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Heat-Resistance and Phase Composition of Ti-Si Coatings on Niobium

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Abstract. A diffusion silicide coatings on refractory under thermal shock. A prospective method of improving their durability is the formation of multi-component coatings. Ti is one of the wide-spread components of such coatings.

In this work, process of simultaneous diffusion saturation of niobium by Ti and Si in powder mixtures has been investigated. The coatings can be divided into two basic types: Nb-Ti solid solutions and Nb and Ti silicides. The coatings of the first type obtained in Ti-Ti₅Si₃ powder mixtures. The complex silicide layers were observed in the packs with higher silicon activity (Ti₅Si₃ - TiSi and TiSi₂-TiSi mixtures). The activities of Ti and Si have been shown to be principal controlling factors in coating phase in composition. The coatings allows to increase heat-resistance of the niobium and niobium alloys up to 2000°C (1,5 hour).

I. INTRODUCTION

The temperature limit for exploitation of traditional diffusion coatings on niobium and its alloys in oxidizing gaseous media does not exceed 1500°C. It is well known that it is possible to increase the limit temperature by combination of deposition methods, by slip-diffusion saturation method for an instance. It's not always acceptable however. Moreover, good coating/base adhesion is not always attainable. So we supposed the coatings described in work [1] to have some anomalous heat resistance for several composition area. This work investigates features of forming for Ti-Si system coatings, their composition and heat resistance in air as well.

II. EXPERIMENT

Phase composition of powder diffusion sources and coatings were studied by X-ray diffraction analysis. The structure and elemental composition of the coatings were studied by microprobe analysis and scanning electron microscopy. Cross-section profiles of elemental distributions in the diffusion zone were obtained using analytical lines of $K\alpha$ -titanium, $K\alpha$ -silicon and $L\beta$ -niobium. Titanium silicides Ti_5Si_3 , $TiSi$, $TiSi_2$ were used as the diffusion source, as well as equilibrium mixtures: $Ti-Ti_5Si_3$, Ti_5Si_3-TiSi , $TiSi-TiSi_2$ with presence of fluoride activators: CaF_2 , MgF_2 , KF , CuF_2 . The elemental composition of the saturating mixture varied from 90 w.% Ti - 10 w.% Si to 46% Ti - 54% Si (stoichiometry $TiSi_2$), activities of the elements in the source be varied widely.

Heat-resistance of the coatings were tested for coated wire Nb samples (diameter: 2mm, length: 50mm) on a direct current heating plant. The temperature was measured with a color pyrometer SPECTROPIR.

III. RESULTS

To choose the optimal regime of saturation of Nb with two elements simultaneously, a serie of experiments with samples treated in $TiSi_2$ powder at $1000-1200^\circ C$ was set. I was found that a layer of $NbSi_2$ of variable thickness, separated from the metal surface by a thin layer of Nb_5Si_3 , did always form. Ti was not found in the coated samples, treated at $1000^\circ C$. However, it started penetrating into $NbSi_2$ at temperatures of $1100-1200^\circ C$. The distribution of Ti in the $NbSi_2$ layer is uneven because of its preferential diffusion along the silicide grains' boundaries. The experiment's results show that Ti concentrates on the grain boundaries of $NbSi_2$ phase, slightly penetrating inside the grains too.

Since the major interest was namely co-diffusion of Ti and Si into niobium, the saturation was performed at $1200^\circ C$. It was shown that two areas on the composition range are to be distinguished: for the Ti-rich mixture, the dominant process is titanization of niobium, while since Si content exceeds 26%, the growth of silicide-type coatings takes place. Fig.1 shows distribution of Ti, Si and Nb in a coating formed at $1100^\circ C$ (CaF_2 activator). A zone of solid solution Nb-Ti with slight presence of Si (< 0,5%) is formed on the sample surface. This effect is attributed to the dependence of mutual diffusion coefficient on the solution composition: Nb concentration being increased, D Nb-Ti decreases by several orders of magnitude, compare to the Ti-rich zone [2]. Thus the inner part of the coating actually

Fig.1. The depth distribution of the elements in diffusion zone after the treatment of niobium in
 (a) $\text{Ti-Ti}_5\text{Si}_3$ (90 w.% Ti - 10 w.% Si) - 3 w.% CaF_2 ;
 (δ) Ti_5Si_3 - 3 w.% CaF_2 ; 1300°C, 2 hours

plays the part of the diffusion barrier. The consequence is high (> 50%) concentration of saturating element in the diffusion layer. This confirms that Ti_5Si_3 in this case almost an inert diluent. Diffusion saturation, performed with Ti_5Si_3 powder, is accompanied by Nb_5Si_3 growing layer on the base metal surface and characterised with minimal process speed. The Ti concentration in the coating is < 0,1%. Obviously, Ti diffusion is being limited on the inner mass transfer stage.

For titanium siliconizing of Nb in the mixtures with high activity of Si the growth of $NbSi_2$ alloyed by Ti may be observed. On the inner boundary of the coating a thin layer of Nb_5Si_3 phase occurs. Due to quantitative analysis results, Ti concentration increases slightly along the diffusion path from the source of $TiSi_2$ to TiSi. The diffusion of Ti atoms in the $NbSi_2$ layer runs mostly along the grain boundaries. It should be mentioned that of the alloyed area is thinner than the total coating for the samples treated with TiSi, TiSi-TiSi₂, TiSi₂, (fig.2). X-ray analysis of the given samples showed the parameters of hexagonal lattice of Nb alloyed with Ti to be: $a=0,4773\pm0,0002$ nm, $c=0,6577\pm0,0002$ nm. The composition of the phase zone may be expressed as $(Nb_{1-x}Ti_x)Si_2$. This means that substitution of Nb atoms with Ti in the $NbSi_2$ layer takes place. Thus, the Ti-alloyed coating areas are of disilicides solid solution based on $NbSi_2$ phase.

Treatment in the Ti_5Si_3 -TiSi mixture forms the most structurally complex diffusion zone. The Nb_5Si_3 layer is extra-thick because of some decrease of the Si activity in the source and the slowdown of gaseous phase transport of Si to the sample surface. The Ti concentration of the outer two-phased layer (solid solution based on Ti and Nb disilicides) is about 15 w.%. For conditions of 2-components diffusion saturation, the Gibbs Phase Rule allows appearance and growth of a heterogeneous layer formed by the two phases. In the given conditions this possibility is realized, the zone II (fig.2) of the phase ($TiSi_2$) appearing not only near the surface, but through the whole depth of the ($NbSi_2$ - $TiSi_2$) layer. Formation of such a two-phased layer contributes to the primary diffusion of the alloying metal along the grain boundaries and forms the starting nonhomogeneity of its distribution in the coating. Obviously, the accumulation of Ti takes place at first in the most defective areas of the lattice (junctions of the silicide grain boundaries is an example), which turns further to be the nuclea of the new phase.

A serie of experiments was performed to appreciate the heat-resistance of the optimal composition coatings in air, the result being presented in the table.

Fig.2. The structure of the coating (a) and the depth distribution of the elements in the coating (b) after the annealing of niobium in $Ti_2Si_3 - TiSi$ (70 w.% Ti - 30 w.% Si) - 3 w.% CaF_2 ; $1300^\circ C$, 2 hours

Table

Tests for heat-resistance of Ti-Si-system coatings on niobium

NN	Thickness of the coating, μ	Oxidation temperature, $^{\circ}\text{C}$	Exposition, minutes
1	80	1750	23
		2000	85
2	60	1750	9
		1800	5
		1900	8
		1950	5
		2000	25
3	100	1750	10
		1800	10
		1850	5
		1950	5
		2000	80

Thus, it is established that the maximal temperature limit for the utilization of the coatings of Ti-Si-system on air is 2000°C . The utilization time at 2000°C is 1-1,5 hrs. This is significantly more than for the known diffusion coatings, silicide type specifically.

CONCLUSIONS

Investigations of the diffusion zone on Nb showed, that treatment in the Ti-Ti₅Si₃ leads to titanization of samples yielding the solid solution of Nb-Ti. In a source with high activity of Si the silicide layer is being formed, its composition corresponding to (Nb,Ti)Si₂, at the same time, depending on elements activities alignment, the coating may be monophaseous (solid solution based on NbSi₂) or heterophaseous (solid on NbSi₂ and TiSi₂). Ti diffusion into disilicide niobium layer may be observed at temperature higher than 1100°C , running mostly along the grains boundaries, which leads to nonhomogeneous distribution of the alloying element even in a monophaseous coating.

The increase of the temperature limit for utilization of Ti-Si-system coatings on niobium in air up to 2000°C is established.

Reference

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