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RESEARCH OF PROPERTIES OF PROTECTIVE COATING APPLIED TO THE SURFACE OF REACTION-SINTERED CERAMIC MATERIALS

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Summary. The study describes the properties of the protective coating deposited on the surface of the reaction-sintered silicon carbide and molybdenum disilicide. The technology of increasing the protective ability of the coating of products deposited on the surface on the basis of reactive sintered carbide of silicon and molybdenum disilicide, which operate in an oxidizing environment at high temperature and a sharp change of thermal regime, is investigated. The obtained results showed that the presence of a protective slip layer significantly increases the stability of the deposited silicoboride coating, thus blocking the interaction of silicon hexaboride with the environment, slowing down almost all diffusion processes at the transition of the interaction of diffusion. It has been established that the simultaneous use of both diffusion and slurry coatings enables maximum protection of reaction-sintered ceramic materials based on silicon carbide and molybdenum disilicide against high-temperature gas corrosion. The developed coating ensures maximum resistance to repeated changes in temperature conditions, while cyclic changes destroy products of silicon carbide and molybdenum disilicide without applied protective coating. The proposed protective coating can be recommended for the protection of reaction-sintered ceramic materials operated in high temperatures.

Key words: silicon carbide, molybdenum disilicide, multilayer coating, ceramic materials.

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Statement of the problem. Modern technological methods of processing reaction-sintered ceramic materials based on silicon carbide and molybdenum disilicide do not provide protection at high temperatures during operation. The protective properties of reaction-sintered ceramic materials can be significantly increased by using a diffusion-slip coating. However, it is necessary to take into account the action of the aggressive environment in which the coating will be operated and the diffusion processes that take place at the boundary «coating-slip layer» [1, 2, 3].

Analyses of available investigations and publications. Chemical-thermal treatment involves various areas of improving technological processes and physical-mechanical and chemical properties of reaction-sintered ceramic materials based on silicon carbide and molybdenum disilicide [1, 4]. Products based on silicon carbide and molybdenum disilicide possess low resistance to high temperature operation, to high temperature oxidation, which leads to the destruction of bonds between ceramic grains and to the loss of material strength [5]. A promising way to solve this problem is to study the properties of the protective coating applied to the surface of the reaction-sintered ceramic materials based on silicon carbide and molybdenum disilicide. It is possible to increase heat resistance and ensure the use of products based on silicon carbide and molybdenum disilicide in harsher operating conditions by applying new compositions of protective mixtures on the surface of ceramic materials [6, 7, 8].

Objective of the paper – is to develop a technology that increases the protective ability of the coating applied to the surface of products based on reaction-sintered silicon

carbide and molybdenum disilicide, which operate in an oxidizing environment at high temperatures and sudden changes in thermal regime.

Research results and their discussion. Studies of the stability of the multilayer coating on the reaction-sintered silicon carbide and molybdenum disilicide in argon at temperatures of 1200–1500°C (for silicon carbide) and 1500–1800°C (for molybdenum disilicide) found that silicon hexaboride does not interact with applied protective coating, according to the results, the interaction is so small that it can be neglected. The micro-X-ray spectral analysis of the near-surface protective layers of silicon hexaboride and silicide oxide coating and the diffusion coating-slip layer transition did not reveal the presence of new phase formations [9]. The calculations showed that the decrease in the specific weight loss (Δg) of samples with a multilayer protective coating applied to the surface occurs 3–4 times slower than samples without coating and 1.5–2 times slower than samples with applied silicoboride protective layer. The specific weight gain decreases gradually and can be described by a linear law, which means that the use of diffusion-slip protective coating virtually stops weight loss. Diffusion processes on the surface of the protective silicoboride coating are inhibited. The inertness of refractory oxides inhibits the high diffusion activity of silicon and boron atoms.

The obtained results showed that the presence of a protective slip layer significantly increases the stability of the applied silicoboride coating, while blocking the interaction of silicon hexaboride with the environment. As a result, almost all diffusion processes at the transition of the interaction of the diffusion and liqueur layers are inhibited.

Significant phase and structural changes in the silicoboride coating are observed during high-temperature oxidation. These changes can be minimized by applying a slurry layer of refractory oxides on the surface of the diffusion coating. Therefore, it was of interest to investigate the heat resistance of the proposed multilayer coating on a reaction-sintered ceramic base in the temperature range of 1400–1500°C for silicon carbide and 1500–1650°C for molybdenum disilicide. The kinetic oxidation process can be determined by the effect of the total inertness of refractory oxides to aggressive oxygen atoms.

To assess properly the importance of using a coating to protect reaction-sintered ceramic materials against high-temperature destruction, it is necessary to take into account the results of parametric studies [10]. The dependence of the specific weight loss of samples of silicon carbide and molybdenum disilicide on the heat resistance parameter is shown in table 1.

Table 1

Influence of temperature on specific weight loss (Δg) of silicon carbide and molybdenum disilicide samples ($t = 4 h$)

Coating	<i>SiC</i>			
	Heating temperature, °C			
	1200	1300	1400	1500
diffusion-slip	0.26	0.31	0.38	0.52
diffusion	0.52	0.77	1.01	1.23
without coating	0.96	1.38	1.64	1.98
Protective coating	<i>MoSi₂</i>			
	Heating temperature, °C			
	1500	1600	1700	1800
diffusion-slip	0.21	0.29	0.34	0.39
diffusion	0.38	0.51	0.62	0.68
without coating	0.77	0.97	1.24	1.52

During the studies, samples of reaction-sintered silicon carbide were weighed before and after the tests, which made it possible to determine the change in specific weight gain due to gas corrosion. Studies have shown that there are processes of slow weight gain of reaction-sintered samples of silicon carbide throughout the temperature range (table 2). The intensity of oxidation increases sharply when the temperature reaches 1500°C or more. The following is observed, white gas of silicon oxide (SiO) begins to be released over the surface of silicon carbide samples, and pores and cracks are formed directly in the places of its exit. With increasing evaporation intensity at a temperature of 1550°C, the diffusion-slip coating begins to lose its self-healing properties. Studies have shown that there is a catastrophic destruction of the composite coating and burnout of the base of the reaction-sintered ceramic material. In our opinion, this is due to the high diffusion activity of silicon atoms; and the destruction of ceramics begins with the depth of the material [11]. The formation of silicon oxide gas occurs in the material itself, and when it comes to the surface, channels begin to form, through which aggressive oxygen penetrates from the gaseous medium and the coating begins to lose its protective properties.

The obtained results have showed that with increasing duration of oxidation processes from 40 to 160 hours at temperatures of 1450°C and 1500°C there is a gradual increase in the proportion of samples of reaction-sintered silicon carbide (Table 3). Observations have shown that at a temperature of 1450°C protective multilayer coating almost completely protects ceramics against oxidation; and when the temperature rises to 1500°C or more and the duration of the oxidation process increases, protective diffusion-slip coating begins to lose gradually its properties. The reaction-sintered ceramic material itself cannot withstand such a load and the destruction process begins in the middle.

Table 2

Weight gain of silicon carbide and molybdenum disilicide samples during oxidation ($t = 40 h$)

<i>SiC</i>				
Heating temperature, °C	1400	1450	1500	1550
Specific weight gain, mg/cm^2	0.0168	0.0197	0.0216	0.0328
<i>MoSi₂</i>				
Heating temperature, °C	1500	1550	1600	1650
Specific weight gain, mg/cm^2	0.0194	0.0217	0.0325	0.0672

For disilicide molybdenum samples, the analysis of the obtained results shows that the specific weight gain increases gradually with the increase of temperature during the oxidation process (Table 2). An increase in temperature above 1600°C causes a high oxidation intensity. The appearance of white gas begins to be observed above the surface at a temperature of 1650°C, and a further increase in temperature leads to the formation of micropores and cracks, the coating is intensely exfoliated. As a result, in some areas the coating is separated from the ceramic base, which causes catastrophic destruction of the protective diffusion-slip coating.

Some areas of the surfaces under study become unprotected during high-temperature gas corrosion, the process of burning the reaction-sintered ceramic base begins and molybdenum disilicide becomes completely unsuitable for further use.

The results have showed that with increasing duration of oxidation processes from 40 to 100 hours at temperatures of 1600°C and 1650°C, the weight of ceramic disilicide molybdenum samples gradually increases (Table 3). The change in specific weight (Δg) can be described by a linear law, and with increasing exposure, the weight begins to increase very sharply. At a temperature of 1600°C, a composite coating applied to the ceramic surface is able

to protect the reaction-sintered molybdenum disilicide against gas corrosion, and at a temperature of 1650 C there is a gradual and further increasing loss of protective properties of the proposed multilayer coating.

Table 3

Oxidation kinetics of silicon carbide and molybdenum disilicide samples

Heating temperature, °C	<i>SiC, mg/sm²</i>			
	Test duration, <i>h</i>			
	40	80	120	160
1450	0.019	0.021	0.027	0.032
1500	0.024	0.038	0.056	0.067
<i>MoSi₂, mg/sm²</i>				
1600	0.032	0.046	0.054	0.061
1650	0.057	0.088	0.106	0.121

The next step of our research was to conduct micro-X-ray spectral analysis of diffusion-slip heat-resistant coating. The obtained results have showed that after 12 hours of aggressive high-temperature oxidation, the concentration of elements applied to the surface of the protective layer remains virtually unchanged (Table 4).

Table 4

Results of micro-X-ray spectral analysis of the composite coating on the surface of silicon carbide and molybdenum disilicide

Base material	Temperature, °C	Concentration of elements, wt %						
		<i>Si</i>	<i>Mo</i>	<i>Zr</i>	<i>Y</i>	<i>Hf</i>	<i>Al</i>	<i>B</i>
<i>SiC</i>	before testing	22.8	12.8	1.9	2.5	1.6	1.4	56.3
	1450	22.5	12.4	1.9	2.4	1.5	1.4	55.8
<i>MoSi₂</i>	before testing	24.7	15.8	3.6	3.9	2.3	1.9	47.9
	1600	24.3	15.5	3.5	3.8	2.1	1.9	47.6

The next stage of the research was to study the effect of repeated changes in temperature. The influence of cyclic heating and cooling of ceramic samples on the quality of diffusion-slip coating during high-temperature gas corrosion was studied. The obtained research results showed that repeated (for SiC ~ 30 cycles at 1400°C, for MoSi₂ ~ 20 cycles at 1600°C, cycle duration - 8 hours) heating and cooling of reaction-sintered ceramic samples does not impair the plasticity of the protective coating. These results can be explained by the ability of the slip coating to self-healing at the sites of cracks and micropores due to the presence of molybdenum disilicide.

Thus, it can be concluded that the simultaneous use of both diffusion and slip coating provides the possibility of maximum protection of reaction-sintered ceramic materials based on silicon carbide and molybdenum disilicide against high-temperature gas corrosion. In addition, it provides the possibility to withstand multiple changes in temperature as many times as possible, while cyclic changes destroy products made of silicon carbide and molybdenum disilicide without a protective coating.

Conclusions. The conducted studies have proved that for the protection of reaction-sintered ceramic materials based on silicon carbide and molybdenum disilicide, in particular, in

high-temperature operation, a diffusion-slip coating, which provides a significant increase in service life of products made of ceramic materials should be used.

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ДОСЛІДЖЕННЯ ВЛАСТИВОСТЕЙ ЗАХИСНОГО ПОКРИТТЯ, НАНЕСЕНОГО НА ПОВЕРХНЮ РЕАКЦІЙНО-СПЕЧЕНИХ КЕРАМІЧНИХ МАТЕРІАЛІВ

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Резюме. Наведено результати проведених досліджень властивостей захисного покриття, нанесеного на поверхню реакційно-спеченого карбиду кремнію та дисиліциду молібдену. Метою проведених експериментів було підвищення захисної здатності покриття нанесеного на поверхню виробів на основі реакційно-спеченого карбиду кремнію і дисиліциду молібдену, які працюють в окислювальному середовищі при високій температурі та різкій зміні теплового режиму. Досліджено особливості технологічного процесу підвищення захисної здатності покриття, нанесеного на поверхню виробів на основі реакційно-спеченого карбиду кремнію і дисиліциду молібдену, які працюють у важкому режимі окислювального середовища при високих температурах та різкій зміні параметрів теплових режимів. Проведено мікрорентгеноспектральний аналіз приповерхневих захисних шарів гексабориду кремнію та силіцид-оксидного покриття. На переході дифузійне покриття – шлікерний шар не виявлено присутності нових фазових утворень. Отримані результати показали, що наявність захисного шлікерного шару суттєво підвищує стабільність нанесеного силікоборидного покриття. При цьому блокується взаємодія гексабориду кремнію з навколишнім середовищем, відбувається загальмування майже усіх дифузійних процесів на переході взаємодії дифузійного та шлікерного шарів. Встановлено, що одночасне використання дифузійного й шлікерного покриття забезпечує можливість максимального захисту реакційно-спечених керамічних матеріалів на основі карбиду кремнію та дисиліциду молібдену від високотемпературної газової корозії. Розроблене покриття забезпечує максимальне витримування багаторазових змін температурних режимів, водночас коли циклічні зміни руйнують вироби з карбиду кремнію та дисиліциду молібдену без нанесеного захисного покриття. Запропоноване захисне покриття можна рекомендувати для захисту реакційно-спечених керамічних матеріалів, що експлуатуються в умовах високих температур.

Ключові слова: карбід кремнію, дисиліцид молібдену, багатощарове покриття, керамічні матеріали.

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