SHORT COMMUNICATIONS

Effect of the Grain Size on the Formation of a Nanophase Structure and Tribological Properties of the Friction Surface of a Ceramic Made of Partly Stabilized Zirconium Dioxide

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Abstract—It is found that the wear of the $ZrO_2 + 3 mol\% Y_2O_3$ ceramics with a grain size of 180 nm in the case of dry friction on steel is smaller by a factor of 20–60 than the wear of a ceramic with an average grain size of 700 nm. It is shown that this is due to the fact that a nanophase structure formed on the friction surface of the ceramic with a grain size of 180 nm consists of ferroelastic nanodomains of the nontransformable *T* phase.

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It is known [1] that a typical feature of nanocrystalline (nanostructural, nanophase) materials (NM) is the size of individual objects forming their structural basis, which should not exceed ≈ 100 nm at least in one dimension. A transition of the material to the nanostructural state is accompanied by considerable improvement of physical and mechanical properties. For example, in [2], nanocrystalline nickel with an elevated hardness was obtained by pressing and fritting of an ultradisperse powder.

As a rule, ceramics of partly stabilized zirconium dioxide (PSCD) is prepared from powders by their pressing and fritting. It was demonstrated in a large number of publications [3–5] that a rapid cooling from the temperature of formation of the cubic (F) phase (which is ≥ 1600 K for ZrO₂ + 3 mol%Y₂O₃) leads to diffusionless transformation of the F phase into an intermediate tetragonal (T) phase [3]. In this case, internal stresses increase and a $I_{(002)}/I_{(200)}$ texture is formed [4]. The T phase experiences twinning [3–5], but is not transformed into the monoclinic (M) phase even in the case of mechanical fracture of the sample [3]. During friction of the PSCD ceramic with a grain size from 600 to 2000 nm on steel at a velocity >2 m/s, the *M* phase is not observed on the friction surface of the sample [6], but the $I_{(002)}/I_{(200)}$ texture is formed. A comparison of the behavior of PSCD ceramic samples with various porosities in friction shows [7] that the wear of samples with a higher porosity for the same grain size \approx 700 nm and for a sliding velocity of 2.5 m/s is smaller. In this case, the F phase is irreversibly transformed into the T phase and the $I_{(002)}/I_{(200)}$ texture is

formed, while the *T* phase is partly transformed into the *M* phase.

This study aims at analysis of the wear of finegrained PSCD ceramic in the $ZrO_2 + 3mol\%Y_2O_3$ system during friction on steel. For comparison, we chose a coarse-grained PSCD ceramic $ZrO_2 + 3mol\%Y_2O_3$, which was used earlier in [7]. Thus, experiments were made on two samples: fine-grained sample no. 1 with an average grain size of 180 nm and coarse-grained sample no. 2 with a grain size of 700 nm. In the course of dry sliding friction, we studied the wear of the ceramics, the evolution of the phase composition of the material, and the formation of a texture and a nanostructure on the friction surface.

In accordance with the technique described earlier in [7, 8], cylindrical samples 8 mm in diameter were prepared from the TZ-3Y powder manufactures at TOSOH by cold isostatic pressing and fritting in air. Sample nos. 1 and 2 were fritted at T = 1623 and 1773 K, respectively. The friction surfaces of the samples were polished before the experiments. The initial data for the samples are given in Table 1. The density of the ceramic was measured by hydrostatic weighing. The grain size was determined using scanning microscopy. Hardness HV_{10} and crack resistance $K_{IC}(RT)$ were measured by microindentation.

As a rider during sliding, we used a polished disk made of the 40KhN steel (GOST no. 4543-71) tempered to a hardness of 55HRC. The sliding velocity of a ceramic sample on steel was 2.5 m/s. Sliding was performed in a circle 100 mm in diameter. The pressure of the ceramic sample against the rider was 1.4 MPa. The

Sample no.	<i>d</i> , nm	ρ_{ex} , g/cm ³	P*, %	<i>HV</i> ₁₀ , GPa	$K_{IC}(RT)$, MPa m ^{1/2}	Average wear rate over 30 min, mg/s
1	180	6.04	0.98	12.0	3.60	3.3×10^{-2}
2	700	6.08	0.33	12.3	3.94	5×10^{-2}

Table 1. Physical and mechanical properties of original samples

Note: Porosity is $P = (1 - \rho_{ex}/\rho_t) \times 100\%$ and the theoretical density is $\rho_t = 6.1$ g/cm³ for 0% concentration of the *M* phase.

Table 2. RPA data, lattice parameters, and texture of samples before testing

Sample no.	Phase composition								
					<i>T</i> pl	F phase	Texture		
	<i>M</i> , vol. %	<i>T</i> , vol. %	<i>F</i> , vol. %	<i>a</i> , nm	c, nm	$\sqrt[3]{a^2c}$, nm	c/a	<i>a</i> , nm	1002/1200
1	0	90	10	0.5091	0.5167	0.5116	1.015	0.5121	0.63
2	0	79	21	0.5078	0.5155	0.5104	1.015	0.5121	0.60

Table 3. RPA data, lattice parameters, texture, and wear of samples after180 min of sliding

Sample Avera		Phase composition				Lattice parameters					
	Average					T and T' phases				F phase	Texture
	wear rate	<i>M</i> , vol. %	<i>T</i> , vol. %	<i>T</i> ', vol. %	<i>F</i> , vol. %	<i>a</i> , nm	c, nm	$\sqrt[3]{a^2c}$, nm	cla	<i>a</i> , nm	1002/1200
1	1.7×10^{-2}	0	70		0	0.5088	0.5159	0.5111	1.014	_	1.14
				30		0.5108	0.5147	0.5121	1.008		
2	1.02	0	81	_	19	0.5091	0.5160	0.5114	1.014	0.5121	0.6

wear of the ceramic was determined by weighing the samples after every 30 min of sliding.

Radiographic analysis of the samples was performed on the DRON-3M setup in CoK_{α} radiation. We studied reflections from the (111) planes of the *M*, *T*, and *F* phases, as well as reflections of tetragonal doublets (002)–(200) and (004)–(400) for determining the $I_{(002)}/I_{(200)}$ texture and the concentration of the *M*, *T*, and *F* phases. X-ray phase analysis (RPA) was carried out in accordance with the technique described in [9, 10]. We compared the phase composition and texture of the friction surface of the ceramic in the initial state and after a wear test lasting 3 h. The results of experiments are given in Tables 1–3 and in Figs. 1 and 2.

The RPA data (Tables 2 and 3 and Fig. 1) show that the *T* and *F* phases are present in the initial state of both fine-grained sample no. 2 and the coarse-grained sample no. 2. The concentration of the cubic phase in sample no. 1 is half the concentration of this phase in sample no. 2, which completely matches the data presented in [11], where the samples prepared from the TZ-3Y powder manufactured at TOSOH were also studied. The RPA data also show that the 3D lattice parameter a_2c of the *T* phase is higher in the fine-grained ceramic, indicating that the concentration of the stabilizing Y_2O_3

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impurity in this ceramic is slightly higher. However, texture $I_{(002)}/I_{(200)} \approx 0.5$ and tetragonality c/a = 1.015 for both samples in the initial state are approximately the same.

The wears of the samples under investigation over the first 30 min differ insignificantly. Upon a further increase in the experimental time, the wear of sample no. 1 becomes much smaller than the wear of sample no. 2. After 60–180 min of sliding, the wear of sample no. 1 is smaller than that of sample no. 2 by a factor of \approx 20–60 (see Fig. 2).

After 180 min of sliding (see Fig. 1 and Table 3), the concentration of the *F* phase in sample no. 1 decreases, while the concentration of the nontransformable twinning *T* phase with tetragonality c/a = 1.008 increases up to 30%. The monoclinic phase is not detected, while the texture increases from 0.6 to 1.14. Sample no. 2 shows virtually no change in the phase composition or texture after 180 min of sliding. It was shown in [6, 7] that this can be due to the reversibility of the $F \longrightarrow T$ and $T \longrightarrow M$ phase transformations in samples with a density close to the theoretical value. In this case, the texture remains unchanged and no monoclinic phase appears.



Fig. 1. X-ray diffraction patterns of ceramic samples before sliding (upper curves) and after 180 min of sliding (lower curves)

This effect can apparently be explained by the formation of ferroelastic domains during friction of sample no. 1 upon martensite transformation $F \longrightarrow T$; these domains are twins with a constant tetragonality [3-5, 12]. The domains are separated by a coherent boundary with a variable tetragonality (i.e., with a variable concentration of the stabilizer). The width of coherent walls with a variable tetragonality depends on the tetragonality of the domains (the width of twin boundaries decreases with the tetragonality) [12]. In accordance with the results obtained in [13], the width of the twinning strip (domain) depends on the grain size and may change from a few nanometers to $\approx 1 \ \mu m$. However, the ratio of the twin width to the grain size remains unchanged. This means that, upon a decrease in the grain size, a nanophase T structure whose properties determine the behavior of the friction surface of the PSCD ceramics can be formed on the friction surface. Apparently, an increase in the concentration of the stabilizing impurity at grain boundaries in a finegrained sample [11] and the observed formation of the



Fig. 2. Decrease in relative wear $\Delta m_1/\Delta m_2$ as a function of friction time (Δm_1 and Δm_2 are the wears of the first and second samples, respectively.

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T phase increase the stability of the T phase on the friction surface and decrease the wear of the ceramic.

Thus, the amount of the cubic phase in a PSCD ceramic (with a grain size of 180 nm) fritted at a temperature of 1623 K is small and, according to [11], this phase is almost entirely localized in the boundary region of grains. During friction, the *F* phase and partly the *T* phase are irreversibly transformed into the *T* phase, which experiences twinning but is not transformed into the *M* phase. This leads to the formation of a nanophase *T* structure on the friction surface, the formation of a texture, an increase in internal stresses, and strengthening of the friction surface. The absence of the $T \longrightarrow M$ transformation is apparently due to the fact that internal stresses emerging during sliding render the metastable *T* phase more stable to the action of external stresses applied in the course of friction.

Fritting of PSCD ceramics at a temperature of 1773 K leads to an increase in the grain size to 770 nm and to an increase in the concentration of the stabilizing impurity in grains near the boundary, which is accompanied by the formation of up to 20% of the cubic phase in the boundary regions of such grains. The density of the sample increases thereby. These circumstances make the $F \longrightarrow T$ and $T \longrightarrow M$ phase transformations reversible. The phase composition and texture do not change during sliding (i.e., the conditions for accumulating internal stresses and for increasing the strength of the friction surface are not created), and the wear of the sample increases.

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