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PERSPECTIVE DIRECTIONS TO INCREASE HEAT TOLERANCE OF SILICONE CARBID AND MOLIBDENUM DISILICIDE BASED MATERIALS

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Resume. *Perspective directions to increase heat-tolerance of silicon carbide and molybdenum disilicide ceramic electric heaters have been outlined based on literary data analysis and research results. The producers of electric heaters solve such complex problem in various ways. The best way is improving ceramic materials production technology, in particular, use of initial materials with the least amount of harmful admixtures. Very often admixtures which get into the products during the manufacturing process influence physical and chemical properties of carbide silicon ceramic materials. They are located on the margins of silicon carbide grains and reduce the effective thermal conductivity of the ceramics, and change its ultimate electrical resistance due to the formation of a conductive grid at grain boundaries. Partial purification of the initial components from metal and other impurities significantly improves the electrical parameters of electric heaters.*

Key words: *silicon carbide, molybdenum disilicide heat tolerance, ceramic materials, protective.*

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Statement of the problem. Silicon carbide and molybdenum disilicide based ceramic materials are used to manufacture high temperature electric heaters [1]. Along with the advantages these materials also have a number of shortcomings impairing their technical and technological properties. High temperature heating causes the growth of silicon carbide and molybdenum disilicide grains, which gather in large blocks and significantly decrease the mechanical strength of electric heaters thus causing their destruction. Silicon carbide endurance in isothermal conditions does not exceed 900 hours, and that of molybdenum disilicide equals to 800 hours. Cyclic operational mode reduces their service life even more. The reason is the uneven detachment of the protective oxide film and formation of unprotected surface areas. In most cases this is due to the reduction of the working area section of the electric heater, which causes its local overheating and failure. Cyclic operational modes of thermal furnaces require maintaining temperature within 1000 ± 500^0C, leading to significant over-consumption of electric power [2]. Operating temperature increase and rapid change in electric heaters thermal modes require improved ways to protect ceramic materials and stimulate the development of new ones.

The **work objective** is to outline the prospective ways to increase heat resistance of silicon carbide and molybdenum disilicide ceramic electric heaters based on the analysis of published data and research results.

Research results. Manufacturers of electric heaters solve such complex problem in various ways. The most practical way is improving the technology of ceramic materials, including the use of raw materials with a minimal amount of harmful impurities [3]. Very often physical and chemical properties of silicon carbide ceramic materials are influenced by impurities getting into the products during the manufacturing process. They are located on the margins of silicon carbide grains and reduce the effective thermal conductivity of the ceramics,

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and change its ultimate electrical resistance due to the formation of a conductive grid at grain boundaries. Partial purification of the initial components from metal and other impurities significantly improves the electrical parameters of electric heaters [3].

High temperature consolidation of molybdenum disilicide based ceramic showed that the amount of silicon introduced in the charge makes the strongest influence on the rheological properties of the material and size of its shear viscosity, as well as the silicide phase average grain size [4]. Silicon reduces the total resistance of ceramics due to its lowest melting point of all the components of the material, and silicon is the last to lose its ability to large plastic deformations. By increasing the silicon content in the charge small grains of silicide phase cause precipitation of molybdenum disilicide grains out of the solution with their subsequent coalescence. If more than 5% silicon is entered to the charge, it slows down the formation stage of the final material structure. The silicon content of less than 5% leads to the formation of a solid frame of fused molybdenum disilicide grains 20 – 40 mm in size, which do not undergo any changes in service.

The process of obtaining electric heaters based on molybdenum disilicide SHS (self-propagating high-temperature synthesis)-extrusion method shows that if the caliber and matrix are heated to 250 – 300^{0}C squeezing fullness increases in 1.2 times, density of the finished rods increases, exfoliation intensity of the surface layer and the amount of cracks decrease, and matrix sealing disappears completely [4].

The introduction of different kinds of supplements to the charge increases physical and chemical properties of ceramic materials based on silicon carbide and molybdenum disilicide [5]. Activation of silicon carbide sintering process is achieved by adding a small amount, approximately 2% of powdered boron, beryllium, aluminum, iron, nickel, cobalt and yttrium. Similarly effective additives are aluminum oxides, hafnium, beryllium and rare earth metals. All the above listed supplements provide ceramic materials with high rates of heat resistance, mechanical stability, resistance to sulfuric and nitric acids, resistance to wear and increased conductivity. However, ceramics operation at high temperatures (above 1200^{0}C) leads to decrease in its strength. Significant increase in physical and chemical properties of silicon carbide products is made possible by the introduction of up to 15% of one or more compounds: Al_2O_3, V_2O_5, Y_2O_3, MgO, Fe_2O_3, Er_2O_3 to the charge. Increase of material density to 98% increases its heat resistance and heat strength, and its ultimate tensile strength in bending at 1400^{0}C exceeds 50 MPa [5]. Material's resistance to oxidation and thermal shocks is highly dependent on the nature and amount of secondary phases formed at grain boundaries under the influence of densifying oxide supplements. Oxygen-free refractory compounds, carbides, nitrides and borides can be successfully used along with oxides as additives [5].

Much attention is paid to the influence of additives on structure and properties of molybdenum disilicide at high temperatures [2]. The material obtained by hot pressing of molybdenum disilicide powder contains 5 – 10% silicon dioxide, presence of which inhibits the growth of $MoSi_2$ grains [2]. Addition of silicon carbide powder reduces the amount of silicon oxide, which is caused by the formation of gaseous oxides (CO, CO_2 and SiO) and pure silicon. To improve the high-temperature properties of hot-pressed $MoSi_2$ it is necessary to add 2% of carbon to the charge [2]. The carbon acts as a deoxidizing agent and promotes the removal of grain boundary phase containing silicon oxide, grain size can increase to 18 – 20 μm. With increase in temperature from 800 to 1400^{0}C viscosity to the destruction of the material is reduced from 4 to 1 $MPa\times m^{1/2}$. If up to 30% of IV-VI metal group borides are entered to the charge, hot-pressed molybdenum disilicide oxidation resistance increases significantly. The bending strength of $MoSi_2$-MeB_2 compositions is 500-700 *MPa* at 1200^0C. The thermal coefficient of linear expansion of the material is $7\text{-}8\times10^{-6}$ deg^{-1}, and heat resistance is 270 – 330^0C.

Another way to increase the physical and chemical properties of ceramics is its strengthening with dispersed particles, crystals and threadlike fibers [6]. Disperse particles of silicon carbide and titanium diboride increase heat resistance of $MoSi_2$ at temperatures 1000 – 1400 ^{0}C. Reinforcing ceramic matrix with 40 – 50 µm long silicon carbide fibers increases its viscosity by 2.4 times, and by more than 5 times with the addition of 0.6 µm zirconium oxide particles. Basis, reinforced with *SiC* fibers, has a high capacity for thermal and chemical resistance as well as resistance to development of cracks and bumps. Destruction energy of such ceramics is close to that of aluminum alloy, which in turn allows to use the ceramic composition for the manufacture of internal combustion engine parts. Improvement of the physical and chemical properties of molybdenum disilicide ceramics can be achieved by reinforcing it with silicon carbide particles and fibers [6]. With the increase of *SiC* volume content from 5% to 40% the viscosity to the destruction increases from 2.7 to 4.5 $MPa\times m^{1/2}$, thus material with 20% silicon carbide has maximum strength. This material can be used to design products that work in oxidizing environments at high temperatures [6]. During extended operation periods refractory compounds interact with the matrix resulting in deterioration of their physical and chemical properties.

Technological disadvantage of *SiC* and $MoSi_2$ products is their low resistance to high temperature oxidation. Negative stages of this process include: the diffusion of oxygen through a silicon dioxide layer; the reaction on the surface division between ceramics and silicon dioxide; counter diffusion of gaseous carbon monoxide through SiO_2 layer. Performance lowering bubbles and cracks appear on the working area of ceramic materials surface [7]. This shortcoming can be eliminated by applying different kinds of protective coatings to the material working surface. The coatings are formed by applying a suspension containing 80% *SiC* and 20% bentonite. Upon application the protective layer is burned in the open air at 1370^0C. In this case material's resistance against oxidation increases and its electrical parameters improve. The working surface of the material is also covered with paste containing molybdenum silicide powder, water and methyl cellulose as an adhesive additive, which eventually is burned in the open air at temperatures 1300 – 1500^0C [7]. The resulting coating protects the ceramic materials from high temperature gas corrosion. Ceramic materials protected this way show a significant increase in the specific load (W/cm^2) in high temperature areas (1500^0C and above).

Operational life of silicon carbide materials increases after their satiation with a suspension comprising $MoSi_2$, water, polyvinyl alcohol and disodium-dibutyl-ortho-phenol-disulfide acid salt with their subsequent burning in an inert environment at a temperature of 1500^0C [8]. The resulting coating provides the ceramic materials at 1480^0C with 2,000 hours of operational life, but the specific load increases with operating temperature increase. *SiC* products heat resistance increase can be achieved by coating their surface with 0.01 mm thick gas-tight silicon carbide layer, but this method is technologically very difficult to perform [8]. High temperature stability and large specific resistance of *SiC* ceramic materials can be achieved by their diffusion saturation with B_4C. The process is carried out as follows: the surface is covered with bakelite varnish, then a layer of technical boron carbide powder or mixture of B_4C and 10% *Si* is applied, followed by heat treatment at first in the open air, then in a protective environment, such as hydrogen at 2200^0C for 1.5 – 2 hours. A layer of cubic *SiC* precipitates on the surface, its mechanical strength is determined by similar values of the thermal expansion coefficients of silicon carbide and ternary compounds of silicon with boron and carbon, and also by a fusible switch between the diffusion layer and ceramic basis. This method has significant drawbacks such as a large number of intermediate manufacturing operations and the complexity of the coating formation process.

Ceramic materials contain up to 20% of free *Si*, which at high temperatures causes the formation of a significant amount of silicon dioxide, located in the pores of the material. Silicon dioxide causes an increase in electrical resistance of the products resulting in their overheating, and a sharp change in temperature conditions leads to the destruction of connections between the grains of ceramics and loss of strength of the material. Failure of at least one heating element requires replacement of all the remaining heaters in the industrial electric furnaces, because due to the aging process their electrical parameters are significantly different from those of new heaters. [9]

Also, studies of the causes of failure of heating elements operating at temperatures 1400 – 1600^0C in a sharp change in thermal conditions were carried out. It was established that ceramic products' operational life is affected by internal oxidation of its heaters' material, the presence of porous and brittle surface layer on the heating element working area, low density of the material, small diameter of necks between grains, and internal stresses in the ceramic heaters. Perspective direction of improving performance of the ceramic heaters is creating on their surface a composite coating in which each layer performs a specific function. Exterior layer, which is a slurry coating, provides heat resistance of the composition, the next one, a barrier coating, prevents interaction of sinter resistant coating component with the base, the main, diffusion layer contributes to relaxation of tensions in the coating after repeated change of temperature, ensures a smooth change of thermal expansion coefficient at the transition from the base to cover, and improves adhesion between the diffused and superimposed parts of the coating. The resulting coating is able to effectively protect silicon carbide and molybdenum disilicide electric heaters from corrosion caused by high temperature gas [10].

Stability studies of silicon carbide and molybdenum disilicide based silicon-boride layer were performed in argon environment. The study of temperature influence on the silicon-boride phase stability on carborundum ceramics in argon environment showed that silicon hexaboride effectively inhibits diffusive movement of carbon and silicon to inert environment – coating margin. Using metallographic analysis, it has been found that silicon hexaboride layer after annealing in argon environment becomes uniform, dense and well-linked to the base, without any cracks or pores in the coating.

The highest percentage of the specific weight loss is seen in uncoated carborundum samples, where Δg increases in direct proportion with heating temperature increase. Specific weight loss of silicon-borated silicon carbide samples is 1.5 – 2 times lower than that of the uncovered ones. We can assume that weight reduction of silicon-borated carborundum samples is due to the fact that in the high-temperature annealing the concentration of boron in the coating changes. Part of boron atoms diffuse on the hexaboride silicon – argon margin, where they react with oxygen (a small part of which is in argon), thus producing the following reaction: SiB_6 +

O_2 –> $SiB_4 + 2BO$, resulting in creation of SiB_4 phase with a thickness of 20±5 μm on the silicon carbide surface. Silicon tetraboride microhardness is 19 ± 0.5 GPa, which is consistent with the data. In addition boron diffuses to the margin phase $SiB_6 – Si_x(B,C)_y$, and its concentration in the ternary compound $Si_x(B,C)_y$ grows by 6.7%. This redistribution of boron concentration in SiB_6 phase promotes growth of silicon tetraboride layer evidenced by X-ray phase analysis and metallographic data analysis methods. The formation of the triple phase on reaction sintered ceramic effectively inhibits further diffusion process of boron into the depth of the base, which significantly increases stability of silicon-boride layer and is an important factor in the development of heat-resistant coating. [8].

Conclusions. Combination of different methods of forming multilayered composite heat-resistant coating will increase the operational parameters of SiC and $MoSi_2$ electric heaters. There have been planned further studies on using activators to increase the protective properties of ceramic materials saturated with silicon and boron.

References

1. Kovbashyn V.I., Bochar I.Y. Tekhnolohichni osoblyvosti formuvannya sylitsydnoho pokryttya na karbidi kremniyu ta dysylitsydi molibdenu, Visnyk Ternopil's'koho natsional'noho tekhnichnoho universytetu, Ternopil', vol. 75, no. 3, 2014. Pp. 127-131. [In Ukrainian].

2. P.S. Kislyj, A.X. Badyan, Kislyj P.S., Badyan A.X., Kindysheva V.S. Vysokotemperaturnye nemetalicheskie nagrevateli, Kyyiv, Naukova dumka, 1991, 166 p. [In Russian].

3. Rahaman M.N. Surfasecharacterisationof silicon nitride and silicon carbide powders, Amer. Ceram. Soc. Bull, no. 8, 1986. Pp. 1171-1176.

4. Buchackij L.M., Nadriin Sh.N., Nagnij A.M. Kinetika uplotneniya i reologicheskie svojstva materialov na osnove disilicida molibdena v oblasti vysokix temperatur, Silicidy i ix primenenie v texnike, Kyiv, In-t probl. Materialovedeniya AN Ukrainy, 1990. Pp. 55-58. [In Russian].

5. Dzyadykevich Yu.V., Kislyj P.S., Zablockaya N.I. Pokrytiya dlya karbidokremnievyx e'lektronagrevatelej, Otkrytiya. Izobreteniya, no. 31, 1991. P. 126. [In Russian].

6. Bochar I.Y., Horbatyuk R.M. Vlastyvosti zakhysnoyi kompozytsiyi, nanesenoyi na poverkhnyu keramichnykh materialiv, Naukovi notatky. Mizhvuzivs'kyy zbirnyk (za napryamom “Inzhenerna mekhanika”. Luts'k, Vypusk no. 24, 2009. Pp. 21-28. [In Ukrainian].

7. Patent 30240 A Ukrayiny, S04V35/56. Sposib obrobky vyrobiv iz karbidu kremniyu ta dysylitsydu molibdenu, Yu.V. Dzyadykevych, I.Y. Bochar, R.M. Horbatyuk (Ukrayina)., no 98020580; zayavleno 03.02.1998; opubl. 15.11.2000, Byul. No. 6-11.

8. Kovbashyn V.I., Bochar I.Y. Vplyv tekhnolohiyi sylikoboruvannya keramichnykh materialiv na vlastyvosti zakhysnykh pokryttiv, Visnyk Ternopil's'koho natsional'noho tekhnichnoho universytetu. Ternopil', vol. 78, no. 2, 2015. Pp. 130-138. [In Ukrainian].

9. Hepworth M.A. Processing, Properties and Applications of Structural Silicon Carbides, Brit. Ceram. Proc., no. 46, 2001. Pp. 113-125.

10. Dzyadykevych Yu.V., Bochar I.Y. Pidvyshchennya zharostiykosti karbidokremniyevykh i dysylitsyd molibdenovykh nahrivnykiv, Mashynoznavstvo, vol. 31, no. 1, 2000. Pp. 11-14.

Список використаної літератури

1. Ковбашин, В.І. Технологічні особливості формування силіцидного покриття на карбіді кремнію та дисиліциді молібдену [Текст] / В.І. Ковбашин, І.Й. Бочар // Вісник Тернопільського національного технічного університету. – Тернопіль, 2014. – № 3 (75). – С. 127 – 131.

2. Кислый, П.С. Высокотемпературные неметалические нагреватели [Текст] / П.С. Кислый, А.Х. Бадян, В.С. Киндышева // К.: Наукова думка, 1991. – 166 с.

3. Rahaman, M.N. Surfasecharacterisationof silicon nitride and silicon carbide powders [Text] / M.N. Rahaman // Amer. Ceram. Soc. Bull, 1986. – № 8. – P. 1171 – 1176.

4. Бучацкий, Л.М. Кинетика уплотнения и реологические свойства материалов на основе дисилицида молибдена в области высоких температур [Текст] / Л.М. Бучацкий, Ш.Н. Надриин, А.М. Нагний //

Силициды и их применение в технике. – К.: Ин-т пробл. Материаловедения АН Украины, 1990. – С. 55 – 58.

5. Дзядыкевич, Ю.В. Покрытия для карбидокремниевых электронагревателей [Текст] / Ю.В. Дзядыкевич, П.С. Кислый, Н.И. Заблоцкая // Открытия. Изобретения, 1991. – № 31. – С. 126.

6. Бочар, І.Й. Властивості захисної композиції, нанесеної на поверхню керамічних матеріалів [Текст] / І.Й. Бочар, Р.М. Горбатюк // Наукові нотатки. Міжвузівський збірник (за напрямом «Інженерна механіка»). – Луцьк, 2009. – Випуск № 24. – С. 21 – 28.

7. Патент 30240 А України, С04В35/56. Спосіб обробки виробів із карбіду кремнію та дисиліциду молібдену [Текст] / Ю.В. Дзядикевич, І.Й. Бочар, Р.М. Горбатюк (Україна). – № 98020580; заявлено 03.02.1998; опубл. 15.11.2000, Бюл. № 6 – 11.

8. Ковбашин, В.І. Вплив технології силікоборування керамічних матеріалів на властивості захисних покриттів [Текст] / В.І. Ковбашин, І.Й. Бочар // Вісник Тернопільського національного технічного університету. – Тернопіль, 2015. – № 2 (78). – С. 130 – 138.

9. Hepworth, M.A. Processing, Properties and Applications of Structural Silicon Carbides [Text] / M.A. Hepworth // Brit. Ceram. Proc., 2001. – № 46. – P. 113 – 125.

10. Дзядикевич, Ю.В. Підвищення жаростійкості карбідокремнієвих і дисиліцид молібденових нагрівників [Текст] / Ю.В. Дзядикевич, І.Й. Бочар. – К.: Машинознавство, 2000. – № 1 (31). – С. 11 – 14.

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ПЕРСПЕКТИВНІ НАПРЯМИ ПІДВИЩЕННЯ ЖАРОСТІЙКОСТІ КЕРАМІЧНИХ МАТЕРІАЛІВ НА ОСНОВІ КАРБІДУ КРЕМНІЮ ТА ДИСИЛІЦИДУ МОЛІБДЕНУ

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Резюме. *На основі аналізу літературних даних і результатів проведених досліджень окреслено перспективні напрями підвищення жаростійкості карбідокремнієвих і дисиліцидмолібденових керамічних електронагрівачів. Виробники електронагрівачів розв’язують таку складну проблему різними шляхами. Найдосконаліший шлях – це вдосконалення технології виготовлення керамічних матеріалів, зокрема використання вихідних матеріалів з мінімальною кількістю шкідливих домішок. Дуже часто на фізико-хімічні властивості карбідокремнієвих керамічних матеріалів впливають домішки, які потрапляють під час виготовлення виробів. Вони розміщуються на межі зерен карбіду кремнію і знижують ефективну теплопровідність кераміки, а також змінюється граничний електроопір за рахунок утворення електропровідної сітки на межі зерен. Часткове очищення вихідних компонентів від металевих та інших домішок суттєво покращує електричні параметри електронагрівачів.*

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

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