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HEAT RESISTANCE COATING FOR NIOBIUM AND TANTALUM - BASE ALLOYS

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Thus, to protect niobium and tantalum from high-temperature gas corrosion within 1200-1500 ^{o}C multilayer coating can be used, which is formed on the preliminary molibdenized niobium and tantalum during successive boron and silicon saturation and then covering the boron-silicide surface with the silicide-oxide composition.

Analysis of the investigated problem

Niobium and tantalum - base alloys are being used for manufacturing of high-temperature machinery products thanks to their unique complex of physical-mechanical and chemical properties. The main disadvantage of refractory metals, which makes the spheres of their application limited, is their low heat resistance. The ways of solving this problem are different, metal surface protection coatings in particular. Diffusion metal and non-metal coatings, slurry and diffusion-slurry compositions [1-2] are used with this purpose. At the same time while developing heat-resistance coatings the researchers realize, that the formed protection layer should meet some demands, the number of which increases greatly while the product operating under sudden change of the heat regime. Such approach makes more difficult the task of raising heat resistance of refractory metals by means of the protection coatings. Efficient direction of the high-temperature oxidation resistance of the niobium and tantalum construction elements is the forming on their surface of multilayer coating, which consists of diffusion and slurry, in which every separate layer has its own function: outer-slurry, provides heat resistance of the slurry part, barrier prevents interreaction of the scale-resistant component of the diffusion part of coating with the base; intermediate promotes strain relaxation in the coating under multiple change of the temperature regime and provides smooth change of the coefficient of the thermal expansion between the base and the coating.

Diffusion part of the coating is obtained by means of the successive saturation of niobium and tantalum by molybdenum at first, and then by boron and silicon. Due to the slurry method silicide-oxide component of the multilayer coating is formed on the niobium and tantalum boron-silicide surface.

In connection with this the process of forming multilayer coating on niobium and tantalum, as well as the efficiency of its application for the oxidation resistance of the refractory metals, are studied in the paper.

Experimental methods

To investigate the forming of multilayer coating on niobium and tantalum the metallography, X-ray-phase and micro-X-ray-spectral analysis methods were used. Data on heat resistance of the coating material is obtained by means of the parametric method [3]. $10 \times 10 \times 2$ mm niobium and tantalum specimens were used for coating. Molibdenizing of niobium and tantalum were carried out in vacuum ($p=1 \times 10^{-3}$ Pa) at 1400 ^{o}C in the powder environment, containing 60% Mo, exposure being 6 h.

Borating of the preliminary molibdenized niobium and tantalum was carried out in the mixture containing (wt. %): B_4C - 60, NaF - 3 and Al_2O_3 - 37%. Temperature - 1050 ^{o}C, isothermal exposure being for niobium 6 h, for tantalum - 12 h.

Preliminary molibdenized niobium and tantalum specimens were saturated by silicon in the powder mixture containing (wt. %): Si - 60, NaF - 3 and Al_2O_3 - 37% at 1100 ^{o}C, exposure being 12 h.

Niobium and tantalum boron-silicide surface was covered by the multilayer coating obtained by mixing the powder filler, bond and liquid phase.

Filler components were: zirconium-yttrium ceramics containing (wh %): 72-78 (ZrO_2 + HfO_2), 22-28 Y_2O_3 and aluminium oxide. Natrium aluminate $NaAlO_2$ was used as a bond, distilled water being a liquid phase. Powder grain size did not exceed 40 mkm. Filler components and natrium aluminate are mixed in the porcelain drum, exposure being 5 h. Suspension is made of the powder mixture and distilled water in proportion 3:1, which is sprayed over the boron-silicide surface of the refractory metals. The first layer contained (wt. 5): $MoSi_2$ - 70, zirconium-yttrium ceramics - 24, $NaAlO_2$ - 6. In

every following layer the content of $MoSi_2$ was decreased in 5%, the amount of filler being increased in the same amount. The layer thickness did not exceed 100 mkm. Every slurry layer was dried in the air during 1 hour, the temperature being smoothly raised up 100 ^oC. Fixation of each layer was carried out while heating the specimens in the air up 1200 ^oC, heating rate being 15 degrees/min. To form heat-resistant silicide-oxide film on the multilayer coating surface niobium and tantalum specimens were heated with the rate of 50 degrees/min up to 1850 ^oC, exposure being 10 min.

Heating of the refractory metals coated specimens was carried out by the direct forcing of the current. Coating testing was carried out in the air within the temperature range 1200 - 1500 ^oC during 10-6000 h in the thermocycling regime: heating, exposure and cooling.

Before measuring the microhardness the device was tested on rock-salt crystals at 0.05 N load, microhardness of which was within 0.2 ± 0.01 GPa.

Results and discussion

Basing on our investigations molibdenizing of niobium and tantalum was carried out. It was found that β and α-solid solution in the depth 180-120 mkm correspondingly is formed on refractory metals, area with different hardness being formed, at the same time the metal core staying elastic.

Metallographic analysis of the successively boron and silicon saturated molibdenized niobium and tantalum specimens testified, that on the metals the coating, consisting of two layers, is formed. The results of the micro-X-ray-spectral and X-ray-phase analysis methods testify that the outer layer consists of desilicide of refractory metal $(Me, Mo)Si_2$, which penetrates in the lower silicide $(Me, Mo)_5Si_3$, and the inner one - boride phase $(Nb, Mo)B_2$ and $(Ta, Mo)B_2$. The cracks and fractures are not available in the coating, which is tightly connected with the base (Fig. 1). The study of the siliconizing kinetics of the preliminary molybdenum-borated niobium and tantalum specimens testified that under saturation the boride layer displaces into the depth of the metal base without change of its size. At the same time it effects the thickness of the silicide layer. It was found, that the greater is the thickness of the boride layer on the metals, the less is the size of the silicide coating (Fig. 2). The silicide phases growth retardation is found the most sufficient on tantalum, where 60 mkm thick boride phase does not allow to obtain the silicide coating of more than 10 mkm. Thus, tantalum deboride, which contains molibdenum, possesses higher barrier properties than that of $(Nb, Mo)B_2$ phase, and can efficiently retard the silicon diffusion in the metal base, when the coating is operating at high temperatures, improving its properties, stability in particular. While comparing the barrier properties of the boride layers, formed on the preliminary molibdenized refractory metals and obtained on the unworked metals [4], it can be stated, that the boride phases $(Nb, Mo)B_2$ and $(Ta, Mo)B_2$ retard silicon saturation of niobium and tantalum in 2 and 3 times more efficiently. It allows to raise sufficiently the operating temperature of products made of niobium and tantalum.
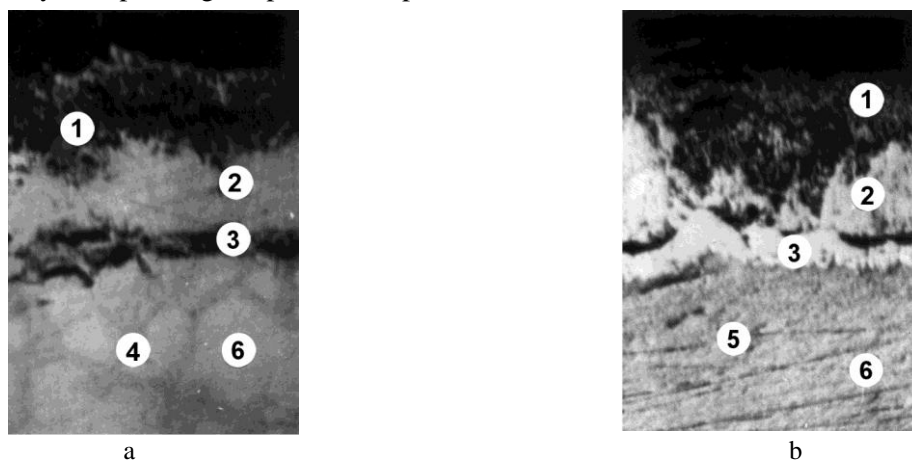

a   b

Figure 1. Microstructure of boronsilicide coating on niobium (a) and tantalum (b): $\times$ 300;
1 - $(Me, Mo)Si_2$; 2 - $(Me, Mo)_5Si_3$; 3 - $(Me, Mo)B_2$; 4 - β -solid solution;
5 - α -solid solution; 6 - base metal; etching: $HF:HNO_3:Y_2SO_4$= 1:1:1 parts.

Basing on the metallographic and X-ray-phase analysis methods of the boron-silicide coating on niobium and tantalum, taking into account the results of the work [5], it can be predicted, that the displacement of the boride phase $(Me, Mo)B_2$ takes place as follows. While siliconizing of the

molibdenum borated metals on the outer boundary of deboride the following reaction takes place: (Me, Mo)B_2 + 2Si = (Me, Mo)Si_2 + 2B; here 2B - quasi-free boron, which causes the appearance of the diffusion flow of the boron layer. As the boron diffusion coefficient in the boride phases is sufficiently greater than that of metal [6], the silicide phase growth and corresponding displacement of the boride phases is caused by the boron atoms diffusion into the depth of the solid solution. The boron atoms diffusion from the outer to the inner boundary of the boride layer, which causes its displacement into the depth of the base, can take place only in the case, when the boron activity gradient is preserved in the boride layer. It can appear in the case, when the reaction of silicon with the boride layer is continuous on its outer boundary. This reaction causes the formation of bonds Me-Si. At the same time some Me-B bonds are developed, and it causes the boron activity growth in the boride layer. As boron is the element which raises the chemical potential of silicon, it is pushed out from the surface area of the boride layer into its depth providing the possibility of appearance of additional bonds Me-Si and the growth of the silicide layer coating. As a result of this process the layer (Me, Mo)B_2 is displaced into the depth of the solid solution without changing of its thickness. Silicide phase (Me, Mo)$_5$Si$_3$ is formed above it, reinforced by the refractory metal (Me, Mo)Si_2 desilicide.
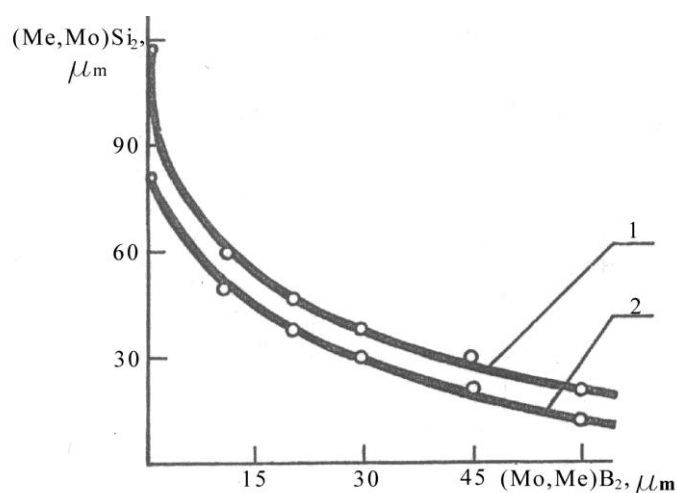

Figure 2. Dependence of thickness of silicide coating on niobium (1)
and tantalum (2) on the thickness of the boride layer (Me,Mo)B_2.

Reaction of transformation on the boundary boride-silicide is the most likely to take place in the area similar to G-P zones. It possesses homogeneous area and the structure which is transitional between the layers structures limiting it. Constant boron activity gradient in the boride layer causes continuous boron diffusion from its outer to inner boundary. The rate of this process is the less, the smaller is the boron activity gradient. Its value depends on the boride layer thickness. The boron activity gradient is smaller, the greater is the boride phase thickness. It is testified by the experimental results.

On the other hand, siliconizing rate of the preliminary borated metals will be determined by the thermodynamical features. The rate of the boride layer displacement will depend on the silicon activity on its outer boundary. On Table 1 the silicon activity in the niobium and tantalum desilicides is presented, which is found basing on the data of the phase forming heat. The silicon sublimation heat at 0 K equals 464 кJ/g • atom. As the calculation results testify, the greatest is the silicon activity in the niobium desilicide.

Table1

Thermodynamic activity of silicon in the niobium and tantalum desilicide

Silicide	Temperature, K				
	1000	1300	1400	1600	1800
NbSi$_2$	$4,9 \cdot 10^{-2}$	$7,6 \cdot 10^{-2}$	$0,8 \cdot 10^{-1}$	$1,3 \cdot 10^{-1}$	$1,8 \cdot 10^{-1}$
TaSi$_2$	$3,3 \cdot 10^{-3}$	$5,2 \cdot 10^{-2}$	$6,5 \cdot 10^{-2}$	$7,9 \cdot 10^{-2}$	$2,2 \cdot 10^{-1}$

The efficiency of the niobium and tantalum siliconizing retardation is determined by the reaction rate of silicon and boron on its outer boundary, which leads to the boron over saturation and

transferring of the boride layer into the depth of the metal [5]. Having in mind, that the boron activity in TaB_2 is lower that in NbB_2 (free energy of forming TaB_2 and NbB_2 at 1000 K equals 188,5 and 154,9 кJ/mol correspondingly), the rate of the boride layer displacement in tantalum must be lower than that in niobium. It is testified experimentally.

Basing on the experiments carried out, one can conclude that the deboride tantalum layer, containing molibdenum, retards siliconizing more efficiently, than the boride phase $(Nb, Mo)B_2$, that is, it possesses barrier properties. Thus, tantalum boride $(Ta, Mo)B_2$ can be used as the products silicon saturation protection.

Retardation of the lower silicide growth $(Me, Mo)_5Si_3$ on niobium and tantalum, which is one of the features of acceleration of the protection oxide film damage, can be obtained by forming of the diffusion layer, possessing barrier properties, on the boundary coating-base [Table 2]. This function is successfully provided by the refractory metals borides [5].

Table 2

Oxidation parameters of multilayer coating on refractory metals

Base	Testing temperature, К	Exposure, * hours		Specific weight loss, g/cm^2		Parabola index, n	Specific weight loss after 500 h of oxidation, g/cm^2		Oxidation activation energy, кJ/mol
		τ_1	τ_2	q_1	q_2		q_1 при T_{min}	q_2 при T_{max}	
Niobium	1473 - 1773	10	1000	$6,0 \cdot 10^{-7}$	$0,5 \cdot 10^{-5}$	2,2	$1,9 \cdot 10^{-7}$	$9,0 \cdot 10^{-6}$	1350,6
Tantalum	1473 - 1773	10	1000	$4,0 \cdot 10^{-7}$	$0,3 \cdot 10^{-5}$	2,3	$1,8 \cdot 10^{-7}$	$4,0 \cdot 10^{-6}$	1410,3

* - testing temperature for niobium and tantalum was 1350 °C.

While studying the regularities of the high-temperature oxidation and damage of the boron-silicide coating on niobium and tantalum, it was found, that only at 1400 °C insufficient changes of the chemical and phase composition were found. Further increase of the temperature to 1500 °C and oxidation exposure causes acceleration of the interreaction processes on both environment coating boundary and coating-base boundary, which results in the oxidation rate growth. At the same time it should be stressed, that while coating testing during 300 hours the oxidation rate is almost equal in both metals (Table 3). Only increase of exposure leads to the oxidation intensification. As the results of metallographic and X-ray-phase analysis methods testify changes in the coatings are available. Deboride phase $(Me, Mo)B_2$ reacts with the metal base and results in the refractory metal monoboride $(Me, Mo)B$ and the displacement of the boride phases into the depth of the metal takes place. At the same time the growth of the lower silicide $(Me, Mo)_5Si_3$ and decrease of the phase layer thickness $(Me, Mo)Si_2$ is observed (Fig.4). It should be stressed, that the layer growth rate $(Ta, Mo)_5Si_3$ is less than that of phase $(Nb, Mo)_5Si_3$. But it does not result in the sufficient growth of the tantalum boron-silicide coating operating time.

Table 3

Data on heat-resistance of multilayer coating on refractory metals

Base	Permissible operating time of coating, hours	Specific loss weight, g/cm^2	Limiting possible operating temperature, К	Maximal possible overheating of composition, К
Niobium	6000	$4,0 \cdot 10^{-4}$	1844	71
Tantalum	6000	$8,0 \cdot 10^{-5}$	1892	119

As the results of the carried out investigations mentioned above testify, the operating time of the boron-silicide coating depends on the high-temperature stability of the deboride phase $(Me, Mo)B_2$, which retards the interrelation of the metal-based silicide phases $(Me, Mo)Si$ and on the heat resistance of the silicide layer $(Me, Mo)B_2$ and its thickness. As the desilicide phases $(Nb, Mo)Si_2$ and $(Ta, Mo)Si_2$ are not able to protect the niobium and tantalum products from the high-temperature oxidation for a long time and the increase of the silicide layer coating thickness (more than 200 mkm), as the experiments testified, causes its scaling from the base, the efficient way of raising the coating heat-resistance is the application of the slurry method for both growing of the total thickness of the coating and changing of its composition by adding some other, more heat-resistant constituents, molibdenum desilicide and refractory oxides in particular [6,7].
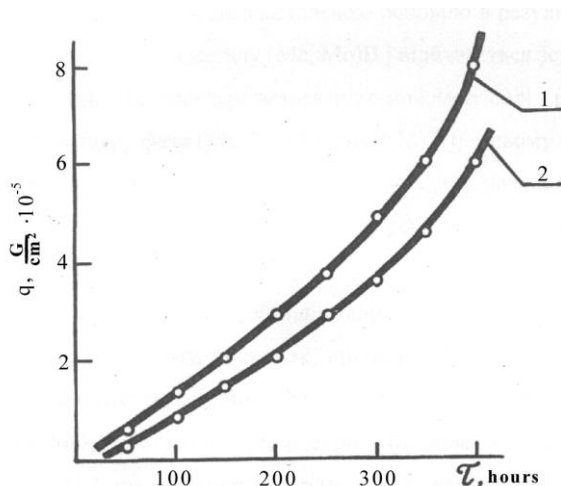
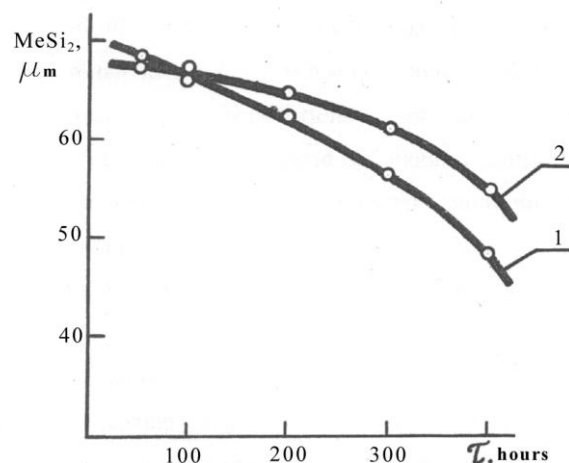Figure 3. Oxidation isotherms of boron-silicide coating on the preliminary molibdenized niobium (1) and tantalum (2): T=1500 ^{o}C; environment - air.

Figure 4. Change of desilicide phase (Me, Mo)Si$_2$ thickness on niobium (1) and tantalum (2) depending on oxidation time: T - 1500 ^{o}C, environment - air; cycle time - 10 h.

Niobium and tantalum specimens were preliminary molibdenized and then successively saturated by boron and silicon, which leads to the formation of phases described above. According to the method mentioned in p.2, the boron-silicide surface was covered with the multilayer slurry coating. After high-temperature heating on the surface of the multilayer slurry-diffusion coating the protection film is formed, which, as the results of the X-ray-phase analysis testified, contains beside silicides, some oxides: ZrSiO$_4$, HfSiO$_4$, YAlO$_3$, Y$_4$Al$_2$O$_9$, etc.

Metallographic analysis testified that the multilayer slurry coating is the MoSi$_2$ - base composition reinforced by the refractory oxides.

The results of investigation carried out testify that the slurry coating thickness must not axceed 250 ± 25 mkm, as while its increasing the microcracks appear and its scaling can be available. Decrease of the coating thickness results in the decrease of the composition operating time.

Thus, it should be concluded, that the application of the slurry method makes possible the formation of the preliminary molibdenized niobium and tantalum multilayer coating on the boron-silicide surface, which is oxidation high-temperature resistant.

Using the method described in [3] the kinetic and temperature dependence of the multilayer composition oxidation was found. It made possible to build up the parametric diagram of the niobium and tantalum multilayer coating heat-resistance and to assess the real coating material oxidation rate due to the relative weight loss values, as well as to calculate the limit coating operating temperature and the maximum possible overheating of the composition material. The growth of the protection film on the multilayer coating is subject to the parabolic law (n~2) and its formation is characterised by the great losses of energy (Table 2). The error in finding the activation energy value is within 2,5-3% and heat-resistance parameter — 4 - 5%. The most sensitive as to the overheating is the niobium coating, the less sensitive - the tantalum coating. It testifies that under sufficient enough operating time of the product (6000 hours), the multilayer composition is sensitive to the raising of the nominal operating temperature. The results obtained make possible to conclude, that the nominal operating temperature of the refractory metals coating can be increased in 70 - 120 K (Table 3).

It should be stressed, that the multilayer coating is less sensitive to the overheating and, as the results of the experiments testify, it is able to be self-treated. It can be covered on both accident damaged surfaces and those on recycling production.

While comparing the operating temperature of coatings and their operating time (Table 4), it should be stressed, that the multilayer slurry-diffusion coating possesses better operating characteristics, as it makes possible to increase in 4 times the operating time of the niobium and tantalum construction elements, which operate in the oxide environment.

Table 4

Heat-resistance of protection coatings on Niobium and Tantalum

Base	Coating	Limiting operating temperature, °C	Operating time, hours	Operating regime	Lite-rature
Combined					
Niobium	(Cr+Ti)-Mo-Si	1300	30	continuous	[8]
Tantalum	- ‖ -	1400	150	- ‖ -	
Metal coating					
Niobium	Sn-Al-Mo	1200	230	- ‖ -	[8]
Tantalum	- ‖ -	1300	100	- ‖ -	
Niobium	Beryllium	1300	30	- ‖ -	[9]
Tantalum	- ‖ -	1375	20	- ‖ -	
Roasting oxide					
Niobium	Al_2O_3 + glass	1375	100	- ‖ -	[10]
Tantalum	- ‖ -	1370	150	- ‖ -	[8]
Complex					
Niobium	$W-ZrB_2$	1700	1	- ‖ -	[8]
Tantalum	$Cr-ZrO_2$	2000	0,2	- ‖ -	[11]
Multilayer					
Niobium	Silicide-oxide composition with boride	1500	5000	periodical and continuous	Investigations carried
Tantalum	and silicide layers	5000	5000		out

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