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STABILIZATION OF ZIRCONIUM OXIDE IN ALUMINUM OXIDE–ZIRCONIUM OXIDE SYSTEM BY COMPLEX STABILIZERS

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Special features of stabilization of zirconium oxide in the aluminum oxide-zirconium oxide system using stabilizers of the yttrium oxide-magnesium oxide system are studied. Optimum regimes for dispersion of the initial components and for final sintering are determined.

Realization of the advantages of ceramics as compared with metal alloys at high temperatures and in corrosive media is hindered because of their brittleness due to defects of the microstructure, the ion-covalent character of the chemical bond, and the low mobility of dislocations.

A substantial increase in the toughness of alumooxide ceramics was attained by the introduction of dispersed zirconium oxide particles [1]. In this case, specific structural states are formed that facilitate maximum energy dissipation in brittle failure of the material. Of considerable importance here is the state of the zirconium dioxide particles in the ceramic matrix, which is in turn governed by its stabilization degree [2]. The high strength characteristics of the materials are due to the high density, fine crystalline composition, and the presence of tetragonal zirconium dioxide, which becomes monoclinic only under the influence of external stresses.

We studied the processes of stabilization of zirconium dioxide in an aluminum oxide matrix using complex stabilizers of the yttrium oxide-magnesium oxide system. An eutectic alloy of 70 wt.% Al_2O_3 + 30 wt.% stabilized ZrO_2 was chosen as the initial composite material. Zirconium dioxide of different degrees of stabilization was produced by altering the content of yttrium oxide (0–6 wt.%) and magnesium oxide (0–3 wt.%).

Stabilization was performed by mixing chemically pure ZrO_2 powder with the components of the stabilizers in the form of solutions of their salts with subsequent vaporization, drying, and annealing of the mixtures at a temperature of 1600°C.

Mechanical mixtures of chemically pure Al_2O_3 with stabilized zirconium oxide were dispersed in an attritor lined with aluminum oxide-based ceramics by balls (beads 0.8–1.6; 1.6–2.5 mm in diameter) of the same alloy. We pressed the mixtures at a pressure of 200 MPa into specimens with a diameter and height of 10 mm, which were sintered in air at 1400–1750°C for 1 h.

We determined the average particle size of the powder mixtures using a Sedi Graph 5100 sedimentograph and the phase composition using a DRON 3.0 X-ray diffractometer in Cu-Ka radiation. The chemical composition and structure of the sintered alloys and fractograms of fractures were studied on a Nanolab scanning electron microscope with a magnification of 1000–10,000 times.

The grain size in the alloys was determined on sections that had been high-temperature-treated in a vacuum furnace at a temperature of 1400°C and a holding time of 1 h.

Based on investigations of the phase composition of the $ZrO_2-MgO-Y_2O_3$ alloys (Table 1) we can say the following.

All three phases – monoclinic, tetragonal, and cubic – are found in all the alloys except alloy 4. The alloy with a Y_2O_3 content of 6 wt.% has no tetragonal phase, is fully stabilized, and contains free yttrium oxide.

Magnesium oxide affects substantially less the stabilization of the high-temperature phase than yttrium oxide does (in alloys 1 and 5, zirconium dioxide is represented mainly by a low-temperature phase, i.e., the

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TABLE 1. Influence of the Composition of Stabilizers on the Phase Composition of Zirconium Dioxide Powders

No. of alloy	Alloy composition, wt.%			Phase content, %		Phase composition
	MgO	Y_2O_3	ZrO_2	Monoclinic phase	Tetragonal (T) phase + cubic phase (K)	
1	3	0	97	73	27	M + K + T
2	2	2	96	19	81	M + K + T
3	1	4	95	7,6	92,4	M + K + T
4	0	6	94	4,4	95,6	M + K + Y_2O_3
5	2	0	98	96	4	M + K + T
6	1	2	97	60	40	M + K + T
7	0	4	96	20,5	79,5	M + K + T

TABLE 2. Influence of the Composition of Stabilizers on the Phase Composition of ZrO_2 in 70 wt.% Al_2O_3 + 30 wt.% Stabilized ZrO_2 Alloys

No. of alloy	Phase composition at a sintering temperature of, °C		Phase content, %			
			M		T + K	
	1500	1750	1500°C	1750°C	1500°C	1750°C
1	M + T + K	M + T + K	77	91	23	9
2	T + K + Y_2O_3	M + T + K	–	71	100	29
3	T + K + Y_2O_3	T + K	–	–	100	100
4	K + Y_2O_3	K	–	–	100	100
5	M + T + K	M + T + K	83	93	17	7
6	M + T + K + Y_2O_3	M + T + K	41	88	59	12
7	K + Y_2O_3	K	–	–	100	100

monoclinic phase); however, it is pertinent to note that the effect of MgO is enhanced in the presence of Y_2O_3 and enhances the stabilizing effect of the latter.

As the investigations showed the production of dispersed mixtures of the powders of aluminum oxide and alloyed zirconium dioxide involves a number of difficulties. Grinding of the Al_2O_3 and stabilized ZrO_2 powders has a different character. Aluminum oxide particles are conglomerates (40–60 μm) of dispersed particles (under 1 μm), which are easily broken down by grinding; alloyed zirconium dioxide particles are monolithic particles (50–60 μm) or the same conglomerates of large particles (over 1 μm) strongly bound to one another. In joint dispersion, the aluminum oxide particles, having reached a size of 0.5–0.6 μm, cease to decrease and start to form strong conglomerates of up to 3–4 μm in size, the zirconium oxide particles continuing to slowly reduce in size down to 0.7–0.8 μm, after which the grinding virtually ceases. In this case, no uniform mixing of finely divided particles of aluminum and zirconium oxides (under 1 μm) is observed. In this connection we carried out separate grinding of the powders of aluminum oxide (to a value of the order of 1 μm) and zirconium oxide (to a value of the order of 0.8 μm) with subsequent joint mixing by grinding to a particle size in the mixture of 0.5–0.7 μm.

Sintered alloys of all the compositions are characterized by a higher degree of stabilization for the high-temperature phases of zirconium oxide as compraed with the powder, which is attributable to the compressing effect of the aluminum oxide matrix, which interferes with the high-temperature–low-temperature phase transitions (Table 2).

The content of the high-temperature phases is higher in all the alloys than in the powders. However, as the sintering temperature increases the degree of stabilization of the high-temperature phases decreases, which is attributable to a number of reasons. A study of sections of microstructures of the sintered alloys revealed a notable grain growth for both zirconium dioxide and aluminum dioxide. Whereas at a sintering temperature of 1500°C the average size of a ZrO_2 grain is under 1 μm and that of an Al_2O_3 grain is under 2 μm, at a temperature of 1750°C they amount to, respectively, 2 and 6 μm. This should reduce the effect of stabilization of the high-temperature phases of zirconium dioxide due to the compression forces of the aluminum dioxide matrix. Furthermore, investigations on the scanning electron microscope showed partial dissolution of the magnesium oxides and yttrium oxides in the aluminum oxide, which was the greater, the higher the sintering temperature. The free yttrium oxide that is observed at a temperature of 1500°C disappears. This reduces the degree of doping of zirconium dioxide by affecting the stability of the high-temperature phases. As in the case of zirconium dioxide powders, the stabilizing effect of magnesium oxide in the alloys is much smaller than that of yttrium oxide.

The study of the fracture fractograms showed that fracturing in alloys that contain Y_2O_3 or Y_2O_3 + MgO occurs both along the grain boundaries and over the grain itself. For alloys that contain only MgO, failure along the grain boundaries is pronounced, which can be attributed to instability of the high-temperature phases and their becoming monoclinic, which causes weakening of the material.

Therefore, the investigations performed showed the possibility of stabilizing high-temperature phases of zirconium dioxide in an eutectic alloy with aluminum oxide using stabilizers of the $MgO-Y_2O_3$ system.

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