Development of Heat-Resistant Coatings for Protection of Niobium and Tantalum from the Oxidizing Effect of Air at Temperatures 1700−1900°C

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The paper presents the results of creating protective coatings on niobium and tantalum samples. These coated samples are tested for heat resistance in air in the temperature range of 1700−1900°C. The coating is formed by the method of activated vacuum diffusion saturation at temperatures of 1150−1310°C. When forming a part of the protective coatings, a layer of slurry is applied to the surface of the samples, followed by chemical and thermal treatment in a vacuum in the presence of NaCl vapours. A thermodynamic analysis of possible chemical reactions taking place in the process of formation of protective coatings is carried out. The developed heat-resistant coatings provide protection of niobium samples from air oxidation at a temperature of 1700°C from 8 to 13.5 hours. Heat-resistant coatings created on samples with Nb and Ta protect them from exposure to an oxidizing environment from 3 to 6.3 hours at a temperature of 1800°C and for 0.5 hours at a temperature of 1900°C.

Key words: protective layer, activated vacuum diffusion saturation, solid non-porous coatings, refractory metals, heat-resistant.

У роботі представлено результати створення захисних покриттів на зразках

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з ніобію та танталу. Ці зразки з покриттями випробовували на жаротрив-
кість на повітрі в інтервалі температур 1700–1900°C. Покриття формували
методом активованого вакуумного дифузійного насичення за температур у
1150–1310°C. Для формування частини захисних покриттів на поверхню
зразків наносили шар шлікеру з подальшим хеміко-термічним оброблен-
ням у вакуумі за присутности парів NaCl. Було проведено термодинамічну
аналізу можливих хемічних реакцій, що мають місце у процесі утворення
захисних покриттів. Розроблені жаротривкі покриття забезпечують захист
зразків з ніобію від окиснення на повітрі за температури у 1700°C від 8 до
13,5 годин. Жаротривкі покриття, створені на зразках з Nb і Ta, захища-
ють їх від впливу окисного середовища від 3 до 6,3 годин за температури у
1800°C та протягом 0,5 години за температури у 1900°C.

Ключові слова: захисний шар, активоване вакуумне дифузійне насичен-
ня, суцільні непористі покриття, тяжкотопкі метали, термостійкість.

1. INTRODUCTION

The problem of protecting refractory metals (niobium and tantalum)
from the influence of oxidizing environments at elevated temperatures
remains relevant today. Previously, they tried to create a protective
layer on the surface of these metals with the help of silicification and
the introduction of refractory components into it. Another method was
preliminary boron saturation of the niobium surface with subsequent
silicification. This method makes it possible to reduce the rate of deg-
radation of the heat-resistant layer on the refractory metal. Currently,
one of the most high-quality methods of protecting niobium from the
influence of an oxidizing environment is a heat-resistant coating,
which is formed using a two-stage technology.

At the first stage, a layer of molybdenum is applied to the niobium
surface, and then the silicification process is carried out. This stage
forms a layer of molybdenum disilicide on niobium. The first stage of
creating this coating—applying a layer of molybdenum is carried out
by the method of ion bombardment condensation (IBO). In the case of
protection of a complex-shaped niobium product, the process of mo-
lybdenum deposition is carried out by gradually applying a layer of
metal to separate areas of the surface of the part. Direct silicification
of niobium does not provide protection of this metal against the influ-
ence of oxidizing environments at temperatures above 1000°C. When
the niobium surface is saturated with silicon, a coating is formed,
which can consist of 3 layers. These are layers consisting of niobium
silicides $NbSi_2$, Nb_5Si_3, Nb_3Si, respectively. All these compounds form
silicon oxide SiO_2 and niobium oxide Nb_2O_5, when exposed to oxidizing
media. Niobium oxide Nb_2O_5 has a powdery structure and does not al-

low creating a continuous non-porous coating on the metal surface. Such a coating does not prevent the penetration of oxygen to niobium and the oxidation of this metal will continue.

One of the ways to eliminate this problem is to saturate the niobium surface with several refractory metals. When the surface is further saturated with silicon, a layer consisting of several refractory silicides is formed on the niobium. Under the action of oxidizing media, a layer consisting of several oxides is formed on such a surface. Depending on the goal, the content of niobium oxide in this surface layer will not be the main one. This can make it possible to form a continuous heat-resistant layer on the surface of niobium, which prevents the penetration of oxygen to the metal. The method of activated vacuum diffusion saturation allows introducing such metals as Ti, Cr, V, Hf, Zr and others into the treated surface. The use of sodium chloride as an activator in this method makes it environmentally friendly [1, 2]. It makes it possible to form uniform diffuse layers even on products with holes of small diameter [3].

The purpose of this work is to create heat-resistant coatings to protect niobium and tantalum from the effects of oxidizing environments at temperatures $T = 1700-1900°C$ by the method of vacuum activated diffusion saturation.

2. MATERIALS AND METHODS

In this paper, the main method of forming heat-resistant coatings on niobium and tantalum was the vacuum diffusion saturation method. An activator (sodium chloride) was used to speed up the processing process. Niobium and tantalum samples had a cylindrical shape with a diameter of 2 mm and a length of 80 mm. This form of samples allows them to be tested for heat resistance on a special stand. On this device, the samples are heated by direct passage of electric current to a given temperature. The temperature of the samples is determined by an optical pyrometer. The measure of heat resistance of the samples is the duration of their work in the air until complete destruction.

Powders of various elements and compounds were used during the chemical and thermal treatment of the samples. Silicon powder of semiconductor purity was used for silicification. When carrying out the process of vacuum activated diffusion borosilication, a powder mixture of the composition Si $(95-97) + B (3-5)$ % wt. was used. In addition, to speed up the process of formation of the protective coating, slurry was used. Slurry was created on the basis of a powder mixture with the addition of a liquid binder. Tsapon-lacquer КО-85 was used as such a substance. Slurry was applied to the surface of the sample before its chemical and thermal treatment. X-ray fluorescence analysis was used to measure the surface composition during the formation of

coatings. For this purpose, flat witness samples were used. These samples were usually used for metallographic research. In this way, the structure and structure of the surface layers on the samples were studied. Another way to conduct research on the process of forming heat-resistant coatings was to use calculations to determine thermodynamically possible chemical reactions that take place in the reaction space during activated vacuum diffusion saturation. The analysis of possible chemical reactions allows us to make assumptions about the mechanism of the transfer of saturating elements and the formation of the surface layer and its composition.

3. RESULTS AND DISCUSSION

To create a heat-resistant coating on niobium and tantalum, it is necessary to create a layer on their surface consisting of several refractory metals. These should be such metals as chromium, zirconium, hafnium, titanium, vanadium, molybdenum, tungsten. Silicon and boron must be introduced into this layer. Due to its physical properties, boron is a component that inhibits the processes of destruction of heat-resistant coatings at elevated temperatures. We have tested various options of protective coatings, which are presented below in Table 1. Under point 1 of this table, a comprehensive protective coating is given. Niobium samples were processed in chromium powder in the presence of NaCl vapours and reduced pressure at a temperature of 1150°C for 6 hours.

During the interaction of NaCl vapours with chromium, 5 chromium chlorides can be formed. In Table 2, column 1 is the reaction number, column 2 is the chemical reaction equation, next column 3 is the reaction temperature, and columns 4 and 5 are the degree of reaction at the specified pressure. The degree of progress of a chemical reaction α is the proportion of starting substances that have reacted according to the reaction. The flow of the activator (sodium chloride) was set by its temperature. During the processes of vacuum diffusion saturation, the temperature of NaCl was maintained in the range of 790−810°C. At these temperature values, the pressure of saturated NaCl vapour varies in the range from 1 to 10^2 Pa. The design of the container is analogous to a Knudsen cell; so, the vapour pressure and composition of the gas medium will be the same throughout the reaction space [4−6]. The process of vacuum activated diffusion chrome plating was carried out at a temperature of $T = 1423$ K and a gas pressure in the reaction space in the range of $1−10^2$ Pa. Under these conditions, the main components of the gas saturation medium will be the lower chromium chlorides CrCl and $CrCl_2$ (reactions 1, 2, Table 2). These compounds interact with the niobium surface according to reactions 3, 4 (Table 2). Chromium plating led to the formation of a surface layer with a composition of

27.9 Nb + 72.1 Cr % wt. Then, a layer of 70 Mo + 20 Ni + 5.4 Ti + 2.8 Si + + 1 B + 0.8 Al % wt. slurry was applied to the surface of these samples and borosilication was carried out.

The composition of the slurry includes titanium, silicon, nickel, boron and aluminium. As thermodynamic analysis shows, when these components interact with NaCl sodium chloride vapours, according to reactions 5−15 (Table 2), chlorides of titanium, silicon, and boron are formed. Therefore, after chemical and thermal treatment, the surface layer has the following composition: 15.75 Si + 8.65 Ti + 28.05 Cr + + 0.25 Ni + 34.3 Nb + 18.8 Mo % wt. This coating provides protection against air oxidation for 8 hours. After chromium plating of niobium samples, a layer containing 72% Cr is formed on the surface. When chrome-plating low-carbon steels, a layer is formed on their surface, the concentration of chromium in which is about 90%. Therefore, it is possible to try to achieve an even higher content of this element on the surface of the sample by varying the niobium chroming regimes.

TABLE 1. Results of comparative heat resistance test of niobium and tantalum samples with protective coatings.

No.	Sub-strate	The process of forming a heat-resistant coating on the sample	Heat resistance test temperature, °C	Heat resistance, h
1	2	3	4	5
1	Nb	The samples were chrome-plated at a temperature of 1150°C for 6 hours, then a layer of 70 Mo + 20 Ni + + 5.4 Ti + 2.8 Si + 1 B + 0.8Al % wt. was applied to them and borosilicated at $T = 1280$°C for 6 hours	1700	8
2	Nb	A layer of 35 MoSi$_2$ + 20 HfB$_2$ + 10 ZrSi$_2$ + 20 VSi$_2$ + + 9 Al + 6 B % wt. was applied to the samples and borosilicated in a mixture of 97 Si + 3 B % wt. at $T = 1300$°C for 7 hours	1700 1800	9 3
3	Nb	A layer of 80 Mo + 13.5 Ni + 6.5 Sn % wt. slurry was applied to the samples and titanated at $T = 1150$°C for 7 hours. After that, the samples were borosilicated at a temperature of $T = 1300$°C for 7 hours	1700	9
4	Nb	The samples were hafniated at a temperature of 1300°C for 6 hours using NaCl vapours. After that, a slurry of the composition 35 HfB$_2$ + 20 ZrSi$_2$ + 20 MoSi$_2$ + + 10 TiB$_2$ + 6.5 Ni + 6.5 Zr + 2 B was applied to the surface of the samples and processed in a mixture of powders 22 Si + 22 ZrSi$_2$ + 22 HfB$_2$ + 31 MoSi$_2$ % wt. at temperature $T = 1300$°C for 7 hours. NaCl was used to speed up the process	1700	9−13.5

Continuation of Table 1.

1	2	3	4	5
5	Nb	The samples were processed in a powder mixture of 40 MoSi$_2$ + 20 HfB$_2$ + 20 VSi$_2$ + 20 Si % wt. in the presence of NaCl steam at a temperature of $T = 1310$°C for 7 hours	1800	5–6.3
6	Ta	The samples were processed in a powder mixture of 40 MoSi$_2$ + 20 HfB$_2$ + 20 VSi$_2$ + 20 Si % wt. in the presence of NaCl steam at a temperature of $T = 1310$°C for 7 hours	1800	5–6.3
7	Nb	The samples were annealed in a mixture of composition 40 Si + 30 HfB$_2$ + 30 ZrSi$_2$ % wt. in NaCl vapours at a temperature of $T = 1300$°C for 7 hours	1900	0.5
8	Ta	The samples were annealed in a mixture of composition 40 Si + 30 HfB$_2$ + 30 ZrSi$_2$ % wt. in NaCl vapours at a temperature of $T = 1300$°C for 7 hours	1900	0.5

Table 1, point 2 shows the method of obtaining a heat-resistant layer on a niobium sample. A layer of 35 MoSi$_2$ + 20 HfB$_2$ + 10 ZrSi$_2$ + 20 VSi$_2$ + 9 Al + 6 B % wt. was applied to this sample, and then borosilication was carried out at a temperature of $T = 1573$ K. During borosilication, the interaction of sodium chloride NaCl vapours with the components of the slurry, as well as silicon and boron, occurs in the reaction space. The aluminium present in the slurry is in a liquid state at the temperature of the chemical and thermal treatment. It acts as a liquid layer on the surface of the sample and facilitates the process of forming a diffusion layer. When NaCl vapours are exposed to boron B [4] present in the slurry, boron chlorides BCl, BCl$_3$ are formed in reactions 12, 13 (Table 2).

The interaction of NaCl steam with molybdenum disilicide MoSi$_2$ leads to the formation of molybdenum dichloride MoCl$_2$ and silicon dichloride SiCl$_2$, reaction 14. The effect of NaCl steam on the slurry component—HfB$_2$, at the appropriate temperature and pressure, leads to the formation of boron chlorides BCl, BCl$_3$ and hafnium chlorides HfCl$_2$, HfCl$_3$, HfCl$_4$, points 15–18 (Table 2). The zirconium disilicide ZrSi$_2$ introduced into the slurry under the influence of NaCl steam forms zirconium chlorides ZrCl–ZrCl$_4$ and silicon chlorides SiCl–SiCl$_4$, points 19–30 (Table 2).

Another component of the slurry is VSi$_2$. When NaCl vapour is exposed to VSi$_2$, vanadium chlorides and silicon chlorides are formed (points 31–41, Table 2).

The formation of the coating according to point 2 occurs by means of processing in a saturating gas environment consisting of molybdenum

dichloride, boron chlorides, hafnium chlorides, zirconium chlorides, vanadium chlorides, and silicon chlorides. The process also involves borosilication of the niobium surface.

As a result of this chemical-thermal treatment, a diffusion layer is formed on the sample, consisting of molybdenum silicides, hafnium silicides, zirconium silicides, vanadium silicides, and it contains boron in the form of a compound. The heat-resistant layer created by this

TABLE 2. The degree of progress of chemical reactions in the reaction space at temperature T and pressure P.

No.	The equation of a chemical reaction	T, K	Degree of conversion α at pressure $P \cdot 10^2$, Pa	
1	2	3	4	5
1	$NaCl\,(g) + Cr\,(s) = CrCl\,(g) + Na\,(g)$	1423	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$
2	$NaCl\,(g) + 1/2Cr\,(s) = 1/2CrCl_2\,(g) + Na\,(g)$	1423	$4 \cdot 10^{-3}$	$1.8 \cdot 10^{-2}$
3	$CrCl\,(g) + 3/8Nb\,(s) = 3/8Cr_2Nb\,(s) + 1/4CrCl_4\,(g)$	1423	1	1
4	$CrCl_2\,(g) + 1/4Nb\,(s) = 1/4Cr_2Nb\,(s) + 1/2CrCl_4\,(g)$	1423	0.87	0.20
5	$NaCl\,(g) + Ti\,(s) = TiCl\,(g) + Na\,(g)$	1553	$4.5 \cdot 10^{-2}$	0.41
6	$NaCl\,(g) + 1/2Ti\,(s) = 1/2TiCl_2\,(g) + Na\,(g)$	1553	$7.6 \cdot 10^{-2}$	0.30
7	$NaCl\,(g) + 1/3Ti\,(s) = 1/3TiCl_3\,(g) + Na\,(g)$	1553	$6.6 \cdot 10^{-2}$	0.19
8	$NaCl\,(g) + 1/4Ti\,(s) = 1/4TiCl_4\,(g) + Na\,(g)$	1553	$1.8 \cdot 10^{-2}$	$4.4 \cdot 10^{-2}$
9	$NaCl\,(g) + Si\,(s) = SiCl\,(g) + Na\,(g)$	1523	$6 \cdot 10^{-3}$	$6 \cdot 10^{-2}$
10	$NaCl\,(g) + 1/2Si\,(s) = 1/2SiCl_2\,(g) + Na\,(g)$	1523	$1.7 \cdot 10^{-2}$	$7.7 \cdot 10^{-2}$
11	$NaCl\,(g) + 1/3Si\,(s) = 1/3SiCl_3\,(g) + Na\,(g)$	1523	$5 \cdot 10^{-3}$	$1.6 \cdot 10^{-2}$
12	$NaCl\,(g) + B\,(s) = BCl\,(g) + Na\,(g)$	1573	$1.5 \cdot 10^{-2}$	0.15
13	$NaCl\,(g) + 1/3B\,(s) = 1/3BCl_3\,(g) + Na\,(g)$	1573	$5 \cdot 10^{-3}$	$1.6 \cdot 10^{-2}$
14	$NaCl\,(g) + 1/6MoSi_2\,(s) = 1/6MoCl_2\,(g) + 1/3SiCl_2\,(g) + Na\,(g)$	1573	$2.3 \cdot 10^{-3}$	$1 \cdot 10^{-2}$
15	$NaCl\,(g) + 1/4HfB_2\,(s) = 1/2BCl\,(g) + 1/4HfCl_2\,(g) + Na\,(g)$	1573	$2 \cdot 10^{-3}$	$1.5 \cdot 10^{-2}$
16	$NaCl\,(g) + 1/5HfB_2\,(s) = 2/5BCl\,(g) + 1/5HfCl_3\,(g) + Na\,(g)$	1573	$5.4 \cdot 10^{-3}$	$3 \cdot 10^{-2}$
17	$NaCl\,(g) + 1/6HfB_2\,(s) = 1/3BCl\,(g) + 1/6HfCl_4\,(g) + Na\,(g)$	1573	$3.2 \cdot 10^{-3}$	$1.4 \cdot 10^{-2}$
18	$NaCl\,(g) + 1/9HfB_2\,(s) = 2/9BCl_3\,(g) + 1/9HfCl_3\,(g) + Na\,(g)$	1573	$3.6 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$
19	$NaCl\,(g) + 1/5ZrSi_2\,(s) = 1/5ZrCl\,(g) + 2/5SiCl_2\,(g) + Na\,(g)$	1573	$3 \cdot 10^{-3}$	$1.6 \cdot 10^{-2}$
20	$NaCl\,(g) + 1/4ZrSi_2\,(s) = 1/4ZrCl_2\,(g) + 1/2SiCl\,(g) + Na\,(g)$	1573	$3 \cdot 10^{-3}$	$2.4 \cdot 10^{-2}$
21	$NaCl\,(g) + 1/6ZrSi_2\,(s) = 1/6ZrCl_2\,(g) + 1/3SiCl_2\,(g) + Na\,(g)$	1573	$8 \cdot 10^{-3}$	$3.5 \cdot 10^{-2}$
22	$NaCl\,(g) + 1/8ZrSi_2\,(s) = 1/8ZrCl_2\,(g) + 1/4SiCl_3\,(g) + Na\,(g)$	1573	$4 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$
23	$NaCl\,(g) + 1/5ZrSi_2\,(s) = 1/5ZrCl_3\,(g) + 2/5SiCl\,(g) + Na\,(g)$	1573	$9 \cdot 10^{-3}$	$5 \cdot 10^{-2}$

Continuation of Table 2.

1	2	3	4	5
24	$NaCl\,(g) + 1/7ZrSi_2\,(s) = 1/7ZrCl_3\,(g) + 2/7SiCl_2\,(g) + Na\,(g)$	1573	$1.5 \cdot 10^{-2}$	$5.9 \cdot 10^{-2}$
25	$NaCl\,(g) + 1/9ZrSi_2\,(s) = 1/9ZrCl_3\,(g) + 2/9SiCl_3\,(g) + Na\,(g)$	1573	$7 \cdot 10^{-3}$	$2.2 \cdot 10^{-2}$
26	$NaCl\,(g) + 1/11ZrSi_2\,(s) = 1/11ZrCl_3\,(g) + 2/11SiCl_4\,(g) + Na\,(g)$	1573	$4 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$
27	$NaCl\,(g) + 1/6ZrSi_2\,(s) = 1/6ZrCl_4\,(g) + 1/3SiCl\,(g) + Na\,(g)$	1573	$1.3 \cdot 10^{-2}$	$6 \cdot 10^{-2}$
28	$NaCl\,(g) + 1/8ZrSi_2\,(s) = 1/8ZrCl_4\,(g) + 1/4SiCl_2\,(g) + Na\,(g)$	1573	$1.9 \cdot 10^{-2}$	$6.6 \cdot 10^{-2}$
29	$NaCl\,(g) + 1/10ZrSi_2\,(s) = 1/10ZrCl_4\,(g) + 1/5SiCl_3\,(g) + Na\,(g)$	1573	$9.1 \cdot 10^{-3}$	$2.6 \cdot 10^{-2}$
30	$NaCl\,(g) + 1/12ZrSi_2\,(s) = 1/12ZrCl_4\,(g) + 1/6SiCl_4\,(g) + Na\,(g)$	1573	$5.2 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$
31	$NaCl\,(g) + 1/3VSi_2\,(s) = 1/3VCl\,(g) + 2/3SiCl\,(g) + Na\,(g)$	1573	$1.7 \cdot 10^{-3}$	$1.7 \cdot 10^{-2}$
32	$NaCl\,(g) + 1/5VSi_2\,(s) = 1/5VCl\,(g) + 2/5SiCl_2\,(g) + Na\,(g)$	1573	$5 \cdot 10^{-3}$	$2.9 \cdot 10^{-2}$
33	$NaCl\,(g) + 1/7VSi_2\,(s) = 1/7VCl\,(g) + 2/7SiCl_3\,(g) + Na\,(g)$	1573	$2.6 \cdot 10^{-3}$	$1 \cdot 10^{-2}$
34	$NaCl\,(g) + 1/7VSi_2\,(s) = 1/7VCl\,(g) + 2/7SiCl_3\,(g) + Na\,(g)$	1573	$2.6 \cdot 10^{-3}$	$1 \cdot 10^{-2}$
35	$NaCl\,(g) + 1/4VSi_2\,(s) = 1/4VCl_2\,(g) + 1/2SiCl\,(g) + Na\,(g)$	1573	$3 \cdot 10^{-3}$	$2.3 \cdot 10^{-2}$
36	$NaCl\,(g) + 1/6VSi_2\,(s) = 1/6VCl_2\,(g) + 1/3SiCl_2\,(g) + Na\,(g)$	1573	$1.6 \cdot 10^{-2}$	$7.4 \cdot 10^{-2}$
37	$NaCl\,(g) + 1/8VSi_2\,(s) = 1/8VCl_2\,(g) + 1/4SiCl_3\,(g) + Na\,(g)$	1573	$6 \cdot 10^{-3}$	$2.1 \cdot 10^{-2}$
38	$NaCl\,(g) + 1/10VSi_2\,(s) = 1/10VCl_2\,(g) + 1/5SiCl_4\,(g) + Na\,(g)$	1573	$4 \cdot 10^{-3}$	$1 \cdot 10^{-2}$
39	$NaCl\,(g) + 1/5VSi_2\,(s) = 1/5VCl_3\,(g) + 2/5SiCl\,(g) + Na\,(g)$	1573	$4 \cdot 10^{-3}$	0.20
40	$NaCl\,(g) + 1/7VSi_2\,(s) = 1/7VCl_3\,(g) + 2/7SiCl_2\,(g) + Na\,(g)$	1573	$7 \cdot 10^{-3}$	$2.6 \cdot 10^{-2}$
41	$NaCl\,(g) + 1/9VSi_2\,(s) = 1/9VCl_3\,(g) + 2/9SiCl_3\,(g) + Na\,(g)$	1573	$3.5 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$

method protects the surface of the niobium sample from oxidation in the air for 3 to 9 hours, depending on the test temperature.

Point 3 of Table 1 shows the result of creating a heat-resistant coating by applying a layer of slip on a sample made of niobium and subsequent titanation. Slurry has a composition of 80 Mo + 13.5 Ni + 6.5 Sn % wt. The tin present in the slicker will be in liquid form during the chemical and thermal treatment. Tin at the processing temperature $T = 1150°C$ will cover the niobium surface with a thin layer.

In this case, molybdenum and nickel will dissolve in it. During titanation in NaCl vapours, according to reactions 5–8 (Table 2), chlorides of this element are formed. Exposure to this gaseous saturation medium will lead to saturation of the niobium surface with molybdenum and titanium. After that, the samples were borosilicated at a temperature of $T = 1300°C$ for 7 hours. As a result of such chemical and thermal treatment of samples, a surface layer consisting of silicides of titanium, molybdenum, nickel and niobium is formed on their surface. Such a coating provides protection of niobium from oxidation in air at a temperature of $T = 1700°C$ for 9 hours.

Point 4 of Table 1 presents another option for creating a heat-resistant coating on niobium. The niobium samples were previously hafniated at a temperature of $T = 1300°C$ for 7 hours. Hafnium powder was used as a saturating mixture, and to accelerate the rate of diffusion saturation, the process was carried out using sodium chloride vapour. This treatment usually results in the formation of a surface layer containing more than 50% wt. hafnium on the niobium sample. A layer of 35 HfB_2 + 20 $ZrSi_2$ + 20 $MoSi_2$ + 10 TiB_2 + 6.5 Ni + 6.5 Zr + 2 B % wt. was applied to the hafniated surface of the samples, and these samples were placed in a powder mixture of the composition 22 Si + 22 $ZrSi_2$ + + 22 HfB_2 + 31 $MoSi_2$ % wt. After that, the process of chemical-thermal treatment of the samples was carried out in NaCl sodium chloride vapours at a temperature of $T = 1300°C$ for 7 hours. Such substances as Si, Zr, HfB2, $ZrSi_2$, $MoSi_2$, and TiB_2 are involved in the process of chemical and thermal treatment. Ni and B components, which are part of the slicker, form a liquid medium on the surface of the sample at the saturation temperature. When the NaCl vapour affects the components involved in the chemical-thermal treatment, a gas-saturated environment is formed. According to points 9−30 of Table 2, its main components will be silicon chlorides, boron chlorides, zirconium chlorides, hafnium chlorides and molybdenum dichloride. This chemical action on the niobium surface will lead to the formation of a diffusion layer. This layer will consist of niobium silicides, zirconium silicides, hafnium silicides, molybdenum silicides, and will contain boron too. Depending on the thermodynamic characteristics of compounds, it is possible to form not only silicides, but also zirconium borides and hafnium borides. This coating provides protection of niobium from exposure to an oxidizing environment at temperature $T = 1700°C$ from 9 to 13.5 hours. Figure 1 shows the structure of the heat-resistant layer on the niobium sample. It was also established that re-forming the surface layer provides an increase in the thickness of the protective layer and slightly increases heat resistance.

Heat-resistant coatings were created on niobium and tantalum samples in accordance with points 5 and 6 of Table 1. These samples were chemically and thermally treated in a powder mixture with a composition of 40 $MoSi_2$ + 20 HfB_2 + 20 VSi_2 + 20 Si in the presence of NaCl vapour at a temperature of $T = 1310°C$ during 7 hours. According to Table 2, at this temperature, silicon chlorides, hafnium chlorides and boron chlorides, vanadium chlorides and molybdenum dichloride will be present in the reaction space; these are reactions 9−11, 14−18, 31−41, respectively.

The influence of the gaseous components of the saturating medium listed above on the niobium surface will lead to the formation of a protective layer consisting of a number of components. These will be niobium silicides, hafnium silicides, vanadium silicides, molybdenum sil-
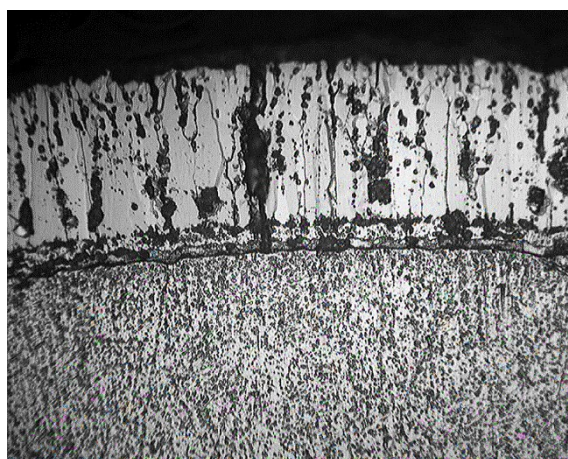
Fig. 1. Image of a cross-section of a niobium sample with a heat-resistant coating obtained according to point 4, Table 1 (×400).

icides, and some boron-based compounds. As you know, each of these metals (niobium, hafnium, vanadium, and molybdenum) has several silicides. If we also take into account possible borides, then, the total number of components of the surface layer turns out to be significant. When the gaseous oxidizing medium acts on this treated niobium surface, a film is formed consisting of oxides of niobium, hafnium, vanadium, and silicon. When creating a protective coating on tantalum, point 6 (Table 1), the picture will be similar. Such coatings provide protection of niobium and tantalum from oxidation in air at a temperature of 1800°C. The conducted studies showed that repeating the process of forming the surface layer leads to an increase in the thickness of the protective coating and, thus, it is possible to increase the heat resistance of the samples to the maximum value.

In Table 1, points 7 and 8 present the method of creating a heat-resistant coating on niobium and tantalum samples. These samples were placed in a powder filling with a composition of $40\ Si + 30\ HfB_2 + 30\ ZrSi_2$ % wt. After that, the samples were chemically and thermally treated in the presence of NaCl vapours at a temperature of $T = 1300°C$ for 7 hours. During this process, a gaseous saturating medium is formed. Silicon, hafnium diboride and zirconium disilicide are included in the powder filling. These components under the influence of NaCl steam at a process temperature $T = 1300°C$ and a pressure of 1 to 10^2 Pa form silicon chlorides, hafnium chlorides and boron chlorides, zirconium chlorides, these are reactions 9−11, 15−18, 19−30 presented in Table 2, respectively. The effect of this gaseous saturation medium on the surface of niobium or tantalum will lead to the formation of a diffusion layer consisting of a large number of compounds. The diffusion

layer on niobium will consist of niobium silicides, hafnium silicides, zirconium silicides, as well as the possible presence of compounds of these metals with boron. A tantalum sample will have a layer of tantalum silicides and components similar to those present on the surface of a niobium sample. Such a complex coating provides protection of niobium and tantalum samples from oxidation in air at a temperature of $T = 1900°C$ for 30 minutes.

Table 2 shows the results of calculations of the possibility of chemical reactions taking place in the reaction space, allowing a deeper understanding of the essence of the process of formation of a protective coating. All reactions describing the interaction of NaCl vapour with the components of the powder saturating mixture proceed with an increase in volume. In this case, they will be better implemented with a decrease in pressure. In addition, with a decrease in pressure, the share of lower chlorides will increase. On the other hand, the reactions describing the interaction of the gaseous saturated medium with the treated surface proceed with a decrease in volume. For example, these are reactions 3, 4 (Table 2). Therefore, when the treated surface is saturated, an increase in pressure will contribute to an increase in the concentration of the injected substance. The composition of the gas saturation medium and the pressure in the reaction space will affect the process of chemical and thermal treatment of samples. The flow of the activator and its pressure in the reaction space depend on the partial pressure of NaCl, which is determined by its temperature. On the other hand, this value is affected by the pumping speed of the vacuum system, which removes the gas mixture from the reaction container. The speed of pumping from the reaction volume depends primarily on the particle size of the powder filler used to saturate the samples. As follows from the above, it is necessary to create optimal conditions to achieve the maximum results of the formation of a diffusion layer on the surface of the samples.

4. CONCLUSIONS

1. The method of vacuum activated diffusion saturation with the use of a preliminary application of a slicker layer on the surface of niobium and tantalum samples allows you to create continuous non-porous coatings on their surface.
2. It was established that repeated application of the surface layer on niobium and tantalum samples leads to an increase in the thickness of the protective coating and helps to increase its heat resistance.
3. Pre-saturation of the niobium surface with such metals as chromium, titanium, hafnium followed by chemical and thermal treatment of the samples helped to increase the heat resistance of the overall coating.
4. As follows from the analysis of the obtained results, it was estab-

lished that preliminary saturation of the niobium surface with refractory metals followed by silicification improves the heat resistance of the coating with an increase in the heat resistance of silicides—chromium, titanium, and hafnium.

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