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FEATURES OF HIGH-STRENGTH COMPOSITE MATERIAL STRUCTURE CREATION

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The basis of technology proposed is use of a sol-gel method for preventing polycrystalline corundum fiber from crystallization during heating to high temperature and for low-temperature synthesis of prescribed phases in a corundum matrix with the aim of improving the operating properties of composite materials based on corundum. As a result of firing a charge based on corundum powder modified with tetraethoxysilane and polycrystalline corundum fiber modified with ethylsilicate-32 at 1360°C materials are created with very good strength properties. The materials exhibit electrical insulation properties and are stable in ionized gas streams at the level of known analogs as a result of creating self-reinforced mullite and β-SiC corundum matrix, reinforced with polycrystalline fiber and rapidly sintered due to presence of silicon oxynitride.

Keywords: structure, CM, mullite, modified fiber, tetraethoxysilane (TEOS), silicon oxynitride, β-SiC.

Progress in the field of high-temperature materials is mainly connected with development of good technology in ceramic materials science. Currently special attention is being devoted to the question of developing and introducing energy saving technology. A significant amount of domestic and overseas publications is devoted to this problem, and also a method for synthesizing heat-resistant materials with prescribed properties.

In order to accelerate scientific and technical progress in various branches of industry, increasing the efficiency of various products, it is necessary to create and introduce new advanced processes and equipment, whose operation is connected with high temperature and other extreme conditions. The intensity of scientific research and development in ceramic materials science gives rise to solution of urgent problems such a requirement for creating new materials for advanced branches of industry, new technology, energy saving, and a reduction in the requirement for scarce materials and environmental protection. The twenty first century is a century of ceramics, since the properties of advanced ceramics are at the boundaries of metals and alloys based on them, and it should resolve very many problems of progress. Improvement of existing high-temperature materials and development of new materials exhibiting a set of properties satisfying specifications of extreme operating conditions is a task requiring a search for new ways of material synthesis. There is increasing interest in use of a sol-gel method in ceramic materials science for low-temperature synthesis of prescribed phases with the aim of improving material operating properties, and also in order to reduce the sintering temperature of materials based on refractory oxides, including those based on corundum. Creation of new composite materials (CM) and implementation of the possibilities of their extensive use are typical trends of contemporary development in science and technology.

Development of high-tech ceramic materials facilitates development of new technology, which as a result of carrying out research at the molecular level makes it possible instead of improving existing materials to create new materials with special properties and for special purposes.

Special possibilities of building the structure of ceramic matrices develop as a result of creating intergranular boundaries of synthesized phases of prescribed composition and morphology with use of silicon alkoxide and a sol-gel composite based upon it.

It follows from published data that there has been inadequate study of methods of modifying refractory fillers, par-

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ticularly various forms of fiber, by introduction of organic additives into a ground system, including organosilicon. Use of silicon alkoxide for this purpose becomes even more popular in CM technology based on refractory fillers, including those based on corundum.

A search for methods for intensifying sintering of different fillers for manufacturing structural and composite ceramics, and their modification during grinding with various surfactants, including organosilicon substances, has led to a choice of a quite universal modifying substance whose use gives the desired result in preparing materials with prescribed properties [1].

As an additive leading to significant structural breakdown of the systematic and non-systematic [2, 3] character in a refractory filler crystal lattice during grinding, silicon alkoxide is used in the form of tetraethoxysilane (TEOS) or ethyl silicate (ETS), which have been used in creating CM based on corundum and fibers using a combined sol-gel binder [4]. Silicon alkoxide additive has also been used during modification of polycrystalline and kaolin fibers.

The task is development and also explanation of features of the CM manufacturing technology with a special structure based on corundum and Al_2O_3-containing fibers, and objects of complex configuration based on it with high density and life within streams of ionizing gases.

The system Al_2O_3–SiO_2 [5 – 8] is fundamental in creating CM based on corundum using kaolin and polycrystalline corundum fiber, modified with addition of silicon alkoxide, since in fact mullitizing of a corundum matrix leads to an increase in strength properties and thermal shock resistance [9]. Mullite synthesis with small amounts of amorphous silica within a corundum matrix commences significantly below 1000°C, decomposition develops at 1100°C, and this intensifies sintering of material based on corundum ad fibers. A film of amorphous silica, covering a fiber surface, reinforces it, slowing down crystallization, and this improves composite material physicomechanical properties.

In this case development of materials reinforced with ceramic fibers started with selection of a production process, which makes it possible to prepare objects with prescribed properties and structure. Key features that have been considered in developing the required materials were the following:

– composite material should exhibit a uniform fine-grained structure, providing good strength properties;

– fiber reinforcing component of a CM should be prevented from recrystallization;

– machining of a raw material surface (workpiece) of the materials developed, since during machining of fired ceramic cracks may form, and an expensive hard alloy tool is required;

– provision of molding for an object of complex configuration from a charge with very fine components and fiber component, and machining of objects using a modified thermoplastic binder.

In order to prepare very fine materials starting components were dispersed and simultaneously mixed in a ball mill. The grinding rate for fibers is significantly greater than for refractory materials, and therefore fibers were charged into a mill after the main components were almost ground to the required size. A modifying addition was made to the mill together with fibers in an amount 1 – 3% of the charge material weight. A considerable increase in workpiece density is noted with use of fibers modified in water. The density of material based on a thermoplastic binder increases more significantly with an increase in firing temperature on introduction into a mix of a considerable amount of modifier (Fig. 1).

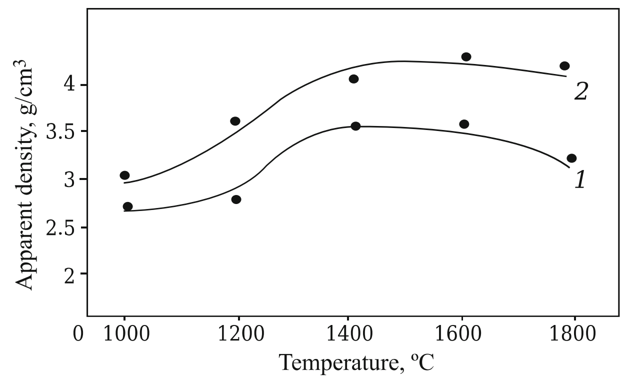

Fig. 1. Dependence of CM based on thermoplastic binder apparent density on sintering temperature and amount of modifier (*1* is 1%, *2* is 3% silicon alkoxide) of polycrystalline Al_2O_3 fiber.

It has been established that a film of amorphous silica modifier applied to a fiber surface amorphizes a fiber surface (Fig. 2) and delays its crystallization. Reaction of ethyl silicate binder with corundum filler has been studied in microsections and micropowders in an MBI 15U4.2 microscope with a high-temperature attachment.

The temperature for appearance of a melt during specimen firing has also been studied. Powders of unfired original materials in immersion preparations on flat polished plates were placed in a heating muffle, whose temperature increase was accomplished at a rate of more than 10 °C/min. Appearance of a melt (Fig. 3) was recorded at 1000 – 1100°C in mixtures of finely ground electrocorundum with ethyl silicate binder.

Appearance of a melt at temperatures lower than normal on reaction of aluminum oxide with amorphous very fine silicon oxide from ethyl silicate binder has a favorable effect on intensifying sintering and preparation of material with low porosity, particularly with high firing temperatures. An increase in material density during sintering facilitates an increase its physicomechanical property indices.

During firing at above 1350°C acicular mullite crystals are synthesized within corundum grains and within the binder part of a corundum matrix (Fig. 4).

Use of silicon alkoxide during grinding refractory compound powders affects the nature of powder dispersion and structure. During grinding there is a change in organic substance structure, the rate of heat of its dissolution, melting temperature, and its other properties. As is well known

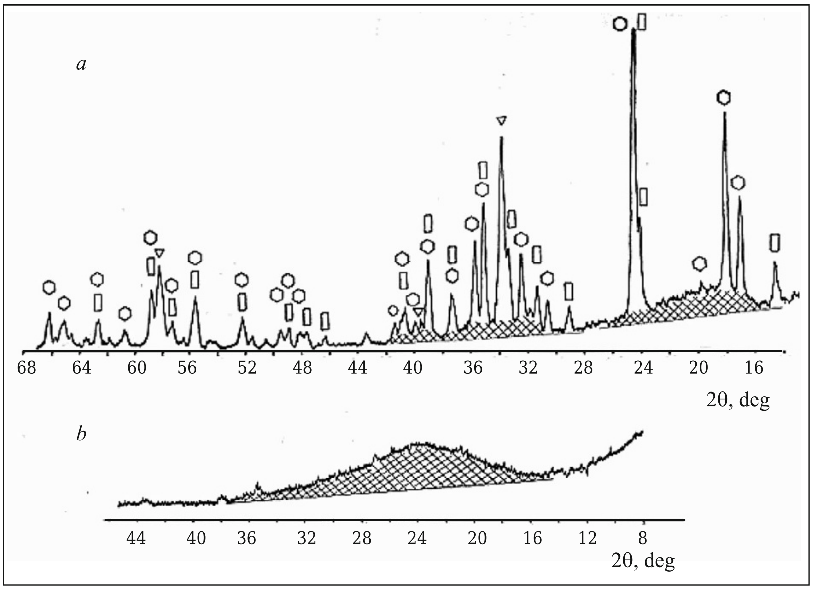

Fig. 2. Diffraction patterns (CU $K\alpha$-radiation) for material fired at 1580°C (*a*, 40 kV, 25 mA) and modified (*b*, 35 kV, 22 mA) polycrystalline fiber: ○) corundum; ▯) mullite; ▽) silicon carbide; ⬡) silicon oxynitride Si_2ON_2.

Fig. 3. Appearance of melt at corundum filler surface. Transmitted light. ×1600.

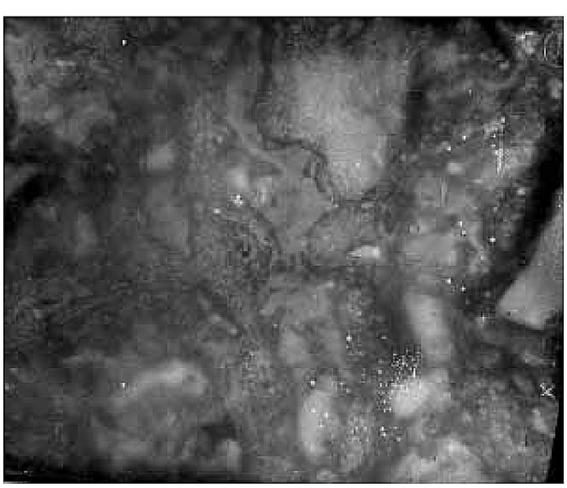

Fig. 4. Corundum matrix mullitization. ×280.

mechanochemical dispersion of high molecular compounds leads to breakdown of weak molecular interaction, and to breakage of valence bonds of the main polymer chain, and as a result of this free radicals of a reactive nature appear, which by reacting with the surface of modified mix components may change their properties and nature of interaction. With conversion of silicon alkoxide a radical (?CH_3) arises, which is a precursor of components for synthesis of silicon carbide and oxynitride, and also silicon nitride.

It is well known that an obligatory condition for SiC synthesis from organosilicon substances is presence of hydrogen in a synthesis medium. In studying electrocorundum modification formation has been established of hydrogen and methane and a change in the amount of them during modification as a result of alternate destruction on polycondensation products of silicon alkoxide hydrolysis on mechanochemical synthesis of compounds. An increase in temperature and pressure observed within microvolumes of ground powder activates mechanochemically conversion of hydrolysis and pyrolysis products, and this leads to creation of pressure within a grinding unit as a result of forming methane and hydrogen, which reduce to silica of a silica cluster skeleton to silicon monoxide. As a result of this within the region of a “magma-plasma” within reactors (cavities of a gel cluster of β-cristobalite structure) in air there is synthesis of refractory compounds β-SiC and Si_2ON_2, and in nitrogen α-Si_3N_4. During synthesis gas pressure within a mill decreases, and mechanical and thermal destruction of products of an organo-inorganic complex (–CH_3)–$(SiO_2)_n$ increases (Fig. 5). Presence of H_2 and CH_4 and a change in pressure during grinding are confirmed by chromatographic analysis and a water manometer respectively. β-SiC is synthesized in the region of 760°C.

Grinding corundum with addition of silicon alkoxide provides stable mechanochemical synthesis of structurally improved metastable mullite phase, which is confirmed by x-ray phase analysis.

Thorough mechanochemical processes during grinding corundum with addition of silicon alkoxide cause breakdown of the α-Al_2O_3 crystal lattice, and as indicated above amorphization of the surface layer of refractory filler, with which amorphized silica of modifying addition is in contact. There is close order self-organization in areas of α-Al_2O_3 disordered structure with amorphous silica in close contact with it at the instant of concentrated impact in the direct of forming cybotaxical groups AlO_4, AlO_6, and SiO_4 in ratios required for mullite synthesis. Mechanochemically synthesize (550°C) mullite is retained at normal temperature for an

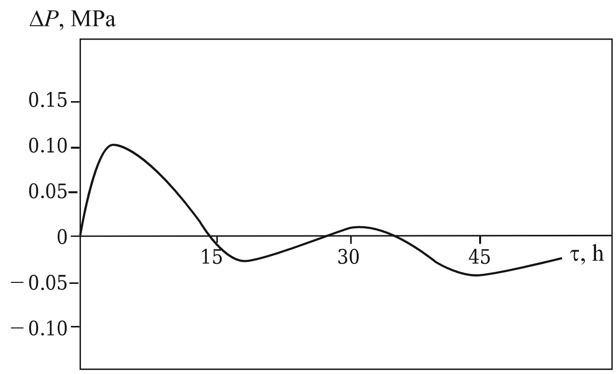

Fig. 5. Change in pressure ΔP in a mill during modification of filler (electrocorundum) with silicon alkoxide during grinding in a ball mill.

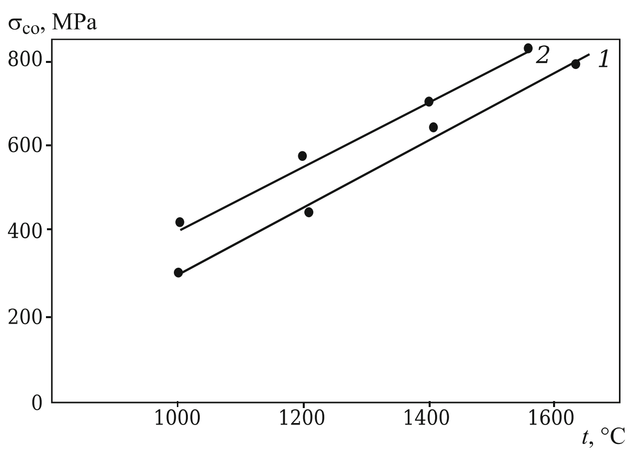

Fig. 6. Dependence of CM ultimate strength in compression σ_{co} on firing temperature *t* and sintering atmosphere: *1*) reducing; *2*) nitrogen.

indefinitely long time, but at elevated temperature its thermal stability falls rapidly. With action of high temperature during firing of modified corundum there is healing of α-Al_2O_3 structural defects. Within modified corundum fired at 1000°C there are only traces of mechanochemically synthesized mullite, and mechanochemically synthesized β-SiC is thermally stable and there is even growth of its nanoparticles during firing. The size of mullite crystals does not exceed 0.1 μm. A band appearing after 1 h of grinding at 750 $cm^{?1}$, answerable for mullite, increases with an increase in grinding duration. As a result of firing at 1360°C material is created with very good strength properties, exhibiting electrical insulation properties (Fig. 6).

Thus, use of corundum filler and polycrystalline fiber powders modified with silicon alkoxide

appeared to be useful for creating CM with a prescribed structure and properties, and objects of complex configuration from them resistant to corrosion in streams of ionized gases, and also in creating high-strength crack-resistant structural ceramics based on silicon carbide and nitride, and dense corundum coatings for protecting graphite from oxidation.

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