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THE STUDY OF TECHNOLOGIES TO IMPROVE PHYSICAL-MECHANICAL AND CHEMICAL PROPERTIES OF REACTION SINTERED CERAMIC MATERIALS ON THE BASIS OF SILICON CARBIDE

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Summary. *The ways of improving physical-mechanical and chemical properties of reaction-sintered ceramic materials based on silicon carbide are described. Various means of processing ceramic materials are studied and analysed. The technologies of obtaining the resulting components, removing free silicon from products, and binding impurities in the surface layers are improved. It is found that the increase of operating temperatures and the use of ceramic materials based on silicon carbide in demanding conditions can be achieved by introducing additives into the mix, strengthening the dispersed particles and applying a protective coating. The synthesis and crystallization of secondary silicon carbide on the grains of primary silicon carbide, and dissolution and recrystallization of submicron particles of primary silicon carbide occur at high temperatures and in the presence of molten silicon. Based on the published data analysis and conducted research, the complex of measures for improving physical-mechanical and chemical properties of reaction sintered ceramic materials based on silicon carbide is proposed.*

Key words: *silicon carbide, heat resistance, ceramic materials, protective coating.*

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Problem setting. Ceramic materials on the base of silicon carbide (carborundum) are widely used in different technique branches due to high temperature firmness, low compactness, high Yung module, low coefficient of warm widening, high firmness, high resistance to wearing out and the erosion deficiency [1]. Among the ceramic materials, the widest extension got self-bound silicon carbide received by reactionary clinkering. It represents by itself almost no-porous two-phase composition, which consists on 80 – 90% of silicon carbide and on 5 – 20% of free silicon [2]. The working temperature increasing and the rigid conditions of exploitation of carborundum products demand the improvement of existing methods of ceramic getting and the development of new ones. This difficult problem solution at present time is reached by different ways.

The uttermost investigations and publications analysis. There are different ways of technology improving and the improvement of physic and mechanic and chemical properties of ceramic materials on the silicon carbide base [3, 4]. The main imperfection of goods on the base of silicon carbide is their low stableness to exploitation at high heating temperatures, high temperature oxidation, connection destruction between the ceramic grains and the material solidity loss [2]. The perspective direction of the given problem solution is the investigation of improving technologies of physic-mechanic and chemical properties of ceramic materials on the silicon carbide base. To increase working temperatures and supply the using under more rigid exploitation conditions of ceramic materials on the base of silicon carbide can be done by the way of admixture insertion into the batch, by the strengthening with dispersed parts and by the coating of deterrent coating.

Research objective is the research of the improving technologies of physic and mechanic and chemic properties of ceramic materials on the base of silicon carbide.

Research results. One of the ways of technology improving is the using for the material receiving advanced initial components, which comprise the minimum quantity of inevitable admixtures [5]. The solidity for the bend in such reactionary and baked material at 1000°C is $630 - 770 \text{ MPa}$ that allows using it for the crucial details producing of gas turbines, diesel engines, and also goods, which work under the conditions of simultaneous action of corrosive medium and high temperatures. Carbide and silicon materials are characterized mainly by covalent type of chemical connection, which differ by little strength. High values of prolonged solidity has the material with the increased grain purity. Insertion even of little quantity of boron, aluminium or carbone admixtures leads at high temperature to among grain destructions. Great impact on physic and mechanic properties (heat conductivity, specific electric resistance, the coefficient of thermo expansion and firmness) of carborundum ceramic realize admixtures, brought into material as with initial components and in the process of its receiving [6]. Arranging mainly on grain limits, admixtures give heat insulation for them and reduce at this time ceramic effective heat conductivity. Equally, with this it is observed the changing of specific heat resistance, as the silicon carbide grains have low heat conductivity, and additive phases create in the material capacity on the grains limits heat conducting grid. Even partial refinement of initial components from metal and other admixtures appreciably increases some carbide and silicon ceramic characteristics.

Great attention at given time is paid to the studying of the granulometric (grain-size) composition and the initial components structure influence on the carborundum ceramic physic and mechanic properties. It is established [7], that the reactionary burnt carbide and silicon material firmness is structurally sensory. The most accessible and affective managing way by material firmness is the size changing and the fraction correlation of carbide and silicon initial powders. Two directions of strong structures formation are possible: carbide and silicon carcass monolithization simultaneously with the diminutium of the concentration of free silicon and structure homogenization [8]. At high temperatures in the presence of silicon melt the synthesis and the reiterative silicon carbide crystallization on the grains of initial SiC , and also dissolution and re crystallization of primary silicon carbide submicronic elements. It leads to the contact reduction, and in the combination with the large compactness – to the creation of local grain accumulation of strong attachments, when initial grading is essentially violated. Structural and transformation role of physic and chemical processes is being increased with the transition to the thin grained compositions. The material firmness is also increased with the level rising of homogeneity of ceramic structure toward the diminution of rupture between the big and small grains SiC , dispersion and more crammed mutual distribution of carbide and silicon and silicon phases, the decrease of medium size of the grain in the multiple factionary creases, given processes can further the formation of solid structures or include them. In the multiple factionary structures case the homogeneous factors influence is developed very apparently, the ceramic firmness is increasing from the big fraction to the middle or small.

Concurrently with the carbide and silicon ceramic quality and grain-size composition for its property improvement significant impact has the technology of material getting, which in particular cases supplies one phase ceramic formation that is close to the mono-crystal silicon carbide as to its properties. With the purpose of increasing of exploitation good baked of reactionary baked carbide and silicon materials characteristics before pressed porous half finished products are soaked in silicon [7]. Such operation improves their working up, wear and corrosive resistance and heat stability, nevertheless, with exploitation temperature increasing the composition firmness is lessening. Lets consider some stages of technology process of improvement of physic and mechanic and chemical properties of carborundum by the way of admixture addition, strengthening and coating.

Admixture consummation. For the activating of carbide and silicon ceramic clinkering processes into the batch is put little additive quantity (1 – 2 mas. %), in the quality of which are used aluminium, boron, beryllium, iron, yttrium, nickel, cobalt powders and others [8]. As effective admixtures can be used aluminium, beryllium, hafnium oxides and rarely land metals. Admixtures provide the material with high thickness, heat resistance and mechanic solidity, the resistance in sulphuric and nitric acids, sufficient heat conductivity and wear resistance. Ceramic exploitation in the high temperature conditions (1200⁰C and higher) leads to the decreasing of its specification figures. Essential improvement of carbide and silicon ceramic physic and mechanic properties is attained by the way of putting into the batch to 15 mas. % one or several following oxides: Al_2O_3 , V_2O_3 , Y_2O_3 , MgO , Fe_2O_3 , Br_2O_3 and others. Simultaneously with the increasing of pressed material thickness, which attains 98%, its thermodynamic ability is augmenting and heat resistance, at 1400⁰C firmness limit on the bend is more than 50 MPa. However, the resistance to the oxidation and thermic strokes heavily depends on the nature and the quantity of secondary phases, which are formed on the grain boundaries by means of thickening oxide admixtures. Concurrently with the oxides in the additive role are successfully used oxygen – free refractory junctions: carbides, nitrides and borides [8].

Strengthening. One of the directions, which gives the possibility to improve ceramic physic and mechanic properties, is its strengthening with the dispersed parts, threadlike crystals and fibers [9]. Consummation into carbide and silicon ceramic disperse parts of carbide and titanium dyboride increases the material heat resistance in the interval 1000 – 1400⁰C. In the case of ceramic matrix reinforcement by SiC fibers with the length 40 – 50 mkm matrix tenacity is enhanced into 2 – 4 times, and at the next part insertion ZrO₂ with the size 0,6 mkm it raises more than 5 times. Ceramics, strengthened by silicon carbide fibers, has high thermic and chemical resistance, the resistance of cracks and stroke development, and also high tenacity. Its destruction energy is approximate to the energy of ruin of aluminium alloys, that allows to use given ceramic composition for the component manufacturing of internal combustion engine [9].

Covering coating. The main imperfection of reactionary baked carbide and silicon composites is their low resistance to the high temperature oxidization. The oxidation process limiting stages are: 1) oxygen diffusion via pellicle SiO₂; 2) on the distribution surface reaction SiC-SiO₂; 3) contrary diffusion of gasiform CO via pellicle SiO₂. As its result, on the composite surface the bubbles are appearing, fissures, that leads to the reduction of material technique characteristics. For the goods manufacturing, which are operated at high temperatures, is recommended baked α -SiC, which doesn't contain free silicon. Such material solidity on the bend can reach 460, and on the pressing 3900 MPa, elasticity module is 410 MPa. It is stable to the oxidization and the gas medium action to 1650⁰C, its thermal conductivity in 10 times higher, than silicon nitride and in 3 times higher, than in stainless steel. However, significant dissention of the firmness coefficients complicates its usage when devising mechanically loaded components. As the research results affirm, the heat resistance of self-fixed silicon carbide depends on the nature and the quantity of among grain secondary phases, and also final residual porosity. Such task solution is reserved by the way of using of different kind protective layers [10].

With the aim of increasing of silicon carbide good resistance to oxidization they are covered (coated) with silicon and are warmed. While this the silicon is filling up the porosities, reducing the material porosity to the level less 2%. Ceramic siliconation and titaniumation does not only protect it from the aggressive medium action, but also avoids the cracks distribution in the outer material layer, and also in 2 times increases the tenacity to the destruction, for instance, at room temperature it is 2,95, and at 1300⁰C – $6 \text{ MPa} \times m^{1/2}$. The firm Ceramic Refractory Co proposes for the construction protection of carbide and silicon ceramic ovens the coating like ET-4, which consists of diminished in size mixture of zirconium and zirconium dioxide in the colloidal suspension form. The coating with the thickness 0,035 – 0,075 mm coat

by means of dispersion. The firm coat cohesion is supplied by means of mechanic and chemical interconnection with the base and is differed from by great stability during exploitation, except of it, the coating has great emissive property. The coating isn't only covered on the production working part, but also on the strengthening fibers, which are used for the composition forming. Coating on the fibers of silicon carbide dioxide zirconium layer with the thickness 70 nm supplies the reserving of fibers mechanic properties under prolonged thermo action of oxidizing medium that affirms the using effectiveness of diffusive barrier on the distribution boundary fiber – matrix [10].

For the coat forming on the goods of reactionary-baked silicon carbide use the suspension, which attains 80 mas. % of highly qualitative silicon carbide 20 mas. % bentonite, which coat on the ceramic, and then anneal on the air at 1370°C [1]. Equally with growing of material firmness to the oxidization also improve its electric variables. It is also known the process of coating on carbide and silicon ceramic goods of paste, which contains the molybdenum silicide powder, water and adhesive admixture – methyl cellulose, with the next coating annealing in the air in the interval 1300 – 1500°C [1]. The coating protects effectively the ceramic construction from high temperature gas corrosion. In the case of given components using for the heating elements, which work at high temperatures, is observed the considerable increasing of specific loading (Vt/sm^2). With the purpose of work resource increasing of carbide and silicon heating elements they are soaked in suspension, which consists of molybdenum disilicide, water, polyvinyl spirit and dynatrium lorthophenol salt of disulphide acid, and anneal in the inert medium at 500°C [1]. Such coating provides with at 1480°C normal heater work during 2000 hours. Nevertheless, under the working temperature increasing drastically increases their specific load.

To increase the carborundum constructions heat resistance is possible by means of coating on them gas impenetrable protective layer of silicon carbide with the thickness to 0,01 mm, but such way is very difficult in technology accomplishment. For the receiving of high thermo resistance and high specific resistance of silicon carbide heating elements authors [10] suggest their diffusive satiation by boron carbide, which is realized by the way of surface moistening with Bakelite lacquer, the given surface girth is realized by means of breaking in by the layer of powder of boron carbide or the boron carbide mixture of 10 mas. % of silicon and the next thermo treatment (firstly in the air, and then in the protective atmosphere; the final stage is the heating in the hydrogen atmosphere at 2200°C during 1,5 – 2 hours.), on the product surface precipitates the layer of cubic silicon carbide. The mechanic firmness of the surface layer is stipulated by, that the coefficient of thermo expansion of silicon carbide and the triple junction of silicon with boron and hydrogen have approximate values, and also floating transition from the diffusive layer to the heater ceramic base. Equally with the advantages the given way has also disadvantages: the great amount of intermediate technology operations and the impossibility to work up the tubular products.

Protective coating application doesn't give necessary results, because of method specification of the product receiving from the reactionary baked carbide and silicon materials they include to 20 mas. % of free silicon. During ceramic exploitation at the limits of high temperatures the availability of incoherent silicon leads to the creation of great amount SiO_2 . Inequality of coefficients of linear widening of silicon dioxide and carbide while temperature changing causes local connection destructions between the grains and the losses of material firmness properties, especially, in the carbide and silicon heaters SiO_2 is accumulated in the porosities, as the result of this the element electric resistance is rising (the so called obsolescence) and the overheating is realized. All this causes additional difficulties when using carborundum heaters, because when one element is broken up the changing of all oven heaters is required, so far as in the working pivots the obsolescence processes are started and their electric parameters drastically differ from new heater variables [3].

Free silicon removing. To increase the effectiveness of coating protective action is possible by the way of preliminary removing of silicon out of carbide and silicon ceramic. Taking into consideration, that the velocity of silicon evaporation out of clear silicon is more higher, than out of carbide and silicon [3], its removing out of material can be realized by thermo way. Before explored researches showed, that the removing of removed silicon can be realized in the non oxidation atmosphere in the interval 1700 – 2000⁰C or in the vacuum ($p = 0,1 \text{ Pa}$) at 1600⁰C. To avoid the contamination of vacuum oven by silicon, that is evaporated, and also by admixtures, which are available in the material, the annealing is necessary to be realized in the medium suitable to absorb the silicon and other additives. On a level with the advantages given way has essential disadvantages: high process requiring the expenditure of much labor and the difficulty in the finishing of long products, apart from, in the examples there is approximately 4 mas. % of free silicon.

Free silicon removing can be realized and by chemical way, as it is known, that it is more active with the lithium hydroxide, natrium, potassium in the comparison with the silicon carbide, which has higher resistance in the different lixivium solutions [3]. The effectiveness of using of chemical removal of silicon out of reactionary baked carbide and silicon ceramic, which contains 10 mas. % of free silicon was explored by the authors of given work. The patterns were plunged into 35% water solution of lithium hydroxide and held during 60 hours. Chemical analysis results affirm, that in the models after the etching there is approximately 5 mas. % of removed silicon. To the given method advantages we can refer the simplicity of technology accomplishment and the possibility of good finishing of any configuration. However, thermo annealing and chemical treatment of reactionary baked carbide and silicon ceramic leads to the porosity growth, the detriment of firmness material properties, and also doesn't supply the total silicon removal. Correspondingly, it is necessary the additional ceramic finishing, as the result of which the free silicon tying and other concomitants was carried out, that are in the material in the refractory junctions. This will lead to the porosity lessening and the improvement of exploitation characteristics of carbide and silicon material.

Admixture tying. Admixture tying is the kind of finishing, which demonstrates the diffusive saturation of reactionary baked carbide and silicon ceramic with boron, as the result of which the silicon borides and other additives will be created. It is known, that silicon borides are characterized with high oxidation resistance, with the joining of high resistance of heat impact, and also have chemical inertness, good emitting ability and high thermo electric parameters [1]. Correspondingly, physic and chemical ceramic properties should be improved.

For some time past in practice it is more frequently used the powder method of borating. It was investigated the ability of its utilization for the binding in carborundum material of silicon and other admixtures, and also the saturation action on the changing of properties of finished material. Ceramic borating was carried out in the mixture, which contained boron carbide, languid stuff and fluoric activator [11]. Boron pattern probation in the air at 1500⁰C showed, that after the standing the test for 100 hours their mass and electric conductivity were changed insignificantly, at the same time as mass and electric conductivity of unfinished examples increased greatly [11].

The other additives binding, which are available in the material, is possible by means of siliconation. Nevertheless, as the investigations showed, the general disadvantage of the diffusive saturation processes is their long duration. The technology time diminution of finishing is possible after using joint boron and siliconation.

Admixture binding by the way of chemic and thermo finishing undoubtedly improves the ceramic physical and chemical properties. But, to increase its temperature exploitation regime is possible only by the way of using of poly layered heat resisting coating. The protective layer should have good adhesion with the ceramic base and should possess the high thermo and electric parameters. Except of it, the values of their coefficients of thermo expansion shouldn't

differ greatly. The components for the formation of highly temperature coating can be: silicon carbide, molybdenum disilicide, zirconium dioxide and yttrium oxide. The composition, created of above mentioned components, owns with good electric properties, and also protects safely from oxidation constructions, which work in the air in thermo cycling regime at 1500°C and higher. Formation on the good surface of the reactionary baked silicon carbide the layer of silicide oxide composition increases considerably their temperature regime and the exploitation term, especially under the conditions of reiterated changing of thermo regime [10].

Conclusions. On the base of literature data analysis and there can be suggested the complex of arrangements directed into the improvement of physic and mechanic and chemical properties of reactionary baked ceramic materials. The combination of determinate methods of carborundum ceramic finishing allows to widen considerably its using range and to increase the exploitation temperature regime. Henceforward we plan the investigations, connected with the development of poly layered thermo resistant coating on the silicon carbide base and molybdenum disilicide.

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ДОСЛІДЖЕННЯ ТЕХНОЛОГІЙ ПОКРАЩЕННЯ ФІЗИКО-МЕХАНІЧНИХ І ХІМІЧНИХ ВЛАСТИВОСТЕЙ РЕАКЦІЙНО-СПЕЧЕНИХ КЕРАМІЧНИХ МАТЕРІАЛІВ НА ОСНОВІ КАРБІДУ КРЕМНІЮ

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Резюме. Описано шляхи покращення фізико-механічних і хімічних властивостей реакційно-спечених керамічних матеріалів на основі карбиду кремнію. Досліджено та проаналізовано різні напрями обробки керамічних матеріалів, зокрема вдосконалення технології отримання вихідних компонентів, видалення вільного кремнію з отриманих виробів та зв'язування домішок у при поверхневих шарах. Встановлено, що підвищити робочі температури та забезпечити використання у жорсткіших умовах експлуатації керамічних матеріалів на основі карбиду кремнію можна шляхом введення добавок у шихту, зміцненням дисперсними частинками і нанесенням захисного покриття. Встановлено, що при високих температурах у присутності кремнієвого розплаву відбувається синтез і кристалізація вторинного карбиду кремнію на зернах первинного карборунду, а також розчинення й перекристалізація субмікронних частинок первинного карбиду кремнію. На основі аналізу літературних даних і проведених досліджень запропоновано комплекс заходів направлених на покращення фізико-механічних і хімічних властивостей реакційно-спечених керамічних матеріалів на основі карбиду кремнію.

Ключові слова: карбід кремнію, жаростійкість, керамічні матеріали, захисне покриття.

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