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FORMATION OF PHASES AND MICROSTRUCTURE OF ZnO AND TiO_2 BASED CERAMIC

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Nanopowders of zinc and titanium oxides were used to obtain samples of Zn_2TiO_4–ZnO ceramic. Phase formation as well as the microstructure and elemental composition of the phases formed were studied by means of electron microscopy. The density and porosity were calculated, and the sizes of grains and pores in the ceramic were determined. The temperature at the zinc titanate forms was determined. It was shown that it corresponds to the sintering temperature of electrocontact materials with this composition. It is proposed that zinc titanate and oxide be used as arc-suppressing and dispersion-hardening additional additives in copper-based electrocontact materials.

***Key words*:** electrocontact materials, metal oxides, zinc titanate, nanopowders, ceramic, microstructure, phase formation.

ZnO nanostructures possess a unique complex of structure, optical, and optoelectronic properties [1]. As a result of solid-phase reactions zinc oxide can form spinel-type compounds in the form of ternary oxides $ZnM^{[3+]}_2O_4$ or $Zn_2M^{[4+]}O_4$ with metals such as Al, Cr, Fe, Ga, In, Sn, Sb, Ti, Mn, and V, which are of technological interest because they possess specific properties which cannot be attained by using ZnO [2 – 6].

Compounds formed by interaction of titanium and zinc oxides — zinc titanate — possess a number of unique physical and chemical properties, as a result of which they are widely used as materials for radioelectronic articles, photoelectrochemical cells, catalysts, gas sensors, and pigments. For this reason a great deal of attention is devoted to studying the synthesis of zinc titanates [7 – 10]. Six chemical compounds of different types, which ortho- and metatitanate have been best studied, form in the system [11]. Zinc orthotitanate Zn_2TiO_4 forms crystals in the form of regular octahedra of the cubic system (lattice parameter $a = 0.846$ nm), while zinc metatitanate $ZnTiO_3$ forms crystals of the hexagonal system — ilmenite (lattice parameters $a = 0.508$ nm and $c = 1.392$ nm).

One practical application of refractory metal oxides, for example, ZnO and TiO_2, is as arc-suppressing and dispersion-hardening phases in electrocontact materials [12 – 14].

The aim of the present work is to investigate the process of phase formation, microstructure, and properties of ceramic based on ZnO and TiO_2 with phase ratio $ZnO : Zn_2TiO_4 \approx 3 : 1$, which is optimal when used as arc-suppressing and hardening phases in electrocontact materials.

EXPERIMENTAL PART

TiO_2 and ZnO nanopowders were used to fabricate ceramic samples. Zinc oxide was obtained by thermal decomposition of zinc hydroxo-carbonate synthesized by mixing water solutions of ammonium hydroxo-carbonate and zinc nitrate. Transmission electron microscopy (TEM) was used to study the morphology and particle-size of the nanopowders. ZnO nanopowder consists of crystallites with average particle size 11 ± 4 nm (Fig. 1*a*). TiO_2 nanopowder was obtained by electric explosion of conductors; the average particle size equals 20 ± 5 nm (Fig. 1*b*).

The nanopowders were mixed in an ethyl alcohol medium by means of ultrasound. This makes it possible to solve two problems: break up conglomerates of nanopowders and

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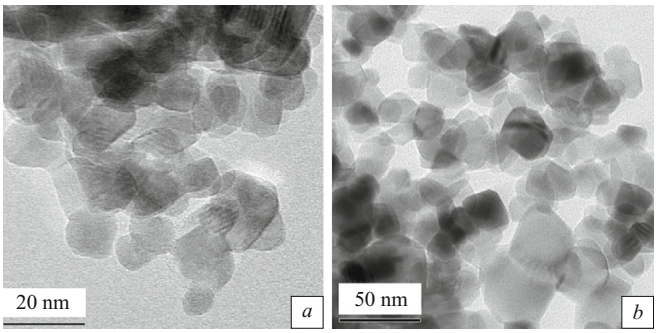

Fig. 1. Electron-microscopic images (TEM) of the initial powders: *a*) ZnO; *b*) TiO_2.

distribute oxides in the batch uniformly. After drying at 80°C a plasticizer (3% solution of polyvinyl butyral in ethyl alcohol) was introduced into the mixture, after which the batch obtained was granulated in order to improve the flowability and compactibility of the batch obtained. The samples were pressed into a rigid matrix under specific pressure $p = 150$ MPa. The sintering was conducted in air; the temperature and the isothermal soaking time are presented in Table 1. The components of the initial batch were taken in the mass ratio TiO_2 : ZnO = 1 : 4, which in accordance with the phase diagram of ZnO–TiO_2 makes it possible to obtain on sintering a ceramic with the phase ratio Zn_2TiO_4 : ZnO = 1 : 3 [15].

The morphology, oxide powder size, microstructure, and elemental composition of the samples were investigated by means of TEM and scanning electron microscopy (SEM) performed with JEM-2100 and JSM-7001F with a system of microanalyzers (Oxford Instruments).

RESULTS AND DISCUSSION

The microstructure and elemental composition of the phases were investigated on pressed compacts and compacts sintered in three regimes. The sintering temperature of the samples was determined in accordance with the following factors: the sintering temperature at 650 °C corresponds to the onset of solid-phase interaction of the ZnO and TiO_2 nanopowders. The temperature 950°C corresponds to the sintering temperature of copper-based electrocontact materials and completion of solid-phase interaction of ZnO and TiO_2 nanopowders; the temperature 1200°C equals the isothermal sintering temperature of ceramic obtained from nanopowders of this composition.

The theoretical density of a compact (5.515 g/cm^3) and the actual density and porosity of pressed compacts and compacts were calculated for the samples (Table 1). The relative of density increased very little as a result of sintering at temperature 675°C and by a factor of 2 at 950°C, but the porosity remained quite high. Sintering at 1200°C, which is close to the sintering temperature of this ceramic, made it possible to obtain higher density.

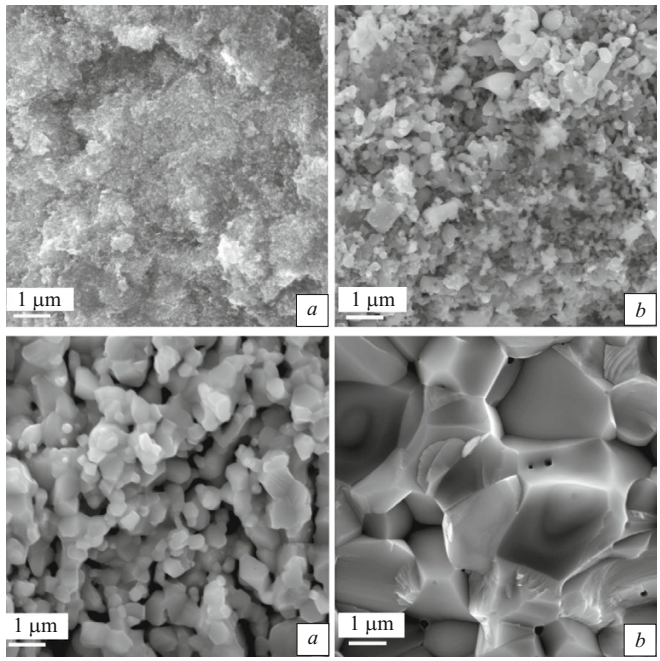

Fig. 2. Electron-microscopic images (SEM) of a fracture surface of the samples: *a*) pressed compact; *b*) sintering at 675°C; *c*) sintering at 950°C; *d*) sintering at 1200°C.

Analysis of the microstructure of fractures of samples yields information on the process of formation of contacts between particles and phase formation upon sintering. The fracture surface of a pressed compact has a fine-grain structure consisting of agglomerates of nanoparticles. The average size of the agglomerates is about 1 μm (Fig. 2*a*). The initial stage of sintering obtains at temperature 675°C; contact arises between particles in agglomerates. During sintering at 950°C necks form in the region of contact and grains no larger than 1 μm are formed (Fig. 2*b*); the relative density of a compact equals 80%. As sintering temperature 1200°C the porosity decreases to 10% and recrystallization occurs, as a result of which grain growth to several microns occurs (Fig. 2*c*).

The elemental composition of the phases formed at sintering temperatures 675, 950, and 1200°C is determined on microsections of samples by means of energy-dispersive microanalysis. The regions from which spectra of the charac-

TABLE 1. Sintering Regimes and Density of TiO_2 and ZnO Based Ceramic

Experimental no.	Sample	Sintering temperature, °C	Isothermal soaking time, h	Density, g/cm^3	Relative porosity, %
1	Pressing	–	–	2.1	60
2	Compact 1	675 ± 5	2	2.3	55
3	Compact 2	950 ± 5	2	4.1	20
4	Compact 3	1200 ± 5	2	4.5	10

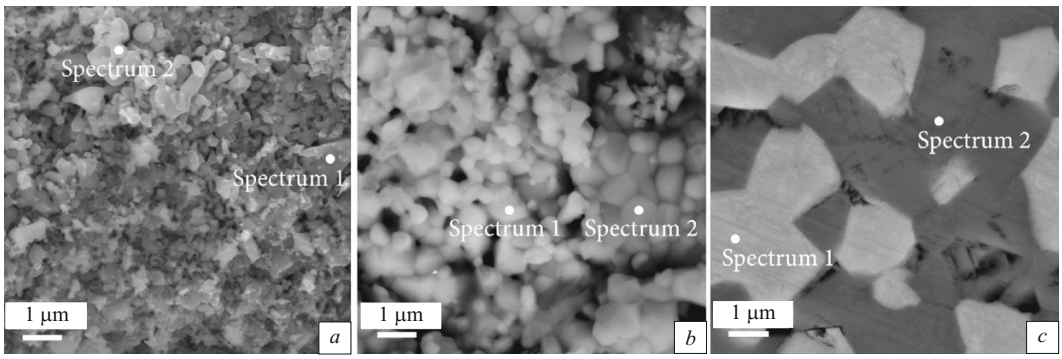

Fig. 3. Electron-microscopic images (SEM) of microsections of sintered samples at temperatures: *a*) 675°C; *b*) 950°C; *c*) 1200°C.

TABLE 2. Elemental Composition of Phases in Sintered Samples of TiO_2 and ZnO based Ceramic

Spectrum no.*	Content of elemental atoms, %, in samples fired at temperature								
	675°C			950°C			1200°C		
	O	Ti	Zn	O	Ti	Zn	O	Ti	Zn
1	51.28	1.52	47.20	57.38	13.29	29.33	48.96	–	51.04
2	51.35	1.76	46.89	52.62	–	47.37	57.06	13.93	29.01

* See Fig. 3.

teristic x-ray radiation were obtained are displayed in Fig. 3; the elemental composition is presented in Table 2.

Electron-microscopic images of the microstructure of microsections (see Fig. 3) were obtained in back-scattered electrons; this makes it possible to distinguish phases by atomic mass. If composition nonuniformities are present in the sample material, the image obtained in back-scattered electrons has well-distinguished phases with sharp boundaries and graded grey coloration. Oxygen and the heavier zinc are present in the light-grey grains, while zinc and the lighter titanium and oxygen were found in the darker grains. Thus, on the basis of the elemental composition (Table 2) the following phases are present in the samples: only zinc and oxygen (ZnO) are present in the first phase and titanium, zinc, and oxygen (Zn_2TiO_4) are found in the second phase.

Grains in which only titanium and oxygen are present, i.e. upon sintering all of the titanium oxide interacted with zinc oxide with zinc orthotitanate being formed, are absent in the sintered samples. The volumetric ratio of zinc titanate and zinc oxide is approximately 1 : 3.

CONCLUSIONS

Ceramic with the required ratio of the phases Zn_2TiO_4 and ZnO was obtained on the basis of zinc and titanium oxide nanopowders.

The sintering temperature, equal to 950°C, is optimal from the standpoint of the formation of the disperse phases Zn_2TiO_4 and ZnO, whose sizes correspond to less than 1 μm. Energy-dispersive analysis shows that the sintering temperature 950°C is adequate for completion of all solid-phase interactions.

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