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FORMATION OF MATERIAL PRESCRIBED PHASE COMPOSITION FROM REFRACTORY FILLER SILICA POWDER MODIFIED WITH ALKOXIDE AND SOL-GEL COMPOSITE

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Creation of ceramics and refractories with improved physicomechanical properties is possible with use of nanomaterials in their technology. Introduction of SiC nanoparticles into a ceramic material charge by using modified filler powders is proposed. Fillers modified with tetraethoxysilane during grinding leads to powder crystal structure breakdown and SiC mechanochemical synthesis. The amount of β-SiC synthesized in this way depends on the amount of modifying additive. Results are provided for modified filler phase composition before and after heat treatment at 1000°C, and mechanochemically synthesized SiC thermal stability is established. It is shown that sintering of modified electro-corundum worsens with an increase in amount of synthesized silicon carbide nanoparticles. The difference is demonstrated in phase composition formation with heat treatment of a mixture of modified and normal finely ground electrocorundum with a sol-gel binder and firing up to 1600°C. Silicon carbide nanoparticle synthesis does not exceed 3 – 7 % in both cases. Recommendations are given for use of corundum filler with a different amount of modifying additive.

Keywords: filler, modification, tetraethoxysilane, synthesis, β-SiC nanoparticles, powder sintering, phase composition.

Scientific and technical progress in the field of new technology and in many branches of industry is impossible without creating composite materials with prescribed properties. Development of up-to-date technology and import substitution materials for various branches of industry, including metallurgy, is the main task of ceramic materials science. Use of mechanochemistry and the sol-gel process in creating composite materials makes it possible to improve significantly their physicomechanical properties and operating indices due to creation of prescribed structures and synthesis of prescribed phases.

Use of a sol-gel process and mechanochemical action in order to intensify synthesis of prescribed refractory compounds, and creation of structures providing improved physicomechanical properties of composite materials, refractories, and coatings, is very promising [1 – 8].

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Studies have shown [3, 4, 6] that modification of refractory compound powders, such as corundum, silicon carbide, silicon nitride, and others, during refinement with addition of elemental-organic substances, including tetraethoxysilane (TEOS), or ethyl silicates, provides breakdown of the crystal lattice structure of compounds of a systematic of non-systematic nature, amorphization of filler surfaces, and also synthesis of β-SiC nanoparticles, silicon oxynitride, and some other phases depending on the form of filler and thermodynamic potential of filler component reaction with silica at certain temperatures. A good example of forming prescribed phases of composite material is use of modified TEOS as a filler or ethylic silicate electrocorundum powder due to the fact that diffraction peaks for α- and β-Al_2O_3 do not coincide with peaks for mechanochemically synthesized β-SiC [3], which makes to possible to be sure of synthesizing silicon carbide nanoparticles both during mechanochemical activation, and during heat treatment of gels and their mixtures with filler.

It has been established [3] that during mechanochemical action, even after one hour of grinding electrocorundum with addition of 1% TEOS, β-SiC nanosize particles and silicon oxynitride are synthesized. Results of studying modified electrocorundum are presented in Fig. 1.

During reaction of modified electrocorundum, within which nanoparticles of β-SiC and Si_2ON_2 are already synthesized mechanochemically, with silica sol-gel binder at a heat treatment temperature of 1000°C, mullite formation is not detected by x-ray phase analysis (XPA) (Fig. 2), but thermally stable mechanochemically synthesized compounds β-SiC and Si_2NO_2 are present within diffraction patterns for a corundum matrix.

Reaction of corundum with amorphous SiO_2 within the composition of a sol-gel composite, physicomechanical processes occurring during heat treatment of a mixture of corundum and the composites mentioned above, is of specific scientific interest. Thermal destruction of sol-gel composite affects softening and sintering of self-hardening mixes, and their good wetting capacity makes it possible to distribute these composites in a thin layer over the surface of electrocorundum, both modified and also unmodified by an elemental-organic substance. During polycondensation of polyethoxysilanes [7] around electrocorundum grains, within structural defects and at the surface, there are nuclei of mechanochemically synthesized crystals of silicon oxynitride and β-SiC, there is polycondensation of TEOS hydrolysis products, and as a result there is formation of a cellular carcase of polysiloxane bonds ≡Si–O–Si≡. Their formation provides good strength properties for specimens of these mixes.

A sol-gel composite of stoichiometric composition provides higher casting strength indices. Since a coating consists of a mixture of finely ground electrocorundum with sol-gel composites, then gel thermal destruction within them shifts into a region of higher temperature, both on heating in air and during heat treatment in different atmospheres compared with pure gels. Thermal destruction on heating proceeds with more difficulty, particularly with high rates of an increase in temperature.

Thermal destruction of polycondensation products of ETS-32/80 hydrolysate on heating is accompanied by an exothermic effect at 360°C. With high heating rates and capture in a cristobalite gel carcase of ethoxy groups ($–OC_2H_5$) creation within it of clathrates of radicals ($–CH_3$) is guaranteed, which are a carbon source for synthesizing SiC in matrices using any fillers. Formation of clathrates ($–CH_3$) in a gel cluster followed by creation of an organo-inorganic complex $(–CH_3)–(SiO_2)_n$ guarantees matrix self-reinforcement by β-SiC nanoparticles, and presence of amorphous silica intensifies matrix sintering. On reaction of amorphous silica with corundum surface layer defects there is low-temperature synthesis of mullite even during reaction of sol-gel composite with unmodified electrocorundum (Fig. 3).

Study of the phase decomposition of fired mixes by the XPA method and petrographic studies showed that mullite is observed at all heat treatment temperatures for a mixture of modified filler with sol-gel composites. At 1100°C mullite is observed in an amount of 3 – 4%, both within specimens based on modified electrocorundum and in specimens based

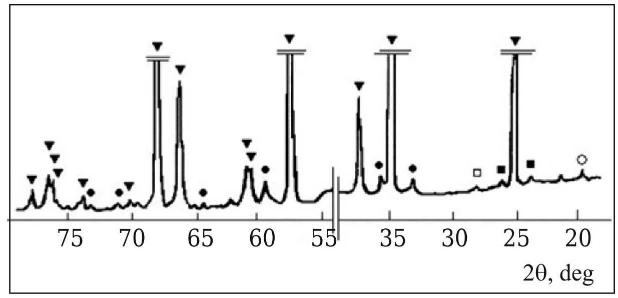

Fig. 1. Phase composition of electrocorundum modified with 1% TEOS after 1 h grinding: ▼) α-Al_2O_3; ●) β-SiC; ○) Si_2ON_2; ■) mullite; □) Si.

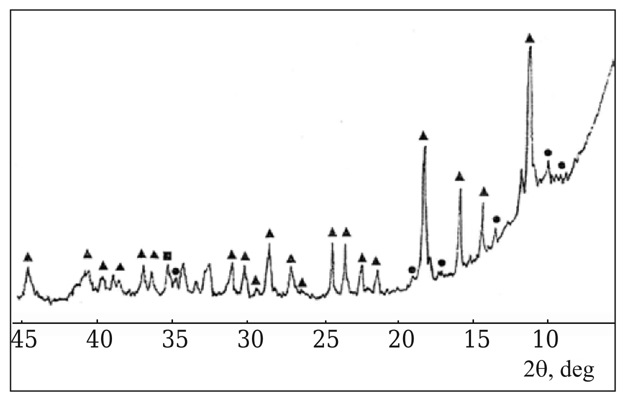

Fig. 2. Phase composition of a mixture of modified electro-corundum and sol-gel composition ETS-32/80 after heat treatment at 1000°C: ▲) Al_2O_3; ●) Si_2ON_2; ■) β-SiC.

in finely ground electrocorundum and sol-gel binder composite ETS 32/80. Material phase composition within these mixes changes differently with an increase in temperature. In specimens of a mix of electrocorundum modified by TEOS and sol-gel composite ETS 32/80, impregnated after drying, and even in mortar ETS 32/80B, there is intensification of mullite formation. The amount of mullite with an increase in temperature grows up to 60% (see Table 1). The amount of melt increases insignificantly with an increase in temperature by 500°C: from 3 – 4 to 5 – 6% with retention of β-SiC in an amount of about 5%. In these mixes β-SiC is present, whose nuclei formed during mechanochemical synthesis from organo-iorganic complex $(–CH_3)–(SiO_2)_n$. It is important to note that as a result of sintering there is formation of a densely sintered outgrowths of corundum grains, intergrown with mullite new formations in the form of particles with a size of 5 – 8 μm, and filamentary crystals with a size from 8 – 15 to 25 μm (Fig. 4). The amount of melt starts to increase at above 1500°C, but it does not exceed 8% at 1600°C.

The phase composition of specimens from mixes based on finely ground corundum and sol-gel composite ETS 32/80

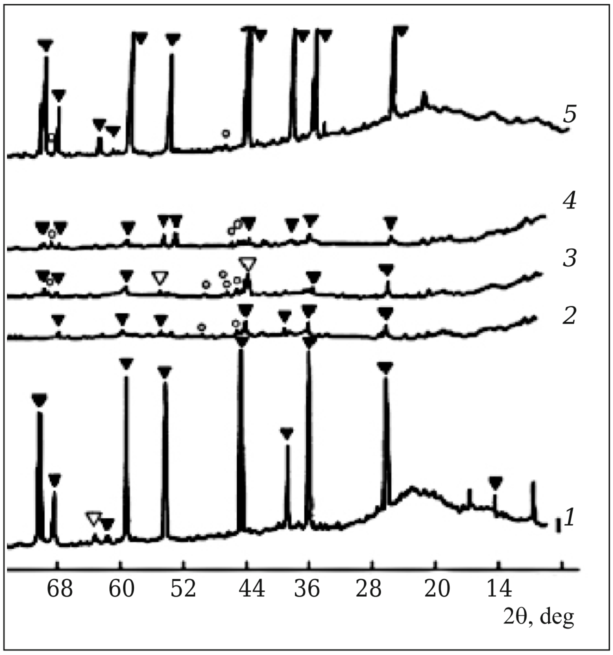

Fig. 3. Diffraction patterns of in situ mixture of electro-corundum and sol-gel binder with heat treatment temperature, °C: *1*) 900; *2*) 1000; *3*) 1100; *4*) 1200; *5*) 1300. Phases: ▼) α-Al_2O_3; ○) mullite; ▽) β-Al_2O_3.

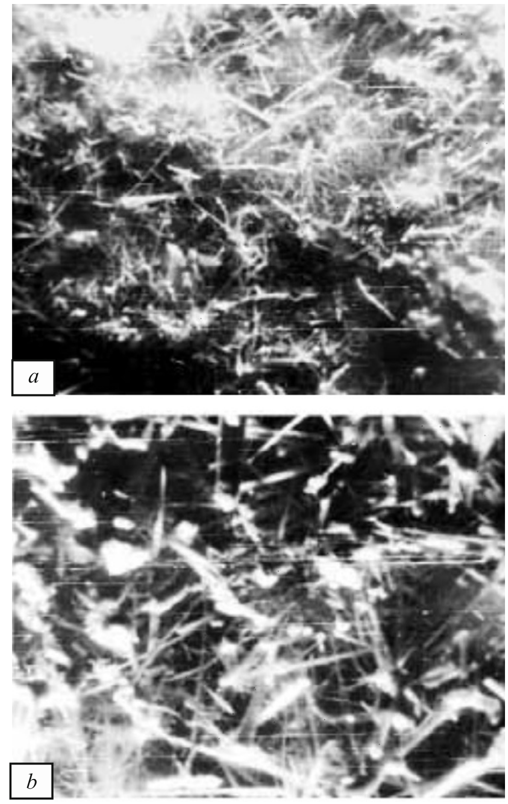

Fig. 4. Mullite synthesis in masses based on modified electro-corundum and sol-gel composition ETS-32/80: *a*) ×2800; *b*) ×12,000.

TABLE 1. Phase Composition of Mix Based on Modified Electro-Corundum and Sol-Gel Composite

Phase	Phase content, wt.%, after firing at temperature, °C				
	1000	1100	1300	1500	1600
Corundum	89 – 93	84 – 85	43 – 45	28 – 29	24 – 26
Mullite	1 – 2	3 – 4	43 – 44	53 – 56	59 – 60
Melt	—	3 – 4	4 – 5	5 – 6	7 – 8
Cryptocrystalline substance	1 – 2	1 – 2	3 – 4	3 – 5	—
β-SiC	2 – 3	3 – 4	4 – 5	4 – 5	4.5 – 6
β-cristobalite	3 – 4	1 – 2	—	—	—

TABLE 2. Phase Composition of Mix Based on Finely Ground Electrocorundum and Sol-Gel Composition

Phase	Phase content, wt.%, after firing at temperature, °C					
	1000	1100	1300	1400	1500	1600
Corundum	87 – 89	83 – 86	80 – 84	77 – 80	74 – 77	67 – 70
Mullite	3 – 4	4 – 5	5 – 6	7 – 8	10 – 12	13 – 15
Melt	—	3 – 4	3 – 4	5 – 6	6 – 7	7 – 8
Cryptocrystalline substance	2 – 3	3 – 4	4 – 5	4 – 3	2 – 3	2 – 3
β-SiC	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5

is represented by corundum and mullite, β-SiC, melt, and cryptocrystalline substance (Table 2).

With an increase in temperature the corundum content decreases from 83 (at 1100°C) to 67% (at 1600°C), and the amount of melt also increases from 4 to 8%, but does exceed 8%. The amount of β-SiC at 1100 – 1500°C is constant, and only at 1600°C increases by 0.5 – 1%. The amount of mullite increases from 6 to 15% with an increase in heat treatment temperature from 1300 to 1600°C (see Table 2). There is no β-cristobalite within this composition. Probably it is within cryptocrystalline substance. XPA shows presence of α-quartz and stishovite at higher temperature. Presence of SiO_2 in different polymorphic phases may affect the increase in amount of melt with an increase in temperature.

Mechanochemical activation of electrocorundum powder and use of ultrafine highly amorphous highly active silica, forming a melt [1] during heat treatment of a mixture of Al_2O_3 and sol-gel composite at 1100°C, facilitates intensification of sintering and formation of filamentary mullite crystals within a corundum matrix.

With an increase in amount of modifying addition during refinement of corundum filler there is intensification of mechanochemical synthesis of silicon carbide, and the amount of β-SiC particles in modified filler increases. The content of synthesized β-SiC is determined by the amount of carbon precursor, formed as a result of mechanochemical ac-

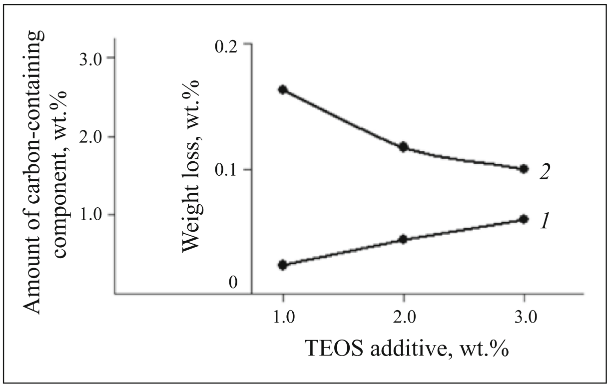

Fig. 5. Dependence of modified electrocorundum powder weight loss after heat treatment at 1000°C (*1*) and amount of carbon-containing components within it (*2*) on amount of TEOS additive.

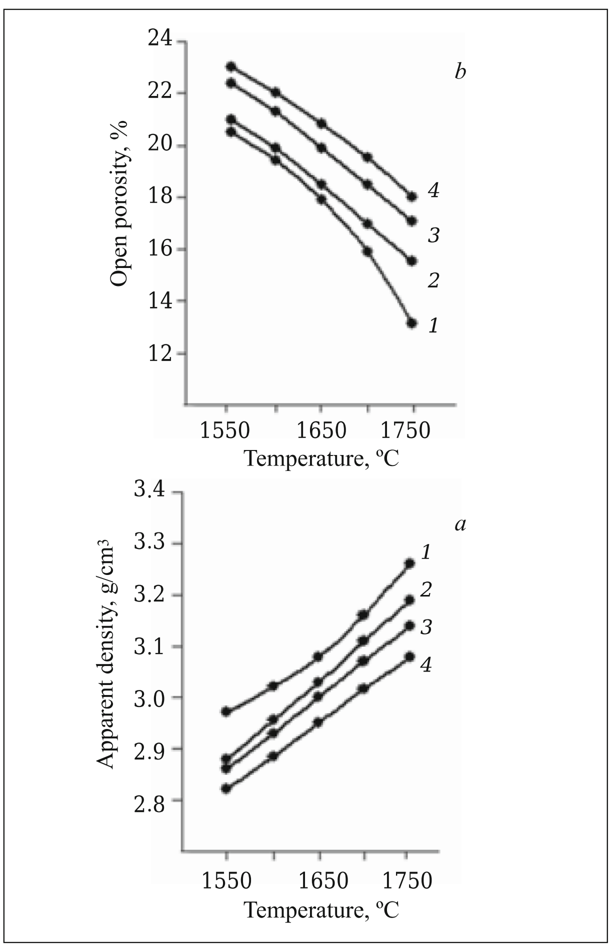

Fig. 6. Dependence of apparent density (*a*) and open porosity (*b*) for a mass of electrocorundum modified with TEOS additive on temperature. Amount of additive shown on curves, wt.%.

tion on organo-inorganic complex (–CH_3)–$(SiO_2)_n$. As studies showed, with use of 1% tetraethoxysilane for powder filler modification the amount of synthesized β-SiC does not exceed 3% (Fig. 5). The amount of carbon-containing component in modified electrocorundum with heating up to 1000°C decreases with an increase in the amount of TEOS modifying addition. This is probably connected with a looser electrocorundum structure, modified with a considerable amount of TEOS, and better access of oxygen to carbon system components, formed during mechanochemical action on elemental organic substance.

The amount of mechanochemically synthesized β-SiC depends on the amount of carbon precursor in modified electrocorundum. With an increase in content in radicals of (–CH_3), ordered and disordered carbon, fullerines C_7 – C_{11}, and other representatives of C precursor forming during TEOS mechanochemical destruction, the synthesized β-SiC content will increase. A study of electrocorundum sintering, modified by a different amount of TEOS, showed that with an increase in amount of mechanochemically synthesized β-SiC in the form of nanoparticles sintering of finely ground electrocorundum worsens (Fig. 6), as also occurs with introduction of normal silicon carbide.

Thus, depending on the purpose of modified electrocorundum it is necessary to select in technology an amount of TEOS modifying addition. In order to create a dispersion-strengthened matrix it is preferable to use 1% addition of elemental organic substance for modifying refractory compound powders [3, 4]. With a requirement for introducing a considerable amount of SiC for self-reinforcement of a matrix it is possible to use powders of refractory filler, modified by 3% TEOS addition.

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