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INFLUENCE OF GAS PHASE COMPOSITION ON THE FORMATION OF Ti-Si COATINGS ON NIOBIUM

M.S. TSIRLIN and S.U. RYBAKOV

Institute of Physical Chemistry of the Academy of Sciences of the USSR, Leninsky pr. 31, Moscow 117915, USSR

Abstract - The elemental and phase composition of diffusion coatings formed on niobium during high temperature gas-substrate interaction has been studied. The packs containing titanium, silicon and fluoride activator have been used for the generation of the gas phase. The coatings can be divided into two basic types: Nb-Ti solid solutions and niobium and titanium silicides. The coatings of the first type have been obtained in Ti-Ti₅Si₃ powder mixtures. The complex silicide layers were observed in the packs with higher silicon activity (Ti₅Si₃-TiSi and TiSi-TiSi₂ mixtures). The equilibrium partial pressures of gaseous components and activities of titanium and silicon in packs and in niobium silicides have been calculated. The activities of titanium and silicon have been shown to be principal controlling factors in coating phase composition.

1.-Introduction.

A diffusion silicide coatings on refractory metals of V-a and VI-a groups exhibit good resistance to high temperature oxidation /1/. However the durability of such coatings on niobium is insufficient, especially under thermal shock /2/. A prospective method of the improving their durability is the formation of multi-component coatings. Titanium is one of the wide-spread components of such coatings /3/. In this work, the process of simultaneous diffusion saturation of niobium by titanium and silicon in the powder mixtures has been investigated. These studies are also useful for the understanding of the general rules of the multi-component diffusion saturation.

2.- Experimental procedures.

The niobium samples (99.99%) in the form of wires (2 mm in diameter and 50-60 mm long) and sheets (10x10x1 mm) were abraded on SiC emery papers, washed in distilled water and treated at 1373-1573 K. The powders of titanium silicides Ti₅Si₃, TiSi and TiSi₂, as well as the equilibrium mixtures of Ti-Ti₅Si₃, Ti₅Si₃-TiSi and TiSi-TiSi₂, were used as the diffusion sources /4/. All the mixtures consisted of the phases, neighboring in Ti-Si phase diagram that prevented the chemical interaction between the mixture components. The grain size of the mixtures was equal to 150-250 μ m. Ca, Mg and K fluorides were used as the activators. 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.

3.-Results and discussion.

The results of the experiments on the annealing of niobium in TiSi_2 packs with different activators are shown in Table 1. It has been found in all the experiments that a NbSi_2 layer was formed at the metal surface and the thin layer of Nb_5Si_3 was formed under NbSi_2 at the metal/coating interface. Titanium has been found in the coatings formed at temperatures above 1473 K and its distribution in the diffusion zone is uneven (Fig.1). The titanium concentration reaches its maximum at the boundaries of NbSi_2 grains. As it can be seen from Table.1, the titanium concentration in the surface zone increases with temperature rise and is almost independent on the activator type and treatment duration.

Fig.1. The depth distribution of the elements in the coating formed after the annealing of niobium in TiSi_2 -3% CaF_2 powder mixture for 2 hrs at 1573 K.

Table 1. The properties of the coatings formed after the annealing of niobium in titanium disilicide packs.

T, K	1373	1473	1573	1573	1573
Activator	KF	MgF_2	MgF_2	CaF_2	CaF_2
Duration, h	2	2	2	2	7
C(Ti), max, %	0	1.8	3.2	3.5	4.0
Coating thickness, μm	28	26	40	30	80

The results of the experiments on the diffusion treatments carried out in different packs for 2 hrs at 1573 K with CaF_2 as an activator are presented in Table 2 and Fig.2. It should be noted that there are two regions on the composition scale of diffusion sources. The use of mixtures with high titanium concentrations leads mainly to the

Fig.2. The coating thickness as a function of the pack composition.

Table 2. The properties of the coatings formed in the process of simultaneous titanizing and siliconizing of niobium (1573 K, 2 h, CaF_2).

Phase and elemental compositions of the packs, %	Thickness of the coating, μm	Phase compositions of the coatings	Max. Ti content in the coatings, %
Ti-Ti ₅ Si ₃ (90Ti-10Si)	36	Nb-Ti sol. solution	57
Ti-Ti ₅ Si ₃ (85Ti-15Si)	21	Nb-Ti sol. solution	53
Ti-Ti ₅ Si ₃ (80Ti-20Si)	10	Nb-Ti sol. solution	15
Ti ₅ Si ₃ (74Ti-26Si)	4	Nb ₅ Si ₃	0.1
Ti ₅ Si ₃ -TiSi (70Ti-30Si)	14	NbSi ₂ -TiSi ₂	15
TiSi (63Ti-37Si)	25	NbSi ₂	4.2
TiSi-TiSi ₂ (60Ti-40Si)	28	NbSi ₂	3.8
TiSi-TiSi ₂ (50Ti-50Si)	32	NbSi ₂	3.5
TiSi ₂ (46Ti-54Si)	30	NbSi ₂	3.5

Fig.3. Thermodynamic activities of the elements in Ti-Si system at 1573 K. The boundaries of the homogeneity regions are shown conditionally.

titanizing of niobium, the silicon concentrations in Nb-Ti solid solutions is being less than 0.5%, while the silicon concentrations in the packs exceeding 26% results in the formation of the silicide phases. The boundary composition separating these two regions is corresponding to Ti_5Si_3 phase. Moreover the minimum process rate together with minimum titanium concentration in the coatings are also related to this phase. The composition of the coating formed in this pack is found to be Nb_5Si_3 . The treatment in Ti_5Si_3 - $TiSi$ packs results in the formation of more complex structures. The thickness of Nb_5Si_3 layer increases substantially and the external layer of the coating consists of the mixture of $TiSi_2$ and $NbSi_2$ phases (or rather the solid

solutions of silicides based on these phases), and titanium concentration in Nb_5Si_3 layer is close to zero. The further increase of silicon concentration in the source leads to the formation of only NbSi_2 phase with titanium concentrations about 3-4% (Table 2).

As the gradient of the chemical potential is the driving force for the isothermal transport of the source components from the pack into the diffusion coating, it is necessary to estimate the thermodynamical activities of the elements participating in this process. The equilibrium compositions of the gas phase generated by pack have been calculated using "Astra-3" code /5/. The thermodynamical properties of TiSi_2 , TiSi and Ti_5Si_3 were found in /6/. The validity of these data were checked by preliminary calculations of the boundaries of the phase regions for Ti-Si system and their comparison with the experimentally determined values /4/.

The calculated dependences of silicon and titanium activities on the pack composition at 1573 K are presented in Fig.3. The critical silicon activities required for the diffusion growth of NbSi_2 and Nb_5Si_3 phases are also shown in Fig.3.

Evidently, the variations of titanium and silicon activities in the range of Si concentrations from pure Si to Ti_5Si_3 phase are rather small and the formation of NbSi_2 coatings is possible in the packs with these compositions. Only Nb_5Si_3 formation is expected if Ti_5Si_3 pack is used as a source (Fig.3). On the contrary, the use of Ti_5Si_3 -Ti packs exhibits the formation of niobium silicides and the formation of Nb-Ti solid solutions should be expected according to Ti-Nb phase diagram. The experimental results (Table 2) confirm the validity of these estimates. The sharp changes in the activities of Si and Ti should be noted in the region of homogeneity of Ti_5Si_3 phase. Really Si concentration of 26% is the boundary one and its decrease below this value leads to the replacement of the siliconizing process to the titanizing one. The calculated silicon and titanium activities in Ti_5Si_3 phase are equal to $7.4 \cdot 10^{-4}$ and $1.1 \cdot 10^{-2}$ at 1573 K respectively and therefore Ti_5Si_3 is a weak source of both Ti and Si which can account for the drop of the rate of the diffusion process in Ti_5Si_3 pack (Fig.2).

The equilibrium pressures of the gaseous components generated by TiSi_2 , TiSi packs with CaF_2 additions are shown in Fig.4. The calculations have shown that TiF_3 molecules are the basic titanium carriers irrespectively of temperature and activator type, whereas SiF_2 molecules are basic carriers of silicon. Titanium content in the gas phase has been shown to increase with temperature both with and without activator. The increase of fluorine pressures results in the higher probability of the combined titanium and silicon transport. It is also worth noting that the introduction of the fluoride activator leads to the increase of $\sum P_i(\text{Ti}) / \sum P_i(\text{Si})$ ratio in gas phase by three orders of magnitude. However higher pressures of alkaline fluorides impede their use in vacuum processes. The results obtained allow some new consideration to be made on the relationship between the composition of the diffusion source and the growth rate of the coating. The comparison of Fig.2 and Fig.3 clearly indicates the coincidence of the coordinates of "the singular point". The reasons of this coincidence were discussed above. It should be only mentioned here that Ti_5Si_3 phase serves as the inert addition in Ti - Ti_5Si_3 and Ti_5Si_3 - TiSi packs. Obviously the application of Ti_5Si_3 phase as a source fits to the minimum at "source composition-coating thickness" diagram.

Fig.4. The partial pressures of the gas phase components vs. temperature in $\text{TiSi-TiSi}_2\text{-CaF}_2$ system.

4.- Conclusions.

The thermodynamic analysis of phase formation during the simultaneous saturation of niobium with titanium and silicon has been carried out. It has been shown that the distinct boundary exists on the scale of element concentration in the packs which separates the regions of preferential transport of titanium or silicon to the coating. This boundary corresponds to Ti_5Si_3 phase stoichiometry.

The calculated data were confirmed experimentally. The layer of Nb-Ti solid solution has been found to form at the niobium surface after the treatment in Ti-Ti₅Si₃ pack. The silicide layer was formed in the packs with high silicon activity. The composition of this layer can be described as (Nb,Ti)Si₂ and it can be single or two phase coating.

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