase of ZrO$_2$, the less the friction coefficient of fine-grained Y-TZP–Al$_2$O$_3$ composite. The curve of CDD size of the tetragonal phase on the friction surface versus the sliding speed has a minimum (Figure 3). As the sliding speed is increased to 2 m/sec, the CDD size decreases. With further increase in the speed to 20 m/sec, the CDD size increases, remaining 33% less than in the initial state (Figure 3). According to [11, 12], the CDD size calculated from the (111) peak profile of the tetragonal phase of ZrO$_2$ can be considered to be the size of intragranular crystallites of the tetragonal phase of ZrO$_2$.

The results obtained indicate that over the entire range of sliding speeds, the intensity ratio for the doublet (002)–(200) of the tetragonal zirconia (Figure 2) on the surface of the fine-grained Y-TZP–Al$_2$O$_3$ ceramics changes so that the c-axis of the tetragonal phase lattice tends to be perpendicular to the friction surface and the average size of its crystallites decreases (Figure 3), especially (to 22 nm) in the region of intensive wear at a sliding speed of 3– 5 m/sec (Figure 1, a). Such structural changes of the friction surface of fine-grained Y-TZP–Al$_2$O$_3$ ceramics may be due to high-temperature plastic deformation in the friction area. For example, the observed increase in I$_{(002)}$ / I$_{(200)}$ with increase in the sliding speed (and, hence, increase in the temperature in the friction area) from 1 to 20 m/sec (Figure 2, a) may be caused by the self-consistent motion of coherent twins in grains of the tetragonal phase [9, 10]. Similar relationships between the ratio I$_{(002)}$ / I$_{(200)}$ and the sliding speed were observed after dry grinding of transformation-toughened course-grained (2–3 μm) Y-TZP ceramics [11] and in studying the tribological characteristics in the range of sliding speeds from 0.2 to 11 m/sec [12]. Another possible cause of the increase in I$_{(002)}$ / I$_{(200)}$ may be high temperature plastic deformation leading to a distortion of grains in the sliding direction, which was observed in Y-TZP ceramics after sliding on steel at a speed of 1–5 m/sec [3].

The curve of wear rate versus sliding speed with a peak at medium speeds (Figure 1, a) is similar to that [3] for relatively coarse-grained (2–3 μm) transformation-toughened Y-TZP–Al$_2$O$_3$ ceramics of the same chemical composition.
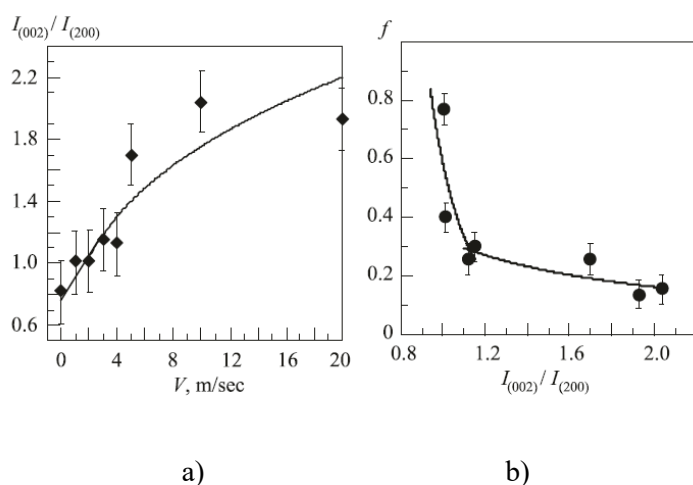
a)   b)

Figure 2. Dependence of the ratio $I_{(002)} / I_{(200)}$ on the sliding speed (a) and friction coefficient (b): in Figure 2a, $I_{(002)} / I_{(200)}$ is the ratio of the tetragonal phase on the polished surface of the sample before friction test.
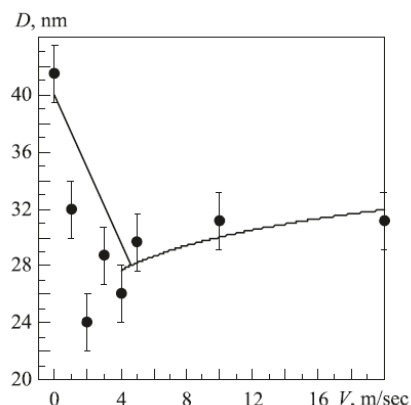
Figure 3. Dependence of the CDD size of the ZrO_2 tetragonal phase of fine-grained Y-TZP–Al_2O_3 composite on the sliding speed.

The presence of the peak indicates that there are at least two factors affecting wear and friction. In the absence of martensitic transformation, the increase in the wear rate with increase in the sliding speed to 5 m/sec (Figure 1, a) may be attributed to the thermomechanical cracking of the friction surface because of the low thermal conductivity of Y-TZP (2 W/(m×K) at 100–1400°C [13] against, for example, 40 W/(m×K) at 25°C for Al_2O_3 [13]), which causes high temperatures in the friction area and high thermal stresses near the surface. Intensive wear is represented by low-scale texture elements on deformed and fractured surface. In such conditions, the friction surface of fine-grained Y-TZP–Al_2O_3 ceramics acquires a microstructure with smallest crystallites of the tetragonal phase (Figure 3) and a crack network with minimum distance between cracks. The quasi-liquid film formed on the friction surface and reducing the contact stresses [3] is responsible for the decrease in the wear rate with increase in the sliding speed from 10 to 20 m/sec. The decrease in the friction coefficient (Figure 2, b) with increasing ratio $I_{(002)} / I_{(200)}$ may be attributed to the intensified plastic deformation of the friction surface, which apparently promotes the formation and fixation of the film on the friction surface. At small (≤2 m/sec) and high (≥10 m/sec) sliding speeds, the wear rate and friction coefficient of the submicron ceramics practically do not differ from those of coarse-grained (1.5 μm) transformation-toughened ceramics of the same chemical composition tested under similar conditions [3]. At medium sliding speeds (~5 m/sec), the fine-grained ceramic composite is worn more intensively (than coarse-grained ceramics [3]), which at high temperatures and plastic strains [3], when the quasi-liquid film has not formed yet, may be due to superplasticity typical of fine-grained ceramic materials.

4. Summary
The dependence of the wear rate on the sliding speed for the fine-grained (0.2 μm) Y-TZP–Al_2O_3 ceramic composite that does not undergo martensitic transformation into a monoclinic phase at a sliding speed of 1–20 m/sec on steel is represented by a curve with a peak at a speed of 5 m/sec. At this speed, the surface is fragmented at different scales: (i) cracks form a network dividing the surface into regions with a minimum average size of 30 μm and (ii) the size of crystallites of the tetragonal phase decreases from 45 nm before friction to 20 nm after friction. It has been shown that the intensity ratio for the doublet (002)–(200) of the tetragonal modification of zirconia is determined by the texture of the friction surface with the c-axis of the crystallite lattice tending to be perpendicular to the friction surface.

Acknowledgement

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