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RESEARCH ON THE PROCESSES OF FORMING HEAT-RESISTANT COATINGS USED TO PROTECT NIOBIUM FROM THE EFFECTS OF OXIDIZING ENVIRONMENTS AT ELEVATED TEMPERATURES

S.G. Rudenkyi, V.I. Zmii, R.V. Kryvoshapka, M.F. Kartsev, O.O. Kornieiev, O.V. Kunchenko, Y.V. Kunchenko, T.P. Ryzhova, I.A. Liashenko, M.Y. Bredikhin
National Science Center "Kharkov Institute of Physics and Technology", Kharkiv, Ukraine
E-mail: kryvoshapkarv@gmail.com

The article presents the results of research on the creation of heat-resistant coatings on niobium samples that provide protection against oxidation in air at temperatures T = 1973 K. Heat-resistant coatings on niobium, obtained by processing in sodium chloride vapors in powders of the composition of [(20-25)Si+(20-24)$ZrSi_2$+(20-24)HfB_2+(30-35)$MoSi_2$] wt.% at a temperature T = 1300 ^{0}C for 6 h and subsequent borosilicification, were approbated. Such heat-resistant coatings provide protection against oxidation in the air for 4…6 h. Complex coating obtained by applying a layer of 20HfB_2+20$MoSi_2$+20$ZrSi_2$+16TiB_2+8.5Ni+8.5Zr+3B+4Si wt.% slip on the surface of the niobium sample and subsequent processing in the [(20-25)Si+(20-24)$ZrSi_2$+(20-24)HfB_2+(30-35)$MoSi_2$] wt.% powder composition at T = 1300 °C for 6 h. The final stage of heat-resistant coating formation was borosilicification. Such a coating provides protection against the influence of an oxidizing environment for 6…10 h. Another method of creating a protective layer was the preliminary vanadium of the surface of the niobium sample followed by complex chemical and thermal treatment. This coating protects against oxidation for 10…12 h.

INTRODUCTION

Refractory metals and alloys are widely used in the creation of rocket and space technology. This is explained by the operating conditions of these devices. But in addition to the influence of both high and low temperatures, there is also the presence of aggressive environments. The materials used in the manufacture of various parts require protection from the effects of oxidizing environments. Heat-resistant coatings are used for this. Niobium or alloys based on it are used in the manufacture of products operating at elevated temperatures. This is explained by the increased strength characteristics of such materials, in contrast to such metals as tungsten and molybdenum. To protect them from oxidation, one of the most widely used materials are heat-resistant compounds, such as molybdenum and tungsten silicides. The influence of oxidizing media on molybdenum silicide at elevated temperatures leads to the formation of volatile molybdenum oxide and silicon dioxide. The last compound protects the product from oxidation. When manufacturing components from niobium or its alloys, in order to create a protective layer on their surface, it is necessary to form a coating using a two-stage technology. The formation of a protective coating on niobium products is carried out by applying a layer of molybdenum to it, followed by silicification. A layer of molybdenum on the surface of the product can be created by ion bombardment condensation (IBC). Silicification of molybdenum is carried out by the method of active vacuum diffusion silicon saturation of the product surface. This method makes it possible to form a uniform protective layer on products that have a complex shape, cavities and small-diameter holes [1, 2]. This technique is used in the formation of a heat-resistant coating on the combustion chambers of uncooled low-thrust jet engines. This part has an asymmetric hourglass shape. In the case when the part has a hole or a long cavity with a small diameter (less than 5 mm), it is practically impossible to ensure the application of a uniform continuous layer of molybdenum over the entire surface of such a product. This leads to the impossibility of creating a guaranteed heat-resistant layer on the surface of such a niobium product. Therefore, the formation of a heat-resistant coating on such products is possible only by the method of vacuum activated diffusion saturation. As it was established, this method allows forming a protective coating even on products with an opening of 0.8 mm [3]. In the case of direct silicification of niobium, a layer of its silicides is formed. Niobium silicides when interacting with an oxidizing environment at elevated temperatures do not provide protection against it. This is explained by the fact that when oxidizing environments act at elevated temperatures on niobium silicide, high-temperature powdered niobium oxide is formed. This compound prevents the creation of a continuous heat-resistant layer on niobium, which prevents the penetration of oxygen into the product. To circumvent this obstacle, we plan to pre-saturate the niobium surface with several refractory metals and then perform vacuum activated diffusion silicification. This approach will create a surface layer consisting of several silicides of refractory metals. In this case, niobium silicide will be only one of the components of the composition of the surface layer.

The purpose of this work is to create a heat-resistant coating on niobium only by the method of vacuum activated diffusion saturation. This coating should provide protection of this metal against the influence of oxidizing environments at elevated temperatures.

MATERIALS AND METHODS

The method of diffusion vacuum activated saturation was used as the main method of forming a protective coating. Sodium chloride NaCl was used to accelerate the process of saturation with the activator. The process of chemical and thermal treatment was carried out in a graphite container. Semiconductor purity silicon powder was used as a saturating medium during vacuum diffusion silicification. Slurry was used when forming a heat-resistant coating on samples. It was prepared by mixing a mixture of powders in a liquid binder. Tsapon varnish KO-85 was used as such a substance. Slurry was applied to the surface of the sample by spreading.

The process of forming a protective coating was carried out on niobium samples. These samples were 100 mm long and 2 mm in diameter. This form of samples allows to test them for heat resistance in air. Such a sample was fixed on a special stand. The sample was heated by direct passage of an electric current, the temperature of which was determined by a pyrometer with an accuracy of ±100 ^{0}C. The heat resistance of the sample was measured by the duration of its operation until burnout. In addition, flat niobium samples were used. These samples were used as witnesses and to measure the surface composition after chemical and heat treatment. The surface composition of the flat sample was determined using X-ray fluorescence analysis (XFA). The metallographic method was used to determine the structure of the protective layer. During the research, one more approach was used – the method of calculating thermodynamically possible chemical reactions. This method makes it possible to understand the mechanism of the formation of the surface layer and the influence of the parameters of the saturation process on it.

RESULTS AND DISCUSSION

Complex silicide coatings of the Cr-Ti-Si, Al-Si-Cr, Mo-Si-B type are usually used to protect niobium and tantalum. At the same time, coatings are used, the composition of which includes Mo, Ti, Cr, Ni, Al, Si, B. According to many authors, preliminary boronization of the surface of refractory metals before forming a heat-resistant coating on them helps to increase its resource. It is not possible to determine the optimal composition of the heat-resistant layer by calculation, so it is necessary to use the empirical method of selecting the appropriate elements. The final stage of processing all samples is borosilication in a powder with a composition of 97Si+3B wt.% in the presence of NaCl steam at a temperature of T = 1300 ^{0}C for 6 h.

Table 1

Results of comparative tests of niobium samples with protective coatings on heat resistance at T=1973 K in air

No	Composition of the surface before processing, wt.%	The composition of the slurry	Processing in a mixture in the NaCl(g) vapor and its mode	Composition of the surface after processing	Heat resistance, h
1	100%Nb	–	Silicification in Si powder at T=1300 ^{0}C, 6 h	$NbSi_2$	0.4
2	100%Nb	–	Processing in powder [(20-25)Si+ (20-24)$ZrSi_2$+ (20-24)HfB_2+ (30-35)$MoSi_2$] wt.% at T=1300 ^{0}C, 6 h	(79.7-8.3)Nb+ (15.4-18.4)Si+ (1.3-1.5)Zr+ (0.26-0.29)Hf+ 0.1Mo wt.% and B	4…6
3	100%Nb	20HfB_2+20$MoSi_2$+ 20$ZrSi_2$+16TiB_2+ 8.5Ni+8.5Zr+3B+ 4Si wt.%	Processing in powder [(20-25)Si+ (20-24)$ZrSi_2$+ (20-24)HfB_2+ (30-35)$MoSi_2$] wt.% at T=1300 ^{0}C, 6 h	(53.4-60)Nb+ (4.1–4.9)Si+ (32.9-38.4)Hf+ (0.9-1.2)Zr+ 2.1Mo wt.% and B	6…10
4	43.1Nb+56.9V after applying vanadium V at T=1270 ^{0}C, 7 h	20HfB_2+20$MoSi_2$+ 20$ZrSi_2$+16TiB_2+ 8.5Ni+8.5Zr+3B+ 4Si wt.%	Annealing of samples with slurry in the mixture 20HfB_2+20$MoSi_2$+20$ZrSi_2$ +16TiB_2+8,5Ni+8,5Zr+3B +4Si wt.% at T=1300 ^{0}C, 6 h	45.3Nb+27.9V+9.2Zr+ 8.8Si+7.5Mo+1.2Ni wt.%	10…12
5	100%Nb	80Mo+11.7Re+6.3 Si+2Al wt.%	The samples were chromium-plated in sodium chloride vapor at T=1150 ^{0}C, 6 h, then the samples were boro-silicated at 1280 ^{0}C, 7 h	–	6
6	100%Nb	50Mo+20.5Cr+21N i+5.5B+3Al wt.%	The samples were boro-silicated at 1280 ^{0}C, 7 h	–	8

The process of activated vacuum diffusion saturation is carried out in a graphite container in powder filling at reduced pressure in the presence of sodium chloride vapor. The container with sodium chloride is maintained at temperature 790…810 ^{0}C. At this temperature, the saturated vapor pressure of sodium chloride is 1…10^2 Pa. Therefore, we will consider the chemical-thermal processes taking place in the reaction container in this pressure range. Earlier, we established that sodium chloride vapor does not dissociate at this pressure up to a temperature of 1600 K. The interaction of sodium chloride vapor with the saturating components occurs by means of chemical action. During silicification, this interaction leads to the formation of silicon chlorides [4]. Depending on the conditions of silicification, the ratio of partial pressures of silicon chlorides can change. At a pressure in the range of tens of pascals and a temperature of the main components of the gas saturation medium are the lower silicon chlorides SiCl, $SiCl_2$. These components form silicides, when interacting with niobium and other metals or alloys. In point 1 (Table 1), the result on the heat resistance of silicified niobium is given. This treatment of niobium leads to the formation of a layer of niobium disilicide $NbSi_2$ on its surface.

Point 2 (see Table 1) shows the result of vacuum activated chemical-thermal treatment of a sample of niobium in powder [(20-24)Si+(20-24)$ZrSi_2$+(20-24)HfB_2+(30-36)$MoSi_2$] wt.% in sodium chloride vapor. The presence of sodium chloride vapor in the powder of the above composition leads to the formation of a multicomponent saturating gas medium. The interaction of the activator vapor with silicon can be described by chemical reactions 1–3 (Table 2). This mechanism was previously established using mass spectrometry methods. The degree of transformation α is the proportion of the starting substances that have reacted according to the reaction equation. The result of this interaction will be silicon chlorides SiCl, $SiCl_2$ and $SiCl_3$. The next component of the powder saturation mixture is silicon disilicide $ZrSi_2$. The effect of sodium chloride vapor on silicon disilicide powder $ZrSi_2$ can be described by reactions 4–15 (see Table 2). The results of this interaction are zirconium chlorides ZrCl, $ZrCl_2$, $ZrCl_3$, $ZrCl_4$ and silicon chlorides SiCl, $SiCl_2$, $SiCl_3$, and $SiCl_4$. There is a compound HfB_2 in the powder filling and under the influence of NaCl vapors, boron chlorides and hafnium chlorides $HfCl_2$, $HfCl_3$, $HfCl_4$ are formed (reactions 16–19). The compound $MoSi_2$ is also present in the powder saturation mixture. According to reaction 20 (see Table 2), the formation of dichlorides of silicon $SiCl_2$ and molybdenum $MoCl_2$ is possible under the influence of sodium chloride NaCl vapors on $MoSi_2$. All these gaseous compounds are present in the reaction space during activated niobium vacuum saturation. The effect of all these gaseous compounds on the surface of niobium leads to the formation of a diffusion layer containing silicon, zirconium, hafnium and partly molybdenum and boron. The latter element cannot be detected by XFA, and its presence was recorded by X-ray structural analysis.

Table 2

The degree of transformation **α** for chemical reactions is occurring in the process of formation of protective coatings on niobium in the reaction space at a temperature of 1573 K

No	The equation of a chemical reaction	The degree of transformation α at pressure P, Pa	
		10^2	1
1	NaCl(g) +Si(s)=SiCl(g)+Na(g)	$1\cdot10^{-2}$	$1\cdot10^{-1}$
2	NaCl(g) +1/2Si(s)=1/2$SiCl_2$(g)+Na(g)	$2.4\cdot10^{-2}$	$1\cdot10^{-1}$
3	NaCl(g) +1/3Si(s)=1/3$SiCl_3$(g)+Na(g)	$7\cdot10^{-3}$	$2\cdot10^{-2}$
4	NaCl(g)+1/5$ZrSi_2$(s)=1/5ZrCl(g)+2/5$SiCl_2$(g)+Na(g)	$3\cdot10^{-3}$	$1.6\cdot10^{-2}$
5	NaCl(g)+1/4$ZrSi_2$(s)=1/4$ZrCl_2$(g)+1/2SiCl(g)+Na(g)	$3\cdot10^{-3}$	$2.4\cdot10^{-2}$
6	NaCl(g)+1/6$ZrSi_2$(s)=1/6$ZrCl_2$(g)+1/3$SiCl_2$(g)+Na(g)	$8\cdot10^{-3}$	$3.5\cdot10^{-2}$
7	NaCl(g)+1/8$ZrSi_2$(s)=1/8$ZrCl_2$(g)+1/4$SiCl_3$(g)+Na(g)	$4\cdot10^{-3}$	$1.3\cdot10^{-2}$
8	NaCl(g)+1/5$ZrSi_2$(s)=1/5$ZrCl_3$(g)+2/5SiCl(g)+Na(g)	$9\cdot10^{-3}$	$5\cdot10^{-2}$
9	NaCl(g)+1/7$ZrSi_2$(s)=1/7$ZrCl_3$(g)+2/7$SiCl_2$(g)+Na(g)	$1.5\cdot10^{-2}$	$5.9\cdot10^{-2}$
10	NaCl(g)+1/9$ZrSi_2$(s)=1/9$ZrCl_3$(g)+2/9$SiCl_3$(g)+Na(g)	$7\cdot10^{-3}$	$2.2\cdot10^{-2}$
11	NaCl(g)+1/11$ZrSi_2$(s)=1/11$ZrCl_3$(g)+2/11$SiCl_4$(g)+Na(g)	$4\cdot10^{-3}$	$1.1\cdot10^{-2}$
12	NaCl(g)+1/6$ZrSi_2$(s)=1/6$ZrCl_4$(g)+1/3SiCl(g)+Na(g)	$1.3\cdot10^{-2}$	$6\cdot10^{-2}$
13	NaCl(g)+1/8$ZrSi_2$(s)=1/8$ZrCl_4$(g)+1/4$SiCl_2$(g)+Na(g)	$1.9\cdot10^{-2}$	$6.6\cdot10^{-2}$
14	NaCl(g)+1/10$ZrSi_2$(s)=1/10$ZrCl_4$(g)+1/5$SiCl_3$(g)+Na(g)	$9.1\cdot10^{-3}$	$2.6\cdot10^{-2}$
15	NaCl(g)+1/12$ZrSi_2$(s)=1/12$ZrCl_4$(g)+1/6$SiCl_4$(g)+Na(g)	$5.2\cdot10^{-3}$	$1.3\cdot10^{-2}$
16	NaCl(g)+1/4HfB_2(s)=1/2BCl(g)+1/4$HfCl_2$(g)+Na(g)	$2\cdot10^{-3}$	$1.5\cdot10^{-2}$
17	NaCl(g)+1/5HfB_2(s)=2/5BCl(g)+1/5$HfCl_3$(g)+Na(g)	$5.4\cdot10^{-3}$	$3\cdot10^{-2}$
18	NaCl(g)+1/6HfB_2(s)=1/3BCl(g)+1/6$HfCl_4$(g)+Na(g)	$3.2\cdot10^{-3}$	$1.4\cdot10^{-2}$
19	NaCl(g)+1/9HfB_2(s)=2/9BCl_3(g)+1/9$HfCl_3$(g)+Na(g)	$3.6\cdot10^{-3}$	$1.1\cdot10^{-2}$
20	NaCl(g)+1/6$MoSi_2$(s)=1/6$MoCl_2$(g)+1/3$SiCl_2$(g)+Na(g)	$2.3\cdot10^{-3}$	$1\cdot10^{-2}$

To accelerate the processes of diffusion saturation, we used the introduction of a liquid phase on the surface oa the treated niobium samples. The process of diffusion saturation through the liquid phase and gas medium at reduced pressure will differ. When considering the liquid phase containing the saturating

element and the gaseous medium phase, the ratio of concentrations per unit of treated surface will be different. The concentration of the saturating element in the liquid phase will be several orders of magnitude higher than in the gaseous medium. But it is necessary to take into account the mobility of atoms in these environments. The mobility of the atoms of the saturating element in the liquid phase is usually lower than in the gaseous medium. But it can be assumed that, under certain conditions, the process of diffusion saturation through an interlayer from the liquid phase will be better than the formation of a diffusion layer in a vacuum. This is possible if the process of diffusion saturation occurs through a layer of a liquid medium that has a small thickness. In this case, rapid mass transfer of atoms of the saturating element will take place. When choosing the materials of the liquid layer used in the formation of diffusion coatings, there are a number of restrictions that must be observed. It is desirable that this liquid medium removes the oxide layer from the surface of the substrate and does not dissolve it. Components of the liquid phase should not form strong chemical compounds with saturating elements, which can prevent their diffusion into the substrate. Saturating elements must dissolve in the liquid phase; otherwise there will be no mass transfer of these substances to the treated surface. As a source of the liquid phase, we use aluminum, copper and eutectics, with a melting temperature lower than the temperature of the chemical-thermal treatment of the samples. This is, for example, a nickel-boron eutectic.

Point 3 (see Table 1) presents the method of processing niobium samples using a slurry. To the powder mixture of the composition $20HfB_2+20MoSi_2+20ZrSi_2+16TiB_2+8.5Ni+8.5Zr+3B+4Si$ wt.% add a solvent – tsapon varnish KO-85. This liquid consistency is applied to the surface of the niobium sample. This sample is placed in a powder filling of the composition [(20-24)Si + (20-24)$ZrSi_2$ + (20-24)HfB_2 + +(30-36)$MoSi_2$] wt.%, which it is annealed in sodium chloride vapor at a temperature of T=1300 ^{0}C for 6 h. Nickel, boron and silicon are included in the slurry. With the ratio of the quantities of nickel and boron, these components form a liquid medium at a temperature of T=1300 ^{0}C. This is confirmed by the appearance of the surface of the samples after chemical and thermal treatment. From the composition of the saturating powder mixture, it follows that the gas environment during the chemical-thermal treatment will be similar to that which took place in the process indicated in Table 1, point 2. The gas saturating environment will contain silicon, zirconium, hafnium and boron chlorides. The introduction of a liquid phase into this process will contribute to the mass transfer of these elements. In addition, the slurry layer is located close to the surface of the sample. It can also help speed up the process of creating a diffusion layer.

Below, Fig. 1 shows the structure of the Nb sample with a protective coating obtained according to point 3 of Table 1. A layer of $20HfB_2 + 20MoSi_2 + 20ZrSi_2$ + +$16TiB_2$+8.5Ni+8.5Zr+3B+4Si wt.% was applied to the surface of the niobium sample. After that, this sample was placed in a powder filling of the composition (25Si+22$ZrSi_2$+22HfB_2+31$MoSi_2$) wt.% and annealed in sodium chloride vapor at a temperature of T=1300 ^{0}C for 6 hours. The final stage of forming a heat-resistant coating on this sample was its borosilication at a temperature of T=1300 ^{0}C for 6 h. During vacuum activated borosilication, in addition to silicon chlorides, boron chlorides BCl, BCl_2, BCl_3 are present in the saturating medium. The presence of boron chlorides during interaction with the treated surface leads to the introduction of boron into the resulting diffusion layer. Under the influence of oxidizing environments on such a surface layer, a heat-resistant coating is formed, consisting of silicon oxide, SiO_2, and boron oxide. This composition better tolerates thermal changes that affect this coating.

Fig. 1 shows that the heat-resistant layer consists of at least 4 layers. Its total thickness is more than 150 μm.

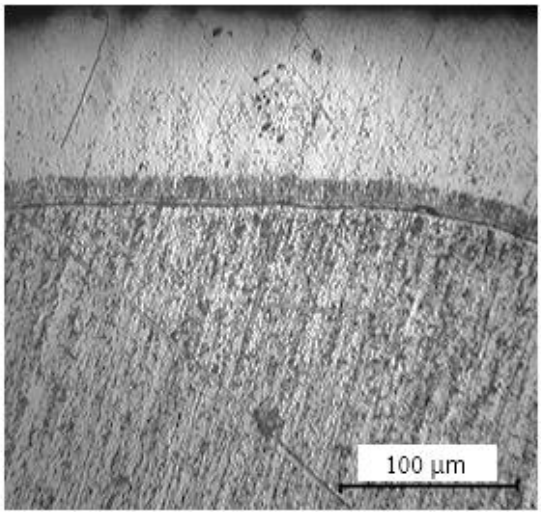

Fig. 1. Cross-sectional structure of the Nb sample processed according to point 3, Table 1

Table 3

The degree of transformation α of chemical reactions occurring during vacuum activated diffusion vanadiation niobium in the reaction space at a temperature of 1543 K

No	The equation of a chemical reaction	The degree of transformation **α** at pressure P, Pa	
		10^2	1
1	NaCl(g)+V(s)=VCl(g)+Na(g)	$1\cdot10^{-3}$	$1\cdot10^{-2}$
2	NaCl(g)+1/2V(s)=1/2VCl_2(g)+Na(g)	$5.8\cdot10^{-2}$	0.24
3	NaCl(g)+1/3V(s)=1/3VCl_3(g)+Na(g)	$4.1\cdot10^{-3}$	$1.3\cdot10^{-2}$
4	VCl(g)+1/2Nb(s)=1/2(NbV)(solid solution)+1/2VCl_2(g)	0.999	0.999
5	VCl(g)+4/5Nb(s)=4/5(NbV)(solid solution)+1/5VCl_5(g)	0.976	$3\cdot10^{-3}$

Item 4 (see Table 1) presents the result of creating a heat-resistant coating using activated vacuum vanadiation. Table 3 below shows the thermodynamically possible chemical reactions occurring in the niobium vanadiation process.

Vanadium with chlorine forms 5 chlorides, but under the given conditions of chemical and thermal treatment, the main components of the gaseous saturation medium will be the compounds VCl, VCl_2, and VCl_3, which are formed in accordance with reactions 1–3 in Table 3. These gaseous compounds interact with the niobium surface. As follows from the data obtained by XFA method, the surface layer of niobium samples after vanadium has a composition of 43.1Nb+56.9V. Fig. 2 shows a cross-section of a niobium sample after vanadium. The surface of niobium has an outer thin layer, 6…7 μm thick, and below it an area 60…80 μm wide, which has a hardness of about 1 GPa, increased compared to the base, the hardness of which is about 0.8 GPa. This indicates that the selected method can be used to form a multicomponent layer of several refractory metals on the surface of niobium products. After that, a layer of $20HfB_2$+$20MoSi$+$20ZrSi_2$+ +$16TiB_2$+8.5Ni+8.5Zr+3B+4Si wt.% was applied to the surface of the samples.

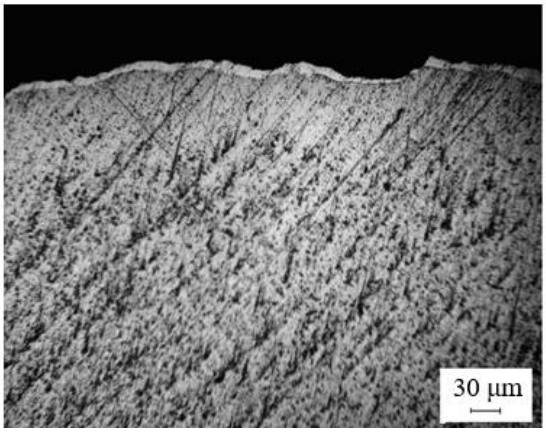

Fig. 2. Photomicrograph of the cross-section of a niobium sample after activated vacuum vanadiation treatment at a temperature of T=1270 ^{0}C for 7 h [5]

This sample with a layer of slurry was placed in a powder filling with a composition of $20HfB_2$+$20MoSi_2$+$20ZrSi_2$+$16TiB_2$+8.5Ni+8.5Zr+3B+ +4Si wt.% and annealing was carried out in sodium chloride vapor at a temperature of T=1300 ^{0}C or 6 h. The surface layer formed on niobium has the composition shown in Table 1. After this treatment, the surface contains, in addition to niobium and vanadium, zirconium, molybdenum, nickel and silicon. But the final stage of formation is borosilication of the samples at a temperature of T=1300 ^{0}C for 6 h. This final stage of forming the protective layer is performed to convert surface components such as niobium, vanadium, zirconium, molybdenum and nickel into their compounds with silicon.

Table 1 in point 5 shows another result regarding the formation of a heat-resistant coating. A layer of 80Mo+11.7Re+6.3Si+2Al wt.% was applied to the surface of the niobium sample. After that, the sample was placed in chromium powder and the process of diffusion vacuum saturation in sodium chloride vapor was carried out. The next stage of formation of the protective layer is borosilicification at a temperature of T= 1280 ^{0}C for 7 h. And the last stage of creating this heat-resistant coating is borosilicification in a powder with a composition of 97Si+3B wt.% at a temperature of T=1300 ^{0}C for 6 h. In this method of forming a heat-resistant coating, aluminum Al was introduced into the composition of the slurry. This component exists in liquid form at the surface layer formation temperature.

A 50Mo+20.5Cr+21Ni+5.5B+3Al wt.% slurry layer was applied to the surface of the niobium samples, item 6, Table 1. After that, these samples were borosilicated at a temperature of T=1280 ^{0}C for 7 h and then again borosilicated at a temperature of T=1300 ^{0}C for 6 h. A small amount of aluminum was introduced into the composition of the slurry. At the aforementioned processing temperatures, aluminum is in liquid form. Such a surface layer on niobium provides protection of the metal against oxidation in air at a temperature of T=1973 K for 8 h.

CONCLUSIONS

1. The method of activated vacuum diffusion saturation makes it possible to form a surface layer on niobium containing several elements at the same time. After silicification of this surface, a diffusion layer is formed on it, which consists of several silicides. And only a part of them is a combination of niobium and silicon.

2. To form a heat-resistant coating, you can use slurry, which is applied to the surface of the sample. After that, the sample undergoes vacuum diffusion saturation with silicon or other elements.

3. It has been established that the introduction of components into the slurry, which at the temperature of the process of forming a protective coating, form a liquid medium, which contributes to the acceleration of the process of creating a diffusion layer.

4. It was established that when using slurry and the method of vacuum activated diffusion saturation, a multi-component and multi-layered structure is formed when forming a heat-resistant coating. As metallographic studies have shown, the coating obtained in this way consists of several continuous and non-porous layers that are firmly bonded together.

5. Using as a criterion the degree of transformation α under the conditions taking place in the reaction space, the main chemical reactions were established. These reactions describe the mechanism of saturation of the niobium surface with vanadium, hafnium, zirconium, boron and silicon depending on the pressure in the reaction space.

REFERENCES

1. Патент №98074. *Спосіб дифузійного насичення поверхонь виробів* / В.І. Змій, Г.М. Картмазов, С.Г. Руденький, від 10.04.2012

2. Патент №98087. *Пристрій для дифузійного насичення поверхонь виробів у вакуумі* / В.І. Змій, Г.М. Картмазов, С.Г. Руденький, від 10.04.2012

3. В.И. Змий, С.Г. Руденький, Е.В. Тимофеева, А.А. Корнеев, В.В. Кунченко, Ю.В. Кунченко,

Т.П. Рыжова, М.Ю. Бредихин. Комплексные жаростойкие покрытия для лопаток газотурбинных двигателей // *Порошковая металлургия*. 2015, №7/8, с. 151-156.

4. В.И. Змий, С.Г. Руденький. Реакционная диффузия и внешний массоперенос при вакуумном активированном насыщении металлов // *ВАНТ. Серия «Физика радиационных повреждений и радиационное материаловедение»*. 1998, в. 5(71), с. 86-88.

5. С.Г. Руденький. *Физико-химические основы активированного вакуумного метода формирования многофункциональных покрытий на металлических и углеродных материалах:* Докт. дис. Харьков: Институт электрофизики и радиационных технологий, 2014.

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ДОСЛІДЖЕННЯ ПРОЦЕСІВ ФОРМУВАННЯ ЖАРОСТІЙКИХ ПОКРИТТІВ ДЛЯ ЗАХИСТУ НІОБІЮ ВІД ВПЛИВУ ОКИСНИХ СЕРЕДОВИЩ ПРИ ПІДВИЩЕНИХ ТЕМПЕРАТУРАХ

С.Г. Руденький, В.І. Змій, Р.В. Кривошапка, М.Ф. Карцев, О.О. Корнєєв, О.В. Кунченко, Ю.В. Кунченко, Т.П. Рижова, І.А. Ляшенко, М.Ю. Бредіхін

Наведено результати досліджень зі створення жаростійких покриттів на зразках з ніобію, що забезпечують захист від окислення на повітрі при температурі T=1973 K. Були апробовані жаростійкі покриття на ніобії, отримані обробкою у парах хлористого натрію у порошках складу [(20-25)Si+(20-24)$ZrSi_2$+(20-24)HfB_2+(30-35)$MoSi_2$] мас.% при температурі T=1300 ^{0}C протягом 6 год та наступного боросиліціювання. Такі жаростійкі покриття забезпечують захист від окислення на повітрі протягом 4…6 год. Комплексне покриття отримане за допомогою нанесення шару шлікеру складу 20HfB_2+20$MoSi_2$+20$ZrSi_2$+16TiB_2+8,5Ni+8,5Zr+3B+4Si мас.% на поверхню зразка з ніобію та подальшої обробки у порошку складу [(20-25)Si+(20-24)$ZrSi_2$+(20-24)HfB_2+(30-35)$MoSi_2$] мас.% при T=1300 ^{0}C протягом 6 год. Завершальною стадією формування жаростійкого покриття було боросиліціювання. Таке покриття забезпечує захист від впливу окисного середовища протягом 6…10 год. Ще одним методом створення захисного шару було попереднє ванадіювання поверхні зразка з ніобію і подальшою комплексною хіміко-термічною обробкою. Таке покриття захищає від окислення протягом 10…12 год.