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METHOD OF REACTION-SINTERED PRODUCTS PROCESSING BASED ON SILICON CARBIDE AND MOLIBDENUM DISILICIDE

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Summary. *The main methods for processing ceramic materials based on reaction-sintered silicon carbide and molybdenum disilicide are described. The technological conditions of nonmetallic ceramic materials processing depending on the oxide silicide composition in the powder mixture are studied and analyzed. It is determined that the increase in the lifetime of ceramic materials based on silicon carbide and molybdenum disilicide can be achieved by introduction of zirconium oxide, yttrium oxide and hafnium oxide. Based on the carried out investigations, optimal conditions for selecting the concentration of these additives, which ensure high saturation speed and improve the operational parameters of the products are proposed. It is also determined that in order to intensify the processing of ceramic materials based on reaction-sintered ceramic materials, various compositions of the silicide oxide composition can be introduced into the saturation medium. Diffusion saturation of ceramic materials with titanium hydride provides high saturation speed and good quality of the surface to be treated. The study of the kinetics of the interaction of silicoboride phase with the carborundum and disilicide with molybdenum base showed that, with increasing heating duration, the thickness of the diffusion coating decreases. The final operation of the process for processing reaction-sintered ceramic materials is to apply silicon-based surface of carbide-silicate and disilicide molybdenum samples of the suspension layer of silicide oxide composition containing molybdenum disilicide, zirconium-yttrium ceramics, and sodium aluminate. The proposed method of processing reaction-sintered ceramic materials increases in 2 and 1.5 times the lifetime of samples based on silicon carbide and molybdenum disilicide. The results of the carried out research show that the proposed method can be recommended for the processing of products based on reaction – sintered carbide silicic acid and disilicide molybdenum materials used for the manufacturing the electric heaters and various types of structural elements of high-temperature equipment.*

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

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Statement of the problem. The technology of reaction-sintered ceramic materials processing based on silicon-carbide and molybdenum disilicide does not provide complete binding of harmful impurities formed in the material when products are obtained [1, 2]. The availability of harmful impurities results in significant deterioration of the technological and operational characteristics of silicon carbide and molybdenum disilicide.

Analysis of the available investigations and publications. Products made of reaction-sintered ceramic materials based on silicon carbide and molybdenum disilicide are widely used in modern high-temperature engineering. However, the availability of impurities, particularly, of silicon, introduced into the material in order to reduce the temperature of products sintering, leads in sintering process to the formation of silicon dioxide (SiO_2). The presence of silicon dioxide increases the electrical resistance and overheating of products made of reaction sintered silicon carbide and molybdenum disilicide. The sharp change in the temperature mode causes the destruction of bonds between the ceramics grains and material strength loss. There are various ways to improve the physical-mechanical and chemical properties of ceramic materials. The most common is coating of the product working surface [3].

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The method of coating formation on the working surface of heater made of silicon carbide (US Patent No. 2003592) which contains 80% of silicon carbide and 20% of bentonite is well known. The protective layer is burned in the air at temperature 1370ºC. The disadvantage of this method is the increase of the heaters specific load at high temperatures (1500ºC and above).

The well-known method for improving the thermal stability of silicon carbide heaters (Inventor's Certificate 133960), which involves several successive processing operations. First, the heater working surface is moistened by bakelite varnish and applied by boron carbide powder or mixture of boron carbide and 10% silicon with further heat treatment: previously in the air, and then in hydrogen medium at 2200ºC for 1,5–2 hours. The layer of cubic silicon carbide is deposited on the product surface. The disadvantage of the proposed method of treatment is a large number of intermediate technological operations and the complexity of protective coating formation process [4].

The method for increasing the heat resistance of heaters from molybdenum disilicide is also known, here the quartz glass is applied to the heater working surface, and then boiled at temperature 1800ºC. The disadvantage of this method is high brittleness of protective coating at room temperature, whereas its electrical resistance sharply changes with temperature growth [5].

Objective of the paper роботи is to propose the method of increasing the products service life on the basis of reaction-sintered silicon carbide and molybdenum disilicide operating in oxidizing medium at temperature range 1500–1600ºC with sharp change in thermal mode.

Results of the investigations. The developed method of reaction-sintered ceramic materials processing on the basis of silicon carbide and molybdenum disilicide is referred to the direct chemical and thermal processing in the field of powder metallurgy and can be recommended in electronics and electrical engineering industry.

The method of reaction-sintered carbide silicon heaters processing is the most approximated one to the described technical result (Inventor's Certificate 1694552), where the unbound silicon is partially removed from the heaters by means of chemical etching, and then saturated with boron with subsequent application of silicide oxide composition to the heaters active part. The disadvantage of this method is the high process complexity and high safety requirements.

The objective of the processing method proposed by us is to increase the products service life on the basis of reaction-sintered silicon carbide and molybdenum disilicide operating in oxidizing medium at temperature range 1500–1600ºC with sharp thermal mode change.

The set objective is achieved first of all by removing silicon dioxide from the products due to their siliconizing in the powder mixture, and then saturating with boron, followed by the application of suspension containing (wt.%): molybdenum disilicide ($MoSi_2$) – 70–80; zirconium-yttrium ceramics (CIS-2) – 15–20 and sodium aluminate ($NaAlO_2$) 5–10.

In order to implement the proposed processing method of reaction-sintered ceramic materials samples of 8x10 *mm* in size made of silicon carbide and silylidide molybdenum electric heaters were used. 12 samples of each type were produced.

To remove silicon dioxide from the materials, the samples were siliconized in the powder mixture containing (wt.%): silicon (Si) – 60; sodium fluoride (NaF) – 5; titanium hydride (TiH_2) – 10; Aluminum oxide (Al_2O_3) (– the rest. The process was carried out in containers made of heat-resistant alloy using the fused shutter. Containers were placed in the thermal furnace with heated air temperature up to 1100ºC, the duration of the saturation process did not exceed 8 hours. Upon the completion of siliconizing process, the containers were cooled together with the oven to the temperature 20ºC, and then powder mixture was unpacked and separated from the samples on the sieve. Siliconized samples after saturation have light gray colour. The constant activity of the mixture is maintained before each use by introducing

5 wt.% silicon (Si), 0.5 wt.% sodium fluoride (NaF) and 1 wt.% titanium hydride (TiH_2). Such mixture can be used up to ten times.

The investigations of the technological process of ceramic materials processing on the basis of silicon carbide and molybdenum disilicide using titanium hydride showed that the introduction of a mixture of 1 to 10% of TiH_2 significantly affects the velocity of the saturation process. Increasing the content of titanium hydride in the powder medium, the saturation capacity of the mixture increases by 1.5-times compared with the use of fluoride activators. Saturation of SiC and $MoSi_2$ in the mixtures containing 10% or more titanium hydride results in container depressurization and saturation process disfunction, therefore it is reasonable to use mixtures containing up to 7% titanium hydride [4].

In order to form the heat-resistant component of the protective coating, the previously silicized samples are boronized in the powder mixture containing (wt.%): amorphous boron (B) – 40; sodium fluoride (NaF) – 5; titanium hydride (TiH_2) – 10 and aluminum oxide(Al_2O_3) – the rest. The process is carried out in containers made of heat-resistant alloy using the fused shutter placed in the thermal furnace with heated air up to 1100ºC, the duration of boronizing process does not exceed 12 hours. When the container is heated, fluorides of boron and boron hybrids are formed, they are boron conveyors to the reaction-sintered ceramics surface. As a result of the atomic boron interaction, hexaboride of silicon is formed. The thickness of the coating layer on silicon carbide and molybdenum disilicide reaches, relatively, 120 and 150 μm. Upon boronizing process completion, the container is cooled with the oven to the temperature 20ºC, and then it is unpacked and the powder mixture is separated from the samples on the sieve. The mixture is stored in the sealed containers to prevent contact with moisture.

The investigation of the kinetics of silicoboride phase interaction with carborundum and disilicide molybdenum base showed that, if the heating duration increases, the thickness of diffusion coating decreases. After annealing at temperature 1200ºC (for 12 hours), the initial thickness of the protective layer on SiC reduces theefold, and at 1500ºC by 40%. The similar phenomenon is observed on molybdenum disilicide samples. The change in the phase coating composition on SiC and $MoSi_2$ occurs from the vacuum medium side. At the same time, there is a slow growth of silicon tetraborate, as the evidence of metallographic and microdurmetric analysis methods results. Since, during heating in vacuum, the surface layer is destroyed and the significant loss of the sample weight is observed, the investigation of silicon hexaboride stability for more than 12 hours is reasonable. To slow down undesired processes on the coating – vacuum surface, the inert medium can be used [2].

As activating additives for diffusion saturation, fluorides of alkaline and alkaline earth metals are used [3]. In order to intensify the process of non-metallic materials processing, the activating additives having the following functions can be introduced into the saturated environment;

- when heated, evaporation or decomposition products of the activator extrude air from the container;
- interact with the surface of the processed material and saturating component;
- remove or restore the oxide films;
- form in the reaction volume the gas phase containing saturation element and transfer it to saturated surface.

Constant activity of the powder mixture before each repeated use is supported by addition of 5% amorphous boron, 0.5% sodium fluoride (NaF) and 1% titanium hydride (TiH_2), the restored mixture can be used from ten to fifteen times.

The final process operation for reaction-sintered ceramic materials processing is the application of suspension layer of silicide oxide composition containing molybdenum disilicide, zirconium-yttrium ceramics and sodium aluminate to silicon-based surface of carbide-silicate and disilicide molybdenum samples. Molybdenum disilicide ($MoSi_2$ – MRTU6-09-5701-68) functions as high temperature binding, zirconium-yttrium ceramics (CIS-2, ТУ14-8-86-73) contains (wt.%) zirconium oxide (ZrO_2) + hafnium oxide (HfO_2) – 72–78, yttrium oxide (Y_2O_3) – 22–28 and is the refractory filler that increases the heat resistance of silicon oxide suspension. The introduction of sodium aluminate suspension ($NaAlO_2$) results in the formation of sodium oxide portion (Na_2O), which is expended to create together with silicon oxide SiO_2 the glass film and refractory component – aluminum oxide (Al_2O_3).

Silicide oxide composition is applied on silicon-based samples based on reaction-sintered silicon carbide and silylidide molybdenum. The composition of silicide oxide compositions (wt.%) is shown in Table 1.

Table 1

Silicide oxide composition

Composition	$MoSi_2$	*ZrY-2*	$NaAlO_2$
I	70	20	10
II	75	17.5	7.5
III	80	15	5.0

The thickness of the coating layer for the periodic coating mode and the working cycle duration of 100 hours is approximately 225 μm. The tests of coated samples (4 pieces of each component) were carried out in accordance with the requirements of the State Standard of Ukraine. The obtained results of the carried out tests of silicon-boronized carbide silicic and silicidicide molybdenum samples with deposited layer of silicide oxide composition are presented in Table 2.

Table 2

Test results

Material	Test temperature °C	Surface durability, *hrs*			
		Proposed			Standard
		Composition I	Composition II	Composition III	
SiC	1500	2000	2500	3000	1500
$MoSi_2$	1600	2200	2600	3500	2000

Conclusions. The obtained results indicate that the proposed method of reaction-sintered ceramic materials processing increases the service lifetime of samples based on silicon carbide and molybdenum disilicide by 2 and 1.5 times. The proposed method can be recommended for the processing of products on the basis of reaction-sintered carbide silicic and silicidicide molybdenum materials used for production of electric heaters and various types of structural elements of high-temperature equipment.

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СПОСІБ ОБРОБКИ РЕАКЦІЙНО-СПЕЧЕНИХ ВИРОБІВ НА ОСНОВІ КАРБІДУ КРЕМНІЮ ТА ДИСИЛІЦИДУ МОЛІБДЕНУ

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Резюме. *Описано основні способи обробки керамічних матеріалів на основі реакційно-спеченого карбіду кремнію та дисиліциду молібдену. Досліджено та проаналізовано технологічні умови обробки неметалевих керамічних матеріалів залежно від складу силіцидоксидної композиції в порошковій суміші. Встановлено, що підвищити ресурс експлуатації керамічних матеріалів на основі карбіду кремнію та дисиліциду молібдену можна шляхом введення оксиду цирконію, оксиду ітрію та оксиду гафнію. На основі проведених досліджень запропоновано оптимальні умови вибору концентрації даних добавок, які забезпечують високу швидкість насичення й покращують експлуатаційні параметри виробів. Також встановлено, що для інтенсифікації процесу обробки керамічних матеріалів на основі реакційно-спечених керамічних матеріалів у насичувальне середовище можна вводити різні склади силіцидоксидної композиції. Дифузійне насичення керамічних матеріалів із використанням гідриду титану забезпечує високу швидкість насичення та добру якість оброблюваної поверхні. Дослідження кінетики взаємодії силікоборидної фази з карборундовою та дисиліцидмолібденовою основою показало, що зі збільшенням тривалості нагрівання товщина дифузійного покриття зменшується. Завершальною операцією способу обробки реакційно-спечених керамічних матеріалів є нанесення на силікоборовану поверхню карбідокремнієвих і дисиліцидмолібденових зразків шару суспензії силіцидоксидної композиції, яка містить дисиліцидмолібдену, цирконієво-ітрієву кераміку і алюмінат натрію. Запропонований спосіб обробки реакційно-спечених керамічних матеріалів підвищує в 2 і 1,5 раза ресурс роботи зразків на основі карбіду кремнію та дисиліциду молібдену. Результати проведених досліджень показали, що запропонований спосіб може бути рекомендований для обробки виробів на основі реакційно-спечених карбідокремнієвих і дисиліцидмолібденових матеріалів, які використовуються для виготовлення електронагрівачів і різного типу конструкційних елементів високотемпературного обладнання.*

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

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