



UDC 621.762

TECHNOLOGICAL CONDITIONS OF DIFFUSIVE BORIDE COATING FORMATION ON SILICON CARBIDE AND MOLYBDENUM DISILICIDE

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Summary. Basic directions of the diffusive boride coating formation on reaction-sintered silicon carbide and molybdenum disilicide are described. Technological conditions of non-metal ceramic materials boriding depending on the consideration of the amorphous boron concentration in the powder mixture are investigated and analyzed. It is determined that it is possible to speed up the rate of saturation process of the silicon carbide and molybdenum disilicide with boron by introducing sodium and aluminum fluorides as activating agents. Based on the carried out researches, optimal conditions for choosing the concentration of activating agents providing high saturation speed and improve operational parameters of the products are offered. It is also defined that to stimulate the process of boriding reaction-sintered ceramic materials, titanium hydride should be introduced into the saturated environment as the activating agent. Diffusion saturation of metals and alloys in hydrogen environment provides high saturation rate and good quality of the treated surface. The results of the carried out investigations prove that the saturation ability of the boride mixture increases significantly by introducing sodium fluoride and titanium hydride into it.

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

Received 11.04.2018

Statement of the problem. The technological process of diffusion siliconizing of reaction-sintered silicon carbide and molybdenum disilicide does not provide complete binding of the harmful impurities formed in the material while producing the products [1, 2]. The availability of harmful impurities, particularly, silicon dioxide, results in significant degradation of technological and operational parameters of SiC and $MoSi_2$.

Analysis of the available investigations and publications. One of the promising trends for improving the physical-chemical properties of reaction-sintered ceramic materials is diffusion saturation with boron resulting in the formation of silicon borides and other impurities. It is known that borides possess high oxidation resistance, which combines with the large thermal-shock resistance. They are chemically passive and have good radiating power and good thermoelectric parameters [3, 4]. Relatively, the physical-chemical properties of reaction-sintered ceramic materials should be improved. In our opinion, the technology of powder boriding method of silicon carbide and molybdenum disilicide for binding silicon and other harmful impurities is advanced. Hence, the process of diffusion saturation of SiC and $MoSi_2$ with boron is investigated.

The objective of the paper is to investigate the technological conditions for the formation of the diffusion boride coating on silicon carbide and molybdenum disilicide.

Results of the investigation. The technological process of silicon carbide and molybdenum disilicide boriding was carried out in containers with fuse gate in the powder mixture containing amorphous boron, fluoride agent and aluminium oxide. The concentration of amorphous boron was changed from 5 to 40 %, and the saturation process was carried out at temperature of 1000 – 1200⁰C for 2 – 12 hours.

Investigation of the technology of non-metallic reaction-sintered materials boriding, depending on the concentration of amorphous boron in a powder mixture, proved that the saturation capacity of such mixture increases with the content of diffusant in the environment up to 20%. Further increase in the amount of amorphous boron does not significantly affect the rate of boriding of SiC and $MoSi_2$, as is evidenced by the values of the samples specific mass gain. According to the X-ray diffraction analysis, the thin layer with the thickness up to $50\mu m$, formed on the surface of silicon carbide and molybdenum disilicide, is the chemical compound – silicon hexaboride (SiB_6). With boron concentration growth (more than 20 %), the thickness of SiB_6 layer increases very slowly, and boron concentration growth (30 % and more) does not sufficiently influence the change of samples mass. Probably, SiB_6 the phase formation slows down the saturation process, and especially the barrier properties of silicon hexaboride become obvious on silicon carbide. Increase of amorphous boron in the content significantly deteriorate the samples quality and results in mixture sintering, consequently preventing their removal from the container. Thus, diffusion boring of silicon carbide and molybdenum should be reasonably carried out in the mixture containing not more than 20 % of amorphous boron.

As the process temperature rises, the saturation capacity of the mixture increases, resulting in the sample specific weight growth. Saturation of reaction-sintered ceramic nonmetallic materials at temperatures above $1100^{\circ}C$ results in the powder mixture baking on the samples surface and its sintering, therefore the boriding temperature of SiC and $MoSi_2$ should not exceed $1100^{\circ}C$.

Fluorides of alkaline and alkaline-earth metals are used as activating agents for diffusion saturation [5]. Intensification of non-metallic materials boriding process can be achieved by introducing activating agents into the saturated environment, which perform the following functions:

- when heated, the products of evaporation or decomposition of the agent drive the air from the container;
- interact with the surface of the treated material and the saturating component;
- remove or restore oxide films;
- form the gas phase containing saturating element in the reaction medium and carry it to saturating surface.

The structure, chemical composition and growth rate of diffusion coatings, as well as their quality, are determined considerably by chemical composition, amount and method of activator introduction. In this regard, the possibility to use for boriding the reaction-sintered ceramic materials of sodium fluoride and aluminium fluoride, which concentration varied from 1 to 10 % for reaction- sintered, is investigated. At the content of activators up to 3 %, the saturation rate of silicon carbide and molybdenum disilicide is approximately the same, which is confirmed by the values of the sample specific mass gain (Table 1).

Table 1

Results of the sample specific mass gain dependence of mass (mg/cm^2) on the content of the fluoride activator in the boride mixture

Base	Activator	Activator concentration, mas. %				
		1	3	5	7	10
SiC	NaF		2,19	2,32	2,58	2,84
	AlF_3	1,43	1,48	1,52	1,6	1,98
$MoSi_2$	NaF	0,46	2,79	3,65	4,72	5,31
	AlF_3	1,37	1,92	2,81	4,05	5,96

Further increases of NaF and AlF_3 concentrations (over 3 %) provide the fast sample weight gain, particularly it is evident on molybdenum disilicide, but a slight increase in the weight gain of silicon carbide samples. The rise of activators (NaF and AlF_3) content in the boride environment results in its saturation ability increase, but baking of the mixture to the samples surface and its sintering occurs. The use of saturated media containing more than 3 % of fluoride activators is not reasonable, as it is almost impossible to remove samples from the container. Thus, SiC and $MoSi_2$ boriding is recommended in mixtures containing no more than 3 % of fluoride activator.

The investigation of the kinetics of the boriding process of ceramic materials samples for 12 hours showed that with an increase in duration there is in the specific weight gain rise in boride samples, resulting in the increase in the coating layer thickness. The results of X-ray diffraction analysis proves that there is no silicon dioxide. Thus, the faster is the specific weight gain growth, the greater is the thickness of the boride coating on the ceramics.

The growth of the layer thickness of boride phase on samples of silicon-carbide and of molybdenum disilicide ceramics is described by the parabolic law. Thus, we can come to the conclusion that the sample specific weight gain growth significantly affects the thickness of the layer of the boride phase SiB_6 . The study of the regularities of the boride layer formation on the samples gives an opportunity to offer the most probable mechanism for the silicon hexaboride layer formation.

The qualitative evaluation of the rate of the boride phase formation on the reaction-sintered ceramics depends on the activity of boron on the phase boundary. The thermodynamic boron activity at saturation temperatures is high providing the high rate of ceramic sample boriding and the formation of silicon hexaboride thick layer on the material surface. It can be assumed that the part of boron (20 – 30 %) is spent on silicon dioxide recovery remained in ceramics.

It is known [6] that diffusion saturation of metals and alloys in hydrogen media provides the high saturation rate and good quality of the treated surface. Hence, it is interesting to investigate the possibility to use metals hydrides of IV-th group as activating agents. We investigated the possibility of using titanium hydride as an activating agent, which at the saturation temperature decomposes with forming atomic hydrogen.

Investigation of the technological process of ceramic materials boriding on the basis of silicon carbide and molybdenum disilicide using titanium hydride proved that the introduction of the mixture from 1 to 10 % of TiH_2 significantly affects the saturation process rate. As the content of the titanium hydride in the powder medium increases, the saturation capacity of the mixture increases in 1.5 time compared with the use of fluoride activators. Saturation of SiC and $MoSi_2$ in mixtures containing 10 % or more of titanium hydride results in container depressurization and saturation process failure. Therefore, it is reasonable to use mixtures containing up to 7 % of titanium hydride.

Analysis of the obtained results gives grounds to conclude that in order to intensify the boriding process of reaction-sintered ceramic materials in saturated environment, it is necessary to introduce fluoride activator and titanium hydride as the activating agent. To determine the effectiveness of the joint action of fluoride activator and TiH_2 , the saturation of SiC and $MoSi_2$ in mixtures containing 20 % of amorphous boron and 1, 3 and 5 % of fluoride activator is studied and the amount of titanium hydride in all experiments is constant (7 %). It is defined that the best saturation power of the boride mixture is achieved with 3 % NaF and 7% TiH_2 , as is evidenced by the values of the samples specific mass gain of reaction-sintered silicon carbide and molybdenum disilicide (Table 2).

Comparison of the values of the sample specific mass gain of reaction-sintered silicon carbide and molybdenum disilicide indicates that boriding of mixtures containing fluoride sodium and titanium hydride are the most effective. The samples specific mass gain increases

twice as compared to saturation in the mixture containing only NaF . Investigation of the boriding samples of $MoSi_2$ showed that the introduction into the powder mixture of sodium fluoride and titanium hydride provides the production of silicon hexaboride on the sample layer with thickness 100 μm , twice as much as the thickness of boride layer obtained by using only NaF . The use of mixtures containing 5 % or more of fluoride activator results in saturation process deterioration. Hence, the use of boron mixtures containing sodium fluoride and titanium hydride is most appropriate.

Table 2

Influence of titanium hydride and fluoride activator on the change of the sample specific mass gain, mg/sm^2

Activator	Content, %	SiC	$MoSi_2$
NaF	1	2,26	5,35
NaF	3	4,05	7,28
AlF_3	1	2,84	5,43
AlF_3	3	3,09	6,45

The investigation of the influence of time on the speed of the boriding process of reaction-sintered ceramic materials showed that, with the increase of the saturation time from 2 to 12 hours, the samples specific mass gain increases approximately with the same rate. Boriding of SiC and $MoSi_2$ over 12 hours results in mixture sintering preventing the samples removal from the container.

On the basis of in-depth study of the agents influence on the saturation process of the reaction-sintered silicon carbide and silicon disilicide with amorphous boron, it is determined that the saturation capacity of the boride mixture increases significantly with the introduction of sodium fluoride and titanium hydride. They provide the mass transfer of the diffusing element from the powder mixture to the surface of the material as the result of saturated element formation, followed by disproportionation and the formation of boron diffusing into the sample depth and interacting with the impurities, resulting in silicon hexaboride formation.

Conclusions. Boriding of reaction-sintered ceramic materials make it possible to bind impurities, particularly silicon, forming silicon hexaboride, which has high stability and heat resistance. The offered technological process provides an opportunity to increase the oxidation resistance of ceramic materials based on SiC and $MoSi_2$ at high temperatures and improves the products operational parameters.

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УДК 621.762

ТЕХНОЛОГІЧНІ УМОВИ ФОРМУВАННЯ ДИФУЗІЙНОГО БОРИДНОГО ПОКРИТТЯ НА КАРБІДІ КРЕМНІЮ ТА ДИСИЛІЦИДІ МОЛІБДЕНУ

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Резюме. Описано основні напрями формування дифузійного боридного покриття на реакційно-спеченому карбіді кремнію та дисиліциді молібдену. Досліджено та проаналізовано технологічні умови борування неметалевих керамічних матеріалів залежно від концентрації аморфного бору в порошковій суміші. Встановлено, що підвищити швидкість процесу насичення карбиду кремнію та дисиліциду молібдену бором можна шляхом введення активуючих добавок фторидів натрію й алюмінію. На основі проведених досліджень запропоновано оптимальні умови вибору концентрації активуючих добавок, які забезпечують високу швидкість насичення й покращують експлуатаційні параметри виробів. Також встановлено, що для інтенсифікації процесу борування реакційно-спечених керамічних матеріалів у насичувальне середовище необхідно вводити активуючу добавку гідрид титану. Якісне оцінювання швидкості утворення боридної фази на реакційно-спеченій кераміці залежить від активності бору на фазовій межі. Термодинамічна активність бору при температурі насичення велика, що забезпечує високу швидкість борування зразків кераміки та утворення товстого шару гексабориду кремнію на поверхні матеріалу. Дифузійне насичення металів і сплавів у водневих середовищах забезпечує високу швидкість насичення та добру якість оброблюваної поверхні. Результати проведених досліджень показали, що насичувальна здатність боридної суміші істотно зростає при введенні в неї фтористого натрію та гідриду титану. Встановлено, що найкраща насичувальна здатність боридної суміші досягається при використанні 3 % фтористого натрію і 7% гідриду титану, про що свідчать величини питомого приросту маси зразків реакційно-спеченого карбиду кремнію та дисиліциду молібдену.

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

Отримано 11.04.2018