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SELF-DIFFUSION OF NIOBIUM IN SOME OF ITS ALLOYS WITH MOLYBDENUM

by

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ABSTRACT: Self diffusion coefficients (D) were obtained for niobium alloyed with 5, 10, 20, 30 and 45% Mo. The values of D were determined from radioactive tracer measurements of Nb^{95} in the form of $Nb_2^{95}O_3$. Lattice parameters were determined by the powder method and both hardnesses and microhardnesses were obtained by standard methods. The self diffusion coefficient of Nb is given as a function of Mo content for temperatures ranging from 1600 to 2100°C while both the activation energy E and the diffusion parameter ln D_0 are given as functions of Mo content. The relation between ln D_0 and E is given by

[redacted]

where $D = D_0 \exp-(E/RT)$. A list of all the diffusion parameters, hardnesses, microhardnesses and lattice parameters is presented for various temperatures and Mo content. Comparisons of E and ln D_0 are made for the Mo-Zr system which also had a linear dependence of ln D_0 as a function of E. In previous studies, the relation $E = \alpha T_{m.p.}$ ($T_{m.p.}$ is the melting temperature) was used to correlate diffusion data. However, $E = \alpha T_{m.p.}$ could not be used for all the experimental data

because the concentration dependence of D had a maximum at 8% Mo, whereas $T_{m.p.}$ diminished monotonically up to 25% Mo and rose about 25% Mo. For Mo contents close to 6.25 at % (about 6.5 wt %) every Nb atom finds itself near another Nb atom at a distance of one Mo atom. Above about 8%, Mo cell distortion arises, complicating the diffusion process; further increases in concentration result in segregation of Mo atoms, changing the concentration dependence of self diffusion. Thus a semiempirical approach yielded E = 176 - 21.7 (% Mo) and the diffusion equations were adjusted accordingly. Orig. art. has: 4 figures, 1 table, 4 formulas.

SELF-DIFFUSION OF NIOBIUM IN SOME OF ITS ALLOYS WITH MOLYBDENUM

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In many cases the stability of materials at high temperatures and stresses is determined not only by the initial mechanical properties, but also by their diffusion parameters. In particular, this holds for alloys based on niobium with Mo, W, V, Zr, Ti and other metals, which have already obtained known application. In spite of this, information about their diffusion parameters is lacking or extremely tentative in the overwhelming majority of cases.

This article gives the results of an investigation of the self-diffusion parameters of niobium and some of its alloys with molybdenum.

The initial materials for the alloys were metallic Nb and Mo of industrial purity. From them we first made thin chips, which we mixed and pressed in the necessary proportion. The obtained briquets were remelted in a MIFI arc furnace with an unexpendable tungsten electrode and a copper water-cooled bottom plate in an argon atmosphere. To obtain a more uniform melt the samples were first subjected to triple or quadruple remelting, and then to 10-hour vacuum homogenizing annealing at temperatures 150-200° below the corresponding liquidus lines (i.e., at 2100-2200°) [1].

Thus we obtained samples of melts with a large-crystalline structure (grain size, 3-5 mm) and containing approximately 5, 10, 20, 30 and 45% Mo. The diffusion mobility of Nb in them was studied by the method of removing layers and measuring the integral activity of the remainder [2]. The radioactive isotope Nb^{95} in the form of $Nb_2^{95}O_5$ was used as the indicator.

The investigation method was analogous to that used in the study of the self-diffusion of niobium in a pure metal [3].

We should note that the diffusion characteristics of niobium established in these tests relate to volume, and not boundary,

processes. This was guaranteed by both the high test temperatures and the large-crystalline structure of the melts used.

The lattice parameters of the melts were calculated from powder patterns (VRS-3 camera with a cassette diameter of 143.4 mm, copper emission, filings annealed in a vacuum). The hardness and microhardness (at loads of 20 g) of the samples were studied by standard methods.

The self-diffusion of niobium in its alloys with molybdenum (5-45% Mo) was studied in the temperature region of 1600-2100°. The basic series of measurements were taken at 1700, 1800, 1900, 2000 and 2100°. The data obtained were used to calculate the self-diffusion parameters of niobium D_0, E, and also $D = D_0 \exp-(E/RT)$. The results of a graphical analysis of the experimental data are generalized in the table and on Figs. 1-3.

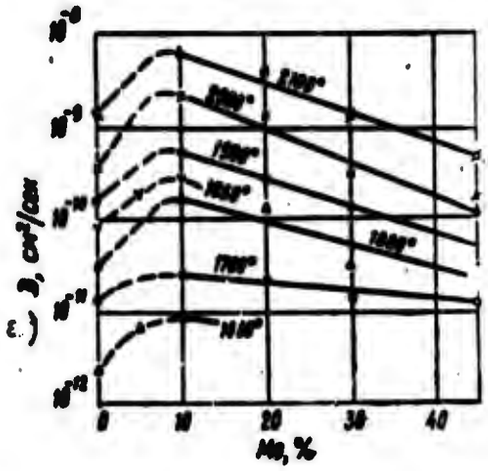

Fig. 1. Dependence of the self-diffusion coefficients of Nb upon temperature and the composition of its alloys with Mo.
KEY: a) D, cm^2/s.

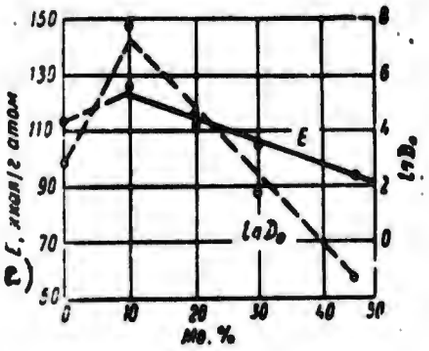

Fig. 2. Dependence of the self-diffusion parameters of Nb upon the composition of its alloys with Mo.
KEY: a) E, kcal/g·atom.

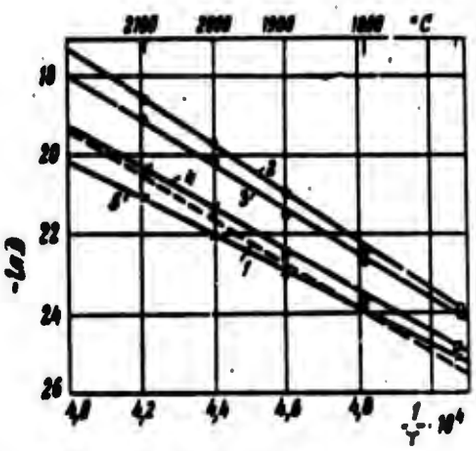

Fig. 3. The effect of temperature on the coefficient of self-diffusion of Nb in its alloys with Mo at a Mo content of: 0 (1), 10% (2), 20% (3), 30% (4) and 45% (5).

a) **Параметры самодиффузии ниобия в его сплавах с молибденом**

b) Содержание Mo, %	c) $a_{эксп}$, kX	d) $a_{аддит}$, kX	e) H_B, кг/мм	f) Микротвердость (P = 20 г), кг/мм	g) D_0, см²/сек	h) E, ккал/моль	i) D (см²/сек) при температурах						
							1600°	1700°	1800°	1850°	1900°	2000°	2100°
0,0*	3,293	3,293	—	—	28,18	113	$3,5 \cdot 10^{-12}$	$1,4 \cdot 10^{-11}$	$5,0 \cdot 10^{-11}$	$9 \cdot 10^{-11}$	$1,7 \cdot 10^{-10}$	$5,6 \cdot 10^{-10}$	$1,6 \cdot 10^{-9}$
5,0	—	—	180	25	—	—	$8,5 \cdot 10^{-12}$	—	—	$2,6 \cdot 10^{-10}$	—	$2,3 \cdot 10^{-9}$	—
10,0	3,267	3,278	200	26	26,92	126	$9,5 \cdot 10^{-12}$	$3,84 \cdot 10^{-11}$	$1,68 \cdot 10^{-10}$	$4,66 \cdot 10^{-10}$	$7,33 \cdot 10^{-10}$	$2,78 \cdot 10^{-9}$	$7,9 \cdot 10^{-9}$
20,0	3,255	3,258	230	32	60,26	112	—	$3,65 \cdot 10^{-11}$	$1,26 \cdot 10^{-10}$	—	$4,39 \cdot 10^{-10}$	$1,75 \cdot 10^{-9}$	$5,2 \cdot 10^{-9}$
30,0	3,232	3,246	305	38	5,26	105	—	$1,55 \cdot 10^{-11}$	$5,02 \cdot 10^{-11}$	—	$1,6 \cdot 10^{-10}$	$4,91 \cdot 10^{-10}$	$1,35 \cdot 10^{-9}$
45,0	3,205	3,220	330	45	0,27	94	—	$1,26 \cdot 10^{-11}$	$3,98 \cdot 10^{-11}$	—	$1,1 \cdot 10^{-10}$	$2,7 \cdot 10^{-10}$	$6,9 \cdot 10^{-10}$

j) * Согласно [3].

KEY: a) Self-diffusion parameters of Nb in its alloys with Mo; b) Mo content, %; c) α_{exp}, kX; d) α_{add}, kX; e) H_B, kg/mm; f) microhardness (P = 20 g), kg/mm; g) D_0, cm^2/s; h) E, kcal/mole; i) D(cm^2/s) at temperatures; j) *according to work [3].

The complex dependence of the self-diffusion coefficients on the composition of the melts draws attention to itself. Introducing the first portions of Mo leads to an increase in D, D_0 and E. However, this occurs only up to concentrations that do not exceed approximately 8% Mo, after which the self-diffusion parameters of Nb monotonically decrease as the Mo content increases. Also, the effect of Mo on D_0 increases noticeably with an increase in temperature.

This temperature effect is evidentally caused by the fact that D_0 and E vary in parallel as the percentage of Mo is changed (see the table). Since the role of the exponential factor decreases with an increase in temperature, and that of the pre-exponential factor increases, the dependence of D on the melt composition is amplified with an increase in temperature.

There is a simple connection between the self-diffusion parameters of Nb in its alloys with Mo (Fig. 4)

$$\ln D_0 = -26{,}9 + 0{,}276\,E, \qquad (1)$$

which also governs the previously established [3, 4, 5] characteristics for pure Nb (see Fig. 4) for both single-crystal and cermet samples.

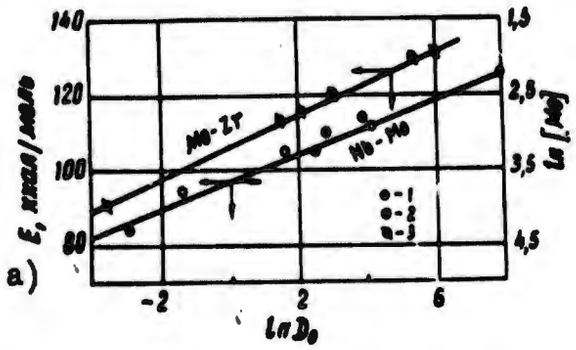

Fig. 4. Interdependence of the self-diffusion parameters of Nb in pure Nb (1) and its alloys with Mo (2), and also of Mo in its alloys with Zr (3).
KEY: a) E, kcal/mole.

Thus, in spite of significant differences in the degree of perfection of their crystalline lattice, the compensating effect, which has been noted many times in an analysis of very diverse processes with the participation of solid phases [4, 6-10], appears rather clearly. In particular, it appears very stably in numerous refractory compositions, e.g., in different Mo alloys. The validity of this is evident from an analysis of the results of thorough investigations [11] of the self-diffusion of Mo in its alloys with Zr subjected to stabilizing annealing and plastic deformation. It turned out that (see Fig. 4) there is a simple correlation between E and D_0 described by the linear dependence

$$\ln D_0 = -25{,}6 + 0{,}24\,E, \qquad (2)$$

that is very similar to (1) for Mo-Nb alloys. These and numerous other examples show that any disturbance of the crystalline grid of a solid caused either by a change in the concentration of point defects and dislocations or by local distortions of the elementary cells during the formation of solid solutions simultaneously affects both D_0 and E.

In their general form the causes of this have been observed many times and are based on the conclusions of the theory of absolute reaction rates and on an analysis of the characteristics of the vacancy mechanism of the diffusion process [8, 12]. In particular, in the latter case we proceed from the evident fact that an elementary act of diffusion preferentially occurs close to the most perturbed sections of the lattice. From this it follows [13] that

$$\ln D_0 = A + \frac{B'}{R T_m} E = A + BE, \qquad (3)$$

i.e., a dependence of the same type as (1) and (2). On the other hand, if we assume, as is frequently done, that $E = \alpha T_m$, then D_0 = const and

$$D = D_0 \exp\left(-\frac{\alpha T_m}{RT}\right). \qquad (4)$$

The validity of expression (4) was examined in a number of works of S. D. Gertsriken [14]. However, it contradicts the compensation effect examined above, which assumes a similarity of the slope of the change in D_0 and E. In connection with this, equation (4) should evidentally be considered a sufficiently flexible semiempirical relationship that successfully generalizes the experimental data in a number of cases. In particular, it clearly cannot be used to generalize all the experimental data given in the table, at least because the concentration dependences of D have a maximum at ≈8% Mo, whereas T_m in Nb-Mo alloys decrease monotonically up to ≈25% Mo, but increase with a further increase in the Mo content.

In connection with what was said about the stability of the interdependence of D_0 and E, the significant differences of the self-diffusion (and diffusion) parameters established by different authors should be explained not only by the perturbing effect of boundary processes (as is most frequently done), but also by the characteristics of the fine structure of the crystalline lattice, the degree of its perfection, and also the type and concentration of its defects. The role of the latter can be exceptionally great.

Turning to an examination of the dependences of the self-diffusion parameters of Nb upon composition, we must bear in mind that before diffusion annealing the samples were subjected to a prolonged high-temperature stabilizing heat treatment at temperatures greatly exceeding the temperature of their recrystallization [15]. Therefore, it is hardly appropriate to assume that the diffusion characteristics of the alloys were affected to any significant degree by the stresses and nonequilibrium distortions of the crystals. Here, the substantial dependence of D, D_0 and E upon Mo content is basically determined by the local disturbances of lattice periodicity and also the changes in the type and symmetry of the bonds that arose during replacement of Nb atoms by

Mo atoms. This was brought about by the differences in the atomic radius of the components (at k = 12, r_{Nb} = 2.94 kX, r_{Mo} = 2.80 kX, Δr = 5%) and the difference in their valence. The rather large negative deflections from the Vegard law are observed in the Nb-Mo system precisely for this reason (see the table, and also works [16, 17]).

The unique concentration dependence of E and D_0 is basically caused by the topography of the Mo atoms in the alloy lattice and the disturbances in the character and periodicity of the lattice field caused by them. Following I. B. Borovskiy and K. P. Gurov [18], we can assume that the diffusion characteristics of Nb-Mo alloys should have extrema at low Mo concentrations caused by the formation of a stable short-range order (of blocks) close to the atoms of the alloying element.

However, this effect can hardly be responsible for the change in the concentration coefficient D close to ≈8% Mo. Here, the following circumstances are evidently more significant. From crystallographic considerations it follows that when up to 6.25 at. % (≈6.5 wt. %) Mo is present in the alloy (and with its statistical distribution) not more than one Mo atom will be located close to each Nb atom. In these conditions as the percentage of Mo increases there will be a linear increase in the number of distortions of the elementary cells, an amplification of the interactions between particles and a complication of the elementary act of diffusion.

A further increase in the Mo concentration brings about a segregation of its atoms, which corresponds to the approach of the concentration coefficients of the parameters of the crystalline grid to its additive value. The arising microheterogeneous structure of the alloys with an increasing number of submicro-regions enriched with Mo atoms changes the concentration dependence of the parameters of self-diffusion. Primarily in these conditions the microregions enriched with Mo and characterized by short interparticle distances are barely effective for the migration of Nb atoms. Therefore, they are unique obstacles for the diffusion flow, causing a progressive decrease of D_0 as the Mo content increases. Conversely, the boundary zones with asymmetric fields become even more favorable than the matrices for the drift of Nb atoms: Diffusion along them is connected with decreased energy complications. Because of these circumstances as the Mo content increases there is a parallel decrease in D_0 and E. Also, the hardness of the alloys increases noticeably (see the table).

Naturally, the above schematic model is evidently valid for not very high Mo concentrations, i.e., in cases when the migration of Nb atoms through microregions enriched with Mo (in comparison with the flow along the boundaries and the matrix) can be disregarded. However, when we go to alloys in which migration through sections basically consisting of Mo atoms is the decisive factor, we can expect the increase of E and D_0. The validity of this is confirmed by the results of work [16], which studied the sintering

conditions of briquets of dispersed Mo and Nb particles. It was established that Mo added to Nb reduces the shrinkage during annealing more than Nb added to Mo. From this we can make the rather plausible conclusion that the coefficient of diffusion of Mo in Nb is greater than that of Nb in Mo. Evidently, this is mainly caused by the difference in the dimensions of the atoms ($r_{Nb} > r_{Mo}$) and in the lattice parameters ($\alpha_{Nb} > \alpha_{Mo}$).

In conclusion let us note that when the changes in the microdistribution of Mo in an alloy (10–45% Mo) are of one type, various semiemperical dependences connecting the diffusion coefficients with different parameters of the component and the system as a whole are fulfilled rather well. For example, since in the examined condition $E \approx 176 - 21.7[\%\ Mo]$, then $\ln D_0 = 21.7 - 6 \ln[\%\ Mo] = -26.9 + 0.276\ E$. Thus, knowing the composition of the alloy, it is easy to calculate E and D_0 analytically or graphically (see Fig. 4).

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