

ENHANCEMENT OF THE HEAT RESISTANCE OF COATINGS FOR THE BLADES OF GAS-TURBINE ENGINES

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To create blades of gas-turbine engines of new generation made of materials based on alloys of the Nb–Si system, we study the surface layer formed on niobium by its silicides with additionally introduced titanium elements. It is shown that the heat resistance of these specimens does not depend on the method of formation of the surface layer and depends only on its thickness. The addition of titanium increases the heat resistance of the specimens at 1350°C depending on its content. We also performed the thermodynamic analysis of the possibility of simultaneous saturation of the surface of niobium with titanium and boron under the action of vapors of the NaCl activator.

Keywords: vacuum-activated diffusion saturation, complex refractory coatings.

Introduction

At present, blades of gas-turbine engines of alloys based on composites of the Nb–Si system are developed in the USA, Germany, other European countries, China, and Japan [1–5]. By using composites of this kind, it is possible to increase the working temperature of the blades up to 1350°C and decrease the specific fuel consumption by 20% because their density (6.6–7.2 g/cm³) is much lower than the density of alloys based on Ni (9.2 g/cm³). Depending on the silicon content of the niobium matrix, one can change the mechanical properties and the oxidation resistance of the material. Compounds of alloys of the Nb–Si system are characterized by high melting points. Thus, in particular, for NbSi₂, it is equal to 1930°C. The composition of the material determines the ratio of the components guaranteeing the maximal strength characteristics and heat resistance of the compounds [6, 7]. Since alloys of the Nb–Si system have higher working temperatures than superalloys based on Ni (whose working temperature is limited by 1200°C), the former can be used in turbines of new generation. However, at high temperatures, they are oxidized, which is explained by crack initiation.

In order to improve the serviceability of these alloys, it is necessary to protect them against the action of high-temperature gaseous media. For this purpose, by the method of vacuum-activated diffusion saturation, we apply protective coatings to their surfaces. Titanium proves to be one of the most efficient elements for the improvement of the oxidation resistance of these alloys. As an activator, we used NaCl [8], which is not decomposed into elements (Na and Cl) in the course of diffusion saturation and, hence, there is no free chlorine in the reaction volume.

The process of mass transfer of saturating substances in the course of thermochemical treatment is accompanied by the formation of gaseous chlorides interacting with the surfaces of treated products and, thus, promoting

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the formation of diffusion layers. Therefore, in this way, it is possible to obtain uniform coatings on the products of complex shape, including their inner hidden domains [9].

The application of other available methods (electron-beam, ion-plasma, and precipitation from the gaseous phase) does not guarantee the attainment of the required properties of the coatings. The ion-plasma and gas-circulation methods are applied most extensively but have numerous disadvantages. Thus, by using the gas-circulation method, it is quite difficult to get uniform coatings, especially on the inner surfaces of the blades. The application of ion-plasma method is connected with high energy consumption and, moreover, by using this method, it is impossible to apply coatings to the inner parts of the blades [10–12].

Methods of Investigations

Specimens with coatings are obtained by using the procedure of vacuum-activated siliconizing of niobium surface and also by titanizing with subsequent siliconizing. The coatings were applied by the method of vacuum-activated diffusion saturation [13, 14]. Niobium specimens (rods 2 mm in diameter and plates 1 mm in thickness, 15 mm in width, and 10 mm in height) were placed in a container. As a saturating mixture, we used Si and Ti powders with particle 0.2–0.5 mm in size. Saturation was carried out both with the help of an activator and in its absence at a temperature of 1080–1300°C in the container under a pressure of residual gases in the vacuum chamber equal to $5 \cdot 10^{-2}$ Pa. The temperature of the activator (sodium chloride) was equal to 800–805°C and its consumption was as high as 1–5 g/h.

We studied the structure of the specimen surface in an MMO-1600 light microscope. In order to investigate the phase composition and structure, we used the CuK_α -radiation. The elemental composition of the surface was determined by the method of X-ray fluorescent analysis with the help of a SPRUT-VM vacuum scanning spectrometer. We tested specimens for high-temperature strength by their annealing in air at 1350°C. Their corrosion resistance was qualitatively estimated by the outward appearance of the specimens and quantitatively evaluated by the mass changes after 5 h of annealing with subsequent cooling (cycle). For this purpose, the specimens with coatings were weighed with an accuracy of 10^{-5} g, and the increment of thickness of the coating was determined by comparing with the initial mass of the specimens (mass losses per unit surface).

Results and Discussion

The structure and phase composition of the coatings depend on the procedure and parameters of their application. Therefore, on niobium specimens, we formed diffusion layers of its silicides either without activators or with a NaCl activator. The surface was saturated with silicon without activators in order to get protective coatings on the specimens containing alloying admixtures, e.g., titanium, which interact with the vapor of sodium chloride and, thus, affect the composition of the surface layer. As the temperature of saturation of the niobium surface with silicon increases, the rate of formation of the diffusion layer becomes higher in agreement with the well-known results from [15]. In Fig. 1, we present the microphotographs of the cross section of specimens with coatings obtained as a result of siliconizing at 1300°C without activators.

The thickness of the diffusion layer after siliconizing for 6 h is equal to 39 μm . Moreover, after saturation for 12 h, it becomes equal to 47 μm . The indicated thickness increases with the duration of holding and, in particular, constitutes 63, 106, and 133 μm after holding for 18, 24, and 30 h, respectively. By the metallographic analysis, we also discovered a clear two-layer structure of the coating. The thickness of the thin inner layer is close to 2 μm in the case of holding for up to 18 h and to 3 μm after holding for 18–30 h. The thickness of the outer layer changes much faster. By the method of X-ray fluorescent analysis, we recorded Si and Nb

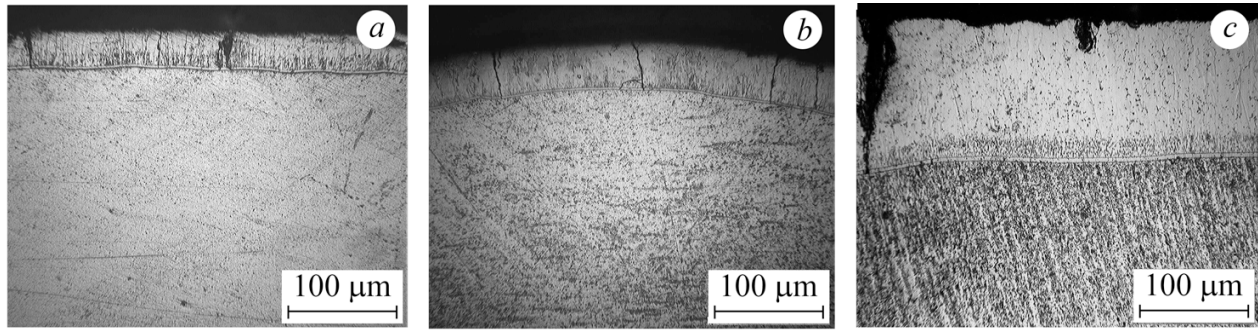


Fig. 1. Microphotographs of the cross section of Nb specimens after siliconizing for 6 (a); 12 (b), and 30 h (c).

Table 1
Contents of Elements and the Phase Composition of the Specimen Surface after Siliconizing

Saturation time, h	Contents of elements, wt.%		Composition of the surface
	Si	Nb	
12	24.63	75.37	NbSi _{1.08}
24	22.3	77.7	NbSi _{0.95}
30	22.8	77.2	NbSi _{0.98}

on the surfaces of the specimens. Furthermore, the results of X-ray phase diffraction analysis enable us to detect the presence of NbSi₂ and Nb₅Si₃ compounds in the coating (Table 1), which is in good agreement with data presented in [16]. The contents of the NbSi₂ and Nb₅Si₃ phases successively increase. The coating is formed mainly due to cross diffusion of Si into the solid matrix of Nb.

Cracks are initiated in the diffusion layer due to the increase in volume in the course of siliconizing of niobium. If the radius of curvature of the niobium surface is small ($r = 1$ mm) and the silicide layer is sufficiently thick (> 200 μm), then the cracks are formed under the action of stresses.

We tested specimens for high-temperature strength also in air at 1350°C. In the course of heating, niobium is noticeably oxidized starting from 200°C. The intensity of oxidation rapidly increases with temperature. After 12 h of siliconizing without activators, the specimens withstand two cycles (10 h). On their surface, after siliconizing for 24 and 30 h, a protective coating is first formed and then, in the course of subsequent oxidation, begins to fail. In total, the specimens withstand 4–5 cycles. For the first cycle (5 h), we observe the formation of a protective SiO₂ coating. Since the affinities of silicon and niobium for oxygen are practically identical, the Nb₂O₅ crystals eventually destroy the continuous SiO₂ film. The rapid growth of the rate of oxidation of niobium at 1000°C and higher is caused not only by the increase in the diffusion rate of oxygen but also by the qualitative changes in the structure of oxide film.

At 1000–1100°C, the low-temperature modification of α-Nb₂O₅ oxide transforms into the high-temperature β-Nb₂O₅, which is accompanied by a significant increase in the volume (by a factor of 2.7) and, hence, by the appearance of internal stresses, local fractures of the film, and its exfoliation [17] leading to a sharp increase in the rate of oxidation of niobium. For the comparison of the kinetics of oxidation, niobium specimens were siliconized with the help of an activator.

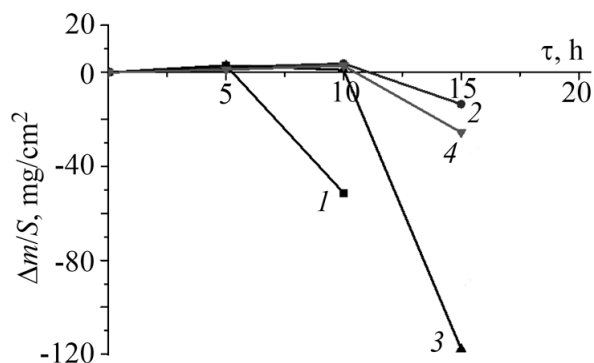


Fig. 2. Time dependence of the relative change in mass of Nb specimens, siliconized without NaCl activator at 1300°C during 12, 24, and 30 h (curves 1–3, respectively) and with activator (curve 4) for 6 h.

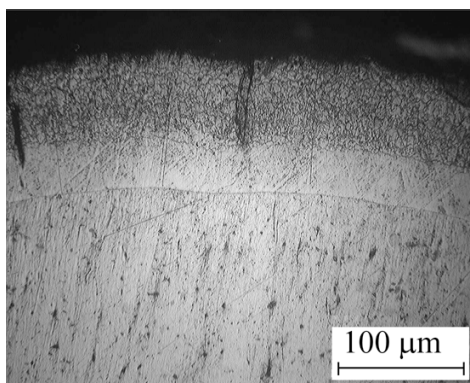


Fig. 3. Microphotograph of the cross section of Nb specimens after titanizing with subsequent siliconizing.

Table 2
Content of Elements on the Specimen Surface after Titanizing at 1080°C
and Subsequent Siliconizing at 1300°C

Saturation time with Ti, h	Saturation time with Si, h	Content of elements, wt.%			Surface composition
		Ti	Nb	Si	
0.5	24	34.9	39.5	25.5	NbTi _{1.66} Si _{2.09}
1	24	35.2	37.9	26.9	NbTi _{1.84} Si _{2.42}
2.5	24	36.4	36.9	26.7	NbTi _{1.92} Si _{2.4}
4	24	45.6	25.2	29.0	NbTi _{3.5} Si _{3.8}
6	24	37.4	34.3	28.2	NbTi _{2.12} Si _{2.73}
8	24	45.9	26.2	27.7	NbTi _{3.39} Si _{3.49}

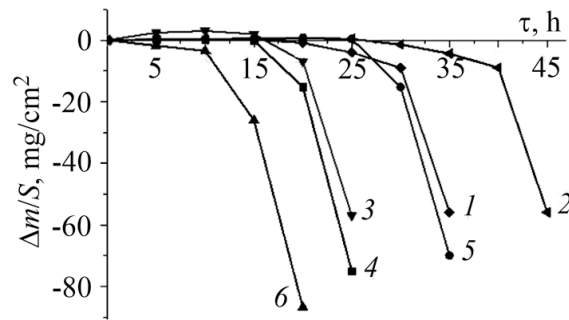


Fig. 4. Time dependence of the relative change in mass of specimens after corrosion tests in air at 1350°C: siliconized during 24 h at 1300°C, preliminarily titanized for 0.5 h at 1080°C (curve 1); 1 h (curve 2); 2.5 (curve 3); 4 (curve 4); 6 (curve 5), and 8 h (curve 6).

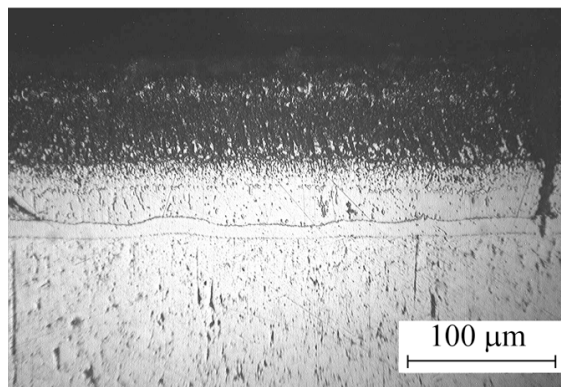


Fig. 5. Microphotograph of the cross section of specimen after annealing during 20 h.



Fig. 6. View of coating after oxidation.

The high-temperature strength of these coatings (Fig. 2) is independent of the method of formation and depends only on the thickness of the coating. The optimal duration of siliconizing is 24 h.

The accumulated results are still insufficient for the commercial application of these materials. One can improve their characteristics by alloying with elements (in particular, with Ti) increasing their refractoriness [18]. It was established that the optimal temperature of titanizing is 1080°C and the duration of saturation affects the amount of titanium on the specimen surface (Table 2). After titanizing with subsequent siliconizing (Fig. 3), the coating has a thickness of about 120 μm and a well-visible two-layer structure.

Table 3
Degree of Transformation of the Reaction at 1070°C

Chemical reactions	Degree of transformation of the reaction under pressure P (Pa)			
	133.3	13.33	1.333	0.133
$\text{NaCl(g)} + \text{TiB}_2\text{(s)}$ $= \text{TiCl(g)} + 2\text{B(s)} + \text{Na(g)}$	$2.7 \cdot 10^{-9}$	$8.5 \cdot 10^{-9}$	$2.8 \cdot 10^{-8}$	$8.5 \cdot 10^{-8}$
$\text{NaCl(g)} + 1/2 \text{TiB}_2\text{(s)}$ $= 1/2 \text{TiCl}_2\text{(g)} + \text{B(s)} + \text{Na(g)}$	$1.7 \cdot 10^{-6}$	$3.6 \cdot 10^{-6}$	$7.8 \cdot 10^{-6}$	$1.7 \cdot 10^{-5}$
$\text{NaCl(g)} + 1/3 \text{TiB}_2\text{(s)}$ $= 1/3 \text{TiCl}_3\text{(g)} + 2/3\text{B(s)} + \text{Na(g)}$	$2.0 \cdot 10^{-5}$	$4.0 \cdot 10^{-5}$	$7.0 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$
$\text{NaCl(g)} + 1/4 \text{TiB}_2\text{(s)}$ $= 1/4 \text{TiCl}_4\text{(g)} + 1/2\text{B(s)} + \text{Na(g)}$	$6.0 \cdot 10^{-24}$	$7.0 \cdot 10^{-23}$	$7.0 \cdot 10^{-22}$	$7.0 \cdot 10^{-21}$
$\text{NaCl(g)} + 1/2 \text{TiB}_2\text{(s)}$ $= \text{BCl(g)} + 1/2 \text{Ti(s)} + \text{Na(g)}$	$4.7 \cdot 10^{-8}$	$1.5 \cdot 10^{-7}$	$4.7 \cdot 10^{-7}$	$1.5 \cdot 10^{-6}$
$\text{NaCl(g)} + 1/4 \text{TiB}_2\text{(s)}$ $= 1/2 \text{BCl}_2\text{(g)} + 1/4 \text{Ti(s)} + \text{Na(g)}$	$2.2 \cdot 10^{-6}$	$4.9 \cdot 10^{-6}$	$1.1 \cdot 10^{-5}$	$2.3 \cdot 10^{-5}$
$\text{NaCl(g)} + 1/6 \text{TiB}_2\text{(s)}$ $= 1/3 \text{BCl}_3\text{(g)} + 1/6 \text{Ti(s)} + \text{Na(g)}$	$1.7 \cdot 10^{-18}$	$1.8 \cdot 10^{-17}$	$1.7 \cdot 10^{-16}$	$1.7 \cdot 10^{-15}$

Comments: (g) gas; (s) solid.

It was discovered (Fig. 4) that, as a result of application of titanium with subsequent siliconizing, the heat resistance of the material at 1350°C insignificantly increases. As the titanium content on the surface of the specimens obtained by the method of vacuum-activated saturation increases, this quantity decreases, most likely due to the growth of the content of lower titanium silicides with lower high-temperature strength than TiSi_2 [18]. Hence, it is necessary to saturate surfaces with other elements, in particular, with Cr, Hf, and also with B and Al.

After long-term cyclic annealing, the presence of cracks in the coating (Fig. 5) leads to the development of corrosion (Fig. 6). By the X-ray phase diffraction analysis, we discovered the Nb_5Si_3 , NbTi_4 , Ti_5Si_3 , TiSi , NbO_2 , SiO_2 , TiO_2 , and Ti_3O_2 phases formed in specimens after annealing at 1350°C in air.

In order to form refractory surface layers on specimens of siliconized niobium, it is necessary to clarify the possibility of simultaneous introduction of titanium and boron by the method of vacuum-activated diffusion saturation. The interaction of these layers with oxidizing media at high temperatures must lead to the formation of protective films of silicon, niobium, titanium, and boron oxides. To determine the possibility of saturation of the surface of siliconized niobium simultaneously with titanium and boron, we performed thermodynamic calculations. In Table 3, we present the results of thermodynamic analyses of possible chemical reactions between the activator, gaseous sodium chloride, and TiB_2 at 1070–1325°C. These results demonstrate that the probability of

Table 4
Contents of Vapor in the Gaseous Atmosphere at 1070°C

Components	Amount of substance in a gas mixture (mole) under pressure P (Pa)			
	133.3	13.33	1.333	0.133
TiCl	$\approx 10^{-10}$	$8.57 \cdot 10^{-9}$	$2.71 \cdot 10^{-8}$	$8.569 \cdot 10^{-8}$
TiCl ₂	$1.65 \cdot 10^{-6}$	$3.582 \cdot 10^{-6}$	$7.717 \cdot 10^{-6}$	$1.662 \cdot 10^{-5}$
TiCl ₃	$2.217 \cdot 10^{-5}$	$3.945 \cdot 10^{-5}$	$7.014 \cdot 10^{-5}$	$1.247 \cdot 10^{-4}$
TiCl ₄	$2.297 \cdot 10^{-5}$	$3.636 \cdot 10^{-5}$	$5.762 \cdot 10^{-5}$	$9.13 \cdot 10^{-5}$
BCl	$4.695 \cdot 10^{-8}$	$1.484 \cdot 10^{-7}$	$4.693 \cdot 10^{-7}$	$1.484 \cdot 10^{-6}$
BCl ₂	$2.339 \cdot 10^{-6}$	$5.048 \cdot 10^{-6}$	$1.087 \cdot 10^{-5}$	$2.341 \cdot 10^{-5}$
BCl ₃	$3.594 \cdot 10^{-5}$	$6.439 \cdot 10^{-5}$	$1.145 \cdot 10^{-4}$	$2.036 \cdot 10^{-4}$
Na	$8.512 \cdot 10^{-5}$	$1.49 \cdot 10^{-4}$	$2.613 \cdot 10^{-4}$	$4.612 \cdot 10^{-4}$
NaCl	0.999915	0.999851	0.999739	0.999539

realization of these reactions increases with temperature. The degree of transformation of a chemical reaction is the fraction of source substances participating in the reaction according to its equation. This quantity is a function of temperature and pressure.

It is easy to see that, in the course of vacuum-activated diffusion saturation, the gaseous medium mainly contains titanium and boron chlorides. The greatest contribution to the transfer of saturating elements is made by the TiCl₂, TiCl₃, and BCl₂ compounds. The results of theoretical evaluation of the reaction yield are presented in Table 4.

CONCLUSIONS

We study coatings obtained by the method of vacuum-activated diffusion saturation from niobium silicides on the specimens of this metal, and the influence of parameters of the process on their high-temperature oxidation. It is shown that, after oxidation at 1350°C, the coating formed on niobium after siliconizing for 12 h without activators withstands two cycles (10 h). In the case of siliconizing of niobium for 24 and 30 h, we observe the formation of a protective coating (for two cycles) whose destruction begins in the course of subsequent oxidation. In total, the specimens withstand 4–5 cycles. In the presence of activator, the high-temperature strength of the coating insignificantly increases. The procedure of titanizing of niobium with subsequent siliconizing improves the corrosion resistance of specimens at 1350°C but their high-temperature strength depends on the titanium content in the composition of the coating. The thermodynamic analysis demonstrates that the protective layer on niobium can be formed by simultaneous saturation of the treated surface with titanium and boron by the method of vacuum diffusion saturation with TiB₂ compound playing the role of the source of these elements. In the course of subsequent siliconizing of this surface, we observe the formation of a protective film, which consists of niobium and titanium silicides alloyed with boron. These coatings protect the surfaces at 1350°C despite the influence of oxidizing media.

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