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COMPOSITION OF THE MIXTURE FOR SILICIZATION AND BORIDING OF PRODUCTS MADE OF SILICON CARBIDE AND MOLYBDENUM DISILICYDE

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Abstract. *The work describes the constitution of the composition for processing ceramic materials, made of reaction-sintered silicon carbide and molybdenum disilicide. The conditions of the technical and technological process of processing non-metallic ceramic materials depending on the composition of silicide and boride powder mixtures were studied and analyzed. It has been established that the improvement of the operational characteristics of powder mixtures for silicification and boronization can be achieved with the help of a complex activator. On the basis of the conducted research, the optimal composition of the mixture is proposed, which ensures high-quality saturation of the treated surface and almost doubles the diffusion saturation with silicon and boron. It was also established that different compositions of silicide and boride mixtures can be used to intensify the process of processing ceramic materials in a saturating environment. Diffusion saturation of ceramic materials is recommended to be carried out using titanium hydride, which ensures the required saturation speed and high quality of the treated surface. The research results showed that the proposed compositions of mixtures for silicification and boronization can be recommended for processing products based on reaction-sintered silicon carbide and molybdenum disilicide materials used for the manufacture of electric heaters and various structural elements of high-temperature equipment.*

Key words**:** *silicification, boriding, silicon carbide, molybdenum disilicide, ceramic materials.*

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1. INTRODUCTION

Existing technologies for the processing of reaction-sintered ceramic materials, such as silicon carbide and molybdenum disilicide, do not provide effective protection against high temperatures during operation. The presence of harmful impurities leads to a significant deterioration in the performance of these materials. In addition, the saturation capacity of the working mixtures (silicides and borides) used to process such materials is very low, which makes it impossible to use them effectively.

In the field of chemical and thermal treatment, modern technologies are used to improve the quality and properties of reaction-sintered ceramic materials based on silicon carbide and molybdenum disilicide [1–8, 13, 14]. Products with such a composition have certain disadvantages, such as insufficient resistance at high temperatures, susceptibility to oxidation, loss of strength, etc. One of the promising ways to solve these problems is to improve technologies that enhance the physical, mechanical and chemical properties of these ceramic materials. The use of new compositions of mixtures for siliconisation and boronisation processes can help to increase operating temperatures and make them more resistant to severe operating conditions.

The objective of this study is to increase the saturation capacity of silicide and boride compositions used to process products made using reaction-sintered silicon carbide and molybdenum disilicide. These products can be used in oxidising environments at high temperatures and significant changes in thermal conditions.

2. EXPERIMENTAL METHODS

The compositions of mixtures obtained by the authors for the technological processing of sintered ceramic materials made of silicon carbide and molybdenum disilicide are classified as chemical and thermal treatment in powder metallurgy and can be recommended for use in the electronics industry and the production of electrothermal devices.

3. RESULTS AND DISCUSSION

Siliconisation process. The most common composition of the siliconizing mixture for products contains silicon and an inactive filler and is carried out in a vacuum (~1300 Pa) at a temperature of 1200–1250°C [9, 16]. Although this composition has its advantages, it also has a number of disadvantages, including the possibility of sintering the mixture and burning it to the surface of the product, as well as the use of mixtures with a high silicon content (over 80%).

The technical result that is closest to the described one is a composition for siliconising products [10], which includes the following components: silicon (Si) in the range of 60 to 80 per cent; sodium fluoride (NaF) in the range of 5 to 10 per cent; the rest is aluminium oxide (Al_2O_3), at a temperature of 1150°C. Among the disadvantages of this mixture composition are the high consumption of silicon and sodium fluoride, as well as the high cost of the mixture. Therefore, there is a need to find ways to improve the processing of reaction-sintered ceramic materials.

The goal is achieved by adding additional components to the mixture used for silicon carbide and molybdenum disilicide siliconisation. Titanium hydride is added to this composition, which already contains silicon, sodium fluoride and aluminium oxide, in the following proportions (by wt%): silicon (Si) – 40 to 60; sodium fluoride (NaF) – 1 to 5; titanium hydride (TiH_2) – 5 to 10; aluminium oxide (Al_2O_3) – the rest.

In the proposed powder mixture, each component performs its own function: silicon acts as a silicate agent, sodium fluoride and titanium hydride act as activators that significantly boost the diffusion saturation process, and aluminium oxide (which is an inert filler) stops the sintering of the main components of the mixture and prevents them from being bonded to the surfaces of the ceramic base.

In this process, components such as silicon (Si), sodium fluoride (NaF) and titanium hydride (TiH_2) are used in powder form with a grain size of up to 100 microns, while aluminium oxide (Al_2O_3) powder has a grain size ranging from 40 to 80 microns.

When using the powder mixture for the first time, all components are thoroughly mixed to obtain a homogeneous mass. Diffusion silicification of reaction-sintered ceramic materials using this mixture composition is carried out in thermal chamber furnaces with an air environment in special containers made of heat-resistant steel.

For diffusion saturation, samples of silicon carbide (SiC) and molybdenum disilicide ($MoSi_2$), were used, which had the following dimensions: length 20 mm; diameter 6–8 mm. Quartz sand, glass with a softening point of 950–1050°C, and asbestos cardboard 1–2 mm thick were used to pack the top of the container. Before the diffusion saturation procedure, the container was packed in the following sequence. A uniform layer of the mixture of components about 20 mm thick was poured onto the bottom of the container, and then the silicon carbide and molybdenum disilicide samples were inserted vertically into this layer of the mixture with a distance of about 5–7 mm between them and 15 mm to the container walls. The specimens were completely covered with the mixture and compacted at the same time, ensuring that the thickness of the mixture layer above the top edge of the specimens was at least 30 mm. After the mixture was poured, an asbestos gasket was placed on top of the 30–40 mm thick layer of sand, which was then compacted. A 20–40 mm thick layer of glass was placed on top of the sand and the container was sealed. After that, the container was put in a thermal chamber furnace and heated to a temperature of 1100°C. The duration of the technological process of diffusion saturation of reaction-sintered ceramic samples was within eight hours.

After completion of the diffusion saturation process, the container was cooled to 20°C together with the oven, after which it was unpacked and the powder mixture was separated from the samples on a sieve. It is recommended to use the working mixture several times, so it was stored in a sealed container to prevent contact with moisture.

The authors of previous studies [11] found that the technological processes of diffusion silicon saturation of silicon carbide and molybdenum disilicide using NaF are slow, and an increase in the process duration (over 8 hours) and activator concentration (over 3%) leads to sintering of the working mixture particles to the surfaces of the tested samples, and in some studies it was found that the mixture itself was sintered. After diffusion siliconisation, the samples of reactive sintered silicon carbide and molybdenum disilicide become light grey in colour. The use of a complex activator (sodium fluoride + titanium hydride) accelerates the process of diffusion saturation twofol

Table 1

Results of applying a complex activator for siliconisation.

Material	Specific weight gain, mg/cm^2			
	composition *«a»*	composition *«b»*	composition *«c»*	prototype
SiC	6,4	9,3	10,7	4,6
$MoSi_2$	11,5	16,8	18	9,9

The powder mixture is kept active before each reuse by adding 0.5% sodium fluoride and 1% titanium hydride. This mixture can be used between 8 and 10 times.

The following compositions of powder mixtures (percentage by weight) were used in the study:

a) silicon (Si) – 40; sodium fluoride (NaF) – 1; titanium hydride (TiH_2) – 5; aluminium oxide (Al_2O_3) – the rest;

b) silicon (Si) – 50; sodium fluoride (NaF) – 3; titanium hydride (TiH_2) – 7; aluminium oxide (Al_2O_3) – the rest;

c) silicon (Si) – 60; sodium fluoride (NaF) – 5; titanium hydride (TiH_2) – 10; aluminium oxide (Al_2O_3) – the rest;

d) silicon (Si) – 80; sodium fluoride (NaF) – 10; titanium hydride (TiH_2) – 5; aluminium oxide (Al_2O_3) – the rest (prototype).

According to the findings of the study, it was established that the use of combined activators for diffusion silicification of ceramic materials made of silicon carbide and molybdenum disilicide can almost double the saturation capacity of silicide mixtures.

The proposed technology has a number of advantages compared to the prototype: reduced diffusion saturation time (by 1.5–2 times), a 50°C reduction in heating temperature, and significant savings in electricity and materials, in particular, silicon and sodium fluoride.

Such compositions of powder mixtures can be effective in the diffusion saturation of reaction-sintered ceramic materials, as well as for refractory metals used in the production of various structural elements for high-temperature equipment.

Technological process of boriding. The process of diffusion saturation of metals and alloys with boron is used to increase their surface hardness and wear resistance. For this purpose, powders are used, including amorphous boron, borax, boron carbide, ferroboron, nickel boron, and their combinations [10, 15]. The most common among these components are amorphous boron and boron carbide.

For boronizing refractory metals, a powder mixture containing boron carbide, an inert diluent and a salt of borofluoric acid is often used, which acts as a process activator. This process is usually carried out in heat-resistant containers with fusible links [12].

The composition of the mixture for boronisation of ceramic products, which contains large amounts of boron carbide (B_4C) and aluminium oxide (Al_2O_3), is similar to the process described above. However, it differs from the prototype in that it is carried out under vacuum (~1300 Pa) at a heating temperature of 1400 °C. The disadvantages of this mixture composition include a large loss of boron carbide and high energy consumption.

The purpose of the proposed technology is to increase the saturation capacity of the boride mixture. This goal is achieved by introducing titanium hydride into the mixtures during the technological process of boronizing ceramics made of silicon carbide and molybdenum disilicide containing amorphous boron, sodium fluoride and aluminium oxide. Their ratio can be as follows: 20–40%; 1.5%, 5–10%, the rest is aluminium oxide.

The components perform important functions: amorphous boron serves as a diffusing agent, sodium fluoride and titanium hydride play the role of activators, while aluminium oxide (which is an inert additive) prevents the components of the mixture from sintering and sticking to the surfaces of the materials being processed. In addition, amorphous boron, sodium fluoride and titanium hydride are typically used in the form of powders with a grain size of up to 100 microns, while aluminium oxide powder has a grain size of 40–80 microns.

Before using the proposed mixture, the components should be mixed until a homogeneous consistency is obtained. To carry out the technological process of diffusion boridining of silicon carbide and molybdenum disilicide using this mixture, air thermal chamber furnaces were used, and the components were in special containers made of heat-resistant steel.

The samples of silicon carbide and molybdenum disilicide materials had the following dimensions: length – 20 mm, diameter – 6–8 mm. The technological process also involved the use of quartz sand, glass with a softening point of 950 to 1050°C and asbestos cardboard with a thickness of 1–2 mm. The packaging of the diffusion boron container was carried out in the same way as for diffusion siliconisation (see above).

After the mixture has been placed, the container is sealed by any known method, using fusible closures. The sealed containers are then placed in a thermal chamber furnace, which is heated to a temperature of 1100°C, and the diffusion saturation process lasted 8 hours.

When the container is heated, the oxidation of amorphous boron begins, leading to the formation of B_2O_3 suboxide, which transports boron to the surface of ceramic samples. At the same time, amorphous boron reacts with sodium fluoride to form boron fluorides (BF_3, BF_2). These compounds react with the surface of the ceramic samples to form atomic boron, which then diffuses into the base. Titanium hydride decomposes under the influence of heat, forming a reducing gas environment that restores oxide films on the surface of ceramic samples. Boron hydrides are also formed, which help transport boron to the substrate. Thus, the joint interaction of oxygen, halogen and hydrogen transfer of boron, as well as the reduction of oxide films present on the surface of ceramic samples, can significantly increase the efficiency of the technology of boron plating ceramics from reaction-sintered silicon carbide and molybdenum disilicide.

At the end of the treatment process, the container and the oven are cooled to a temperature of 20^0C. After that, unpack the container and separate the powder mixture from the samples using a sieve. To prevent possible contact with moisture, the test mixtures must be stored in an airtight container.

Silicon carbide and molybdenum disilicide samples acquire a light grey colour after diffusion hardening. The use of a complex activator (NaF i TiH_2) doubles the speed of the diffusion saturation process, which is confirmed by the results of the authors' studies (see Table 2).

Table 2

Results of the use of a complex activator for boriding.

Material	Specific weight gain, mg/cm2			
	composotion *«a»*	composotion *«b»*	composotion *«c»*	prototype
SiC	2,23	4,51	6,18	1,74
$MoSi_2$	5,35	7,2	9,43	3,42

The results of the research showed that the constant activity of the powder mixtures is maintained before each reuse by adding 0.5% sodium fluoride and 1% titanium hydride. Such mixtures are recommended for use from 8 to 10 times.

The following compositions of the powder mixture were used (in mass percentage):

a) amorphous boron – 20; sodium fluoride – 1; titanium hydride – 5; aluminium oxide – the rest;

b) amorphous boron – 30; sodium fluoride – 3; titanium hydride – 7; aluminium oxide – the rest;

c) amorphous boron – 40; sodium fluoride – 5; titanium hydride – 10; aluminium oxide – the rest;

d) boron carbide – 90; aluminium oxide – the rest (prototype).

The analysis of the obtained results confirms that the use of a combined activator during diffusion boroning of reaction-sintered ceramic materials based on silicon carbide and molybdenum disilicide provides a double increase in the saturation capacity of the boride mixture.

4. CONCLUSIONS

The proposed technological process of silicification has a number of advantages over the prototype:

- the duration of the diffusion siliconisation process is reduced by half;
- reduction of the heating temperature by 50 ^{0}C;
- significant energy efficiency;
- reduced consumption of powder components such as silicon and sodium fluoride.

The developed diffusion boron technology also has advantages over the prototype:

- reduction in the duration of the diffusion boriding process by 1.5 times;
- significant energy efficiency, as the heating temperature is reduced by 300 ^{0}C;
- the powder mixtures can be used for diffusion boron saturation of reaction-sintered ceramic materials, as well as for refractory metals used in the manufacture of various structural elements of high-temperature equipment.

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СКЛАД СУМІШІ ДЛЯ СИЛІЦІЮВАННЯ ТА БОРУВАННЯ ВИРОБІВ ІЗ КАРБІДУ КРЕМНІЮ ТА ДИСИЛІЦИДУ МОЛІБДЕНУ

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Резюме. *Описано склад композиції для обробки керамічних матеріалів з реакційно-спеченого карбіду кремнію та дисиліциду молібдену. Існуючі технології для обробки реакційно-спечених керамічних матеріалів, таких, як карбід кремнію та дисиліцид молібдену, не забезпечують ефективного захисту від високих температур під час експлуатації. Наявність шкідливих домішок призводить до значного погіршення експлуатаційних характеристик цих матеріалів. Крім того, насичувальна здатність робочих сумішей (силіцидних і боридних), що використовуються для обробки таких матеріалів, є дуже низькою, що унеможливлює їх ефективне використання. Досліджено та проаналізовано умови техніко-*

технологічного процесу обробки неметалевих керамічних матеріалів залежно від складу силіцидної та боридної порошкових сумішей. Встановлено, що підвищення експлуатаційних характеристик порошкових сумішей для силіціювання та борування можна досягти за допомогою комплексного активатора. На основі проведених досліджень запропоновано оптимальний склад суміші, який забезпечує високу якість насичення оброблюваної поверхні та майже удвічі прискорює дифузійне насичення кремнієм і бором. Також встановлено, що для інтенсифікації процессу обробки керамічних матеріалів у насичувальному середовищі можна використовувати різні склади силіцидної та боридної сумішей. Дифузійне насичення керамічних матеріалів рекомендується проводити з використанням гідриду титану, що забезпечує необхідну швидкість насичення та високу якість оброблюваної поверхні. Результати досліджень показали, що запропоновані склади сумішей для силіціювання та борування можуть бути рекомендовані для обробки виробів на основі реакційно-спечених карбідокремнієвих і дисиліцид-молібденових матеріалів, що використовуються для виготовлення електронагрівачів та різноманітних конструкційних елементів високотемпературного обладнання.

***Ключові слова**: силіціювання, борування, карбід кремнію, дисиліцид молібдену, керамічні матеріали.*

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