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TRANSLATION

DIFFUSION OF SILICON IN TITANIUM, TANTALUM, MOLYBDENUM AND IRON

By

G. V. Samsonov, M. S. Koval'chenko, et al.

FOREIGN TECHNOLOGY DIVISION

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FIRST LINE OF TEXT

DIFFUSION OF SILICON IN TITANIUM, TANTALUM, MOLYBDENUM AND IRON

by

O. V. Samsonov, M. S. Koval'chenko, et al

The formation on the surface of metals of solid silicide coatings, which are highly resistant to acids, molten salts and certain metals, have high heat resistance and antithermoemission properties, surface saturation by silicon is of great interest for modern technology [1 - 4].

FIRST LINE OF TITLE

The obtainment of silicide coatings by deposition of silicon from gaseous phase on metals of IV-VI groups of the periodical system is described in report [5], iron and steel - in [6]. In report [7] was made the first effort to explain the nature of phases, which will be formed during the saturation of high melting silicon metals.

In the given investigation the authors are trying to make a more thorough investigation of silicon diffusion in titanium, tantalum, molybdenum and iron. Investigation were made on samples of titanium (99.98%), tantalum (99.6% Ta; 0.4% Nb), molybdenum (99.98%), iron (armko-iron) with the utilization of silicon, purified by the method, described in report [8]. The samples were saturated with silicon in an Argon atmosphere from a solid phase bath, which consisted of 97% Si and 3% NH_4Cl. Ammonium chloride was introduced into the batch for which, in order that a certain amount of $SiCl_4$ should be formed between it and the silicon during reaction, which during the decomposition on the surface of the metal with separation of active silicon accelerates the process of diffusion, and HCl vapors, which form in this case, pickle the metal and promote diffusion.

The titanium, tantalum, molybdenum and iron samples were saturated with silicon at temperatures of 600-1200° with a 100° interval, for a period of 4 years with the

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exception, that the time of saturation varied at temperatures of 900, 1000 and 1200° respectively for titanium and iron, molybdenum and tantalum.

The relative change in weight, diameter and height of samples depending upon temperature and time of saturation can be described by empirical equations

$$\frac{\Delta p}{p} = \gamma \sqrt{A\tau}\, e^{-\frac{B}{T}} \qquad (1)$$

where $\frac{\Delta p}{p}$ - relative change in weight, diameter or height; γ - time of saturation; T - absolute temperature; A,B-experimentally designated constants.

Metallographic and x-ray investigations as well as microhardness measurements revealed that during diffusion of silicon in titanium, tantalum, molybdenum and iron, at low temperatures are formed monophase silicide layers, and at higher temperatures (1000-1200°) two phase layer do originate.

Results of measuring layer thickness, phase composition of layers and microhardness at a distance of 20 microns from the outer surface of samples are listed in table.

It has been established on the basis of results in determining the force of piercing silicide coatings [9], that it increases with the increases in silicide layer thicknesses. But electric resistance and piercing strain are to a considerable extent affected by phase composition of the layer, porosity and degree of being separated from the metal base. An increase in the content of silicon in the layer, as a rule, leads to a sharp rise in piercing stress. Piercing stress at identical thickness of silicide layer for various metals is also different (table).

As is evident from the mentioned data, piercing stress rises at a reduction in the degree of defectiveness of unfilled d-sub levels of atoms of transient metals.

Considering the predominant formations during silicon saturation of $TiSi_2$, $TaSi_2$, Mo_3Si_2 and FeSi phases, we have determined the diffusion coefficients by the method, described in [10], and the values of activation energy, listed in table. The temperature dependence graph of the diffusion coefficients are presented in drawing.

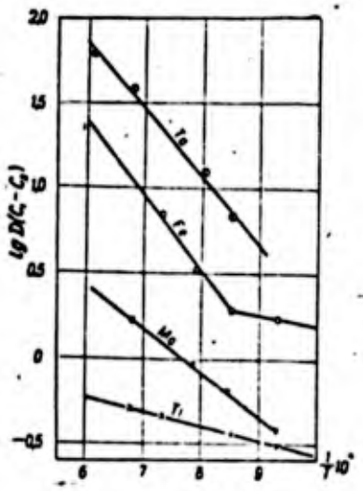

Fig. Temperature dependence of diffusion coefficient of silicon in titanium, tantalum, molybdenum and iron.

It is evident from the results of this investigation, that during diffusion saturation of transient metals with silicon are formed silicide coatings, whereby disilicide phases are not always predominant in the layers, in spite of the fact, as shown by [7], that they may always be formed. The TiSi compounds formed predominantly on titanium correspond to literature data for maximum temperature of formation of this silicide as compared with Ti_5Si_3 and $TiSi_2$ silicides [11].

Formations of FeSi and Mo_3Si_2, as basic phases in silicide layers on iron and molybdenum, apparently, take place in accordance with the known law of conformity between the heat of formation (by 1-g-atom) and melting points of these compounds [12].

In the Fe-Si system to the FeSi compound corresponds a maximum revealed in the liquidus curve and the melting point exceeds the melting point of other iron/silicon compounds. The higher heat of formation of this phase is due to their predominant content in the composition of silicide coatings on iron.

Analogous phenomena are observed during the formation of Mo_3Si_2.

The previously made statement on the effect of purely electron factors on the diffusion of metalloids in metals [7] has been confirmed in this report.

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Table: Thickness, Phase Composition, Microhardness, Piercing Stress of Diffusion Coatings and Magnitude of Diffusion Constants.

1. Metal
2. $\frac{1^1}{N_n}$
3. Temp. °
4. Hour - Year
5. Layer thickness μ
6. Phase comp.
7. Micro hardness at distance of 20 μ from surf. of sample kg/mm^2
8. Piercing stress^2 v
9. Activation energy a, designated analytically cal/mol
10. D_o, cm^2/sec
11. Equations of temperature dependence of diffusion coefficient.
12. Titanium
13. Tantalum
14. Molybdenum
15. Iron

Товщина, фазовий склад, мікротвердість, напруга пробою дифузійних покрить та величин дифузійних констант

1. Метал	2. $\frac{1^1}{Nn}$	3. Температура, °С	4. Час, год.	5. Товщина шару, мк	6. Фазовий склад	7. Мікротвердість на відстані 20 мк від поверхні зразка, кг/мм²	8. Напруга пробою², в	9. Енергія активації a, визначена аналітично, кал/моль	10. D_o, см²/сек	11. Рівняння температурної залежності коефіцієнта дифузії
				other grains						
12. Титан	0,167	800	4	Окремі зерна	TiSi	1000	1,2	5216,4±2367,0	2,99	$D=2,99e^{-\frac{5216,4\pm 2367,0}{T}}$
		900	4	46	$TiSi$, $TiSi_2$	1000				
		900	8	53	$TiSi$, $TiSi_2$	1000				
		1000	4	56	$TiSi$, $TiSi_2$	1000				
		1100	4	70	$TiSi$, $TiSi_2$	1000				
13. Тантал	0,063	900	4	<1	—	—	1,8	21513,2±1671,0	$36,23\cdot10^3$	$D=38,23\cdot10^3e^{-\frac{10756,5\pm 835,5}{T}}$
		1000	4	120	$TaSi_2$	1220				
		1100	4	180	$TaSi_2$	1640				
		1200	2	230	$TaSi_2$	1220				
		1200	4	370	$TaSi_2$	1263				
		1200	6	429	$TaSi_2$	1269				
14. Молібден	0,50	800	4	40	Mo_3Si_2	1520	4,2	13387,5±8416,9	$1,5\cdot10^3$	$D=1,5\cdot10^3e^{-\frac{1687,7\pm 421,0}{T}}$
		900	4	53	Mo_3Si_2, $MoSi_2$	1520				
		1000	1	50	Mo_3Si_2	800				
		1000	2	75	Mo_3Si_2, $MoSi_2$	1310				
		1000	4	110	Mo_3Si_2, $MoSi_2$	1945				
		1000	8	174	Mo_3Si_2, $MoSi_2$	1945				
		1100	4	127	Mo_3Si_2, $MoSi_2$	1145				
		1200	4	165	Mo_3Si_2, $MoSi_2$	1070				
				Solid Solution						
15. Залізо	0,55	700	4	0	Твердий розчин	—	3,0	1553,8 (α-залізо)	2,52	$D=2,52\cdot e^{-\frac{776,5}{T}}$
		800	4	10	—	—				
								22029,0 (γ-залізо)	$14,55\cdot10^3$	$D=14,55\cdot10^3e^{-\frac{11014,5}{T}}$
		900	1	60	—	950				
		900	2	165	—	610				
		900	4	230	FeSi	—				
		900	8	680	FeSi	645				
		1000	4	180	FeSi	640				
		1100	4	220	FeSi	800—1220				

Footnotes to table on page 4.

1 Ratios $\frac{1}{Nn}$ express approximately the degree of incompleteness of d-levels of atoms of transient metals : N-main quantum number, n-number of electrons on the in complete d-level.

2 Piercing stress for coatings of identical thickness.

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