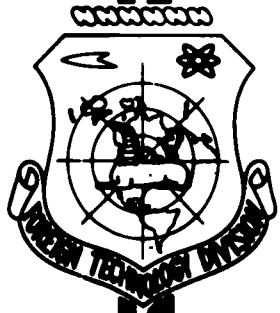
TRANSLATION

INVESTIGATING DIFFUSION MOBILITY OF ZIRCONIUM IN ZIRCONIUM-NIOBIUM ALLOYS

By

G. G. Ryabova and P. L. Grusin



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INVESTIGATING DIFFUSION MOBILITY OF ZIRCONIUM IN ZIRCONIUM-NIOBIUM ALLOYS

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G. G. Ryabova and P. L. Gruzin

Alloys of the zirconium-niobium system arouse greater scientific and practical interest. In recent years the properties of alloys of this system have been investigated by many researchers. Zirconium alloys were found with small additions of niobium, alloys with properties, satisfactory for application of these alloys in the construction of reactors [1, 2], as well as alloys with higher niobium content, characterized by excellent fire and heat resistance [2,3]

Zirconium and niobium - high melting metals. But zirconium, in spite of the high melting point, is distinguished by low heat reasistance. Niobium is characterized by good heat resistance qualities.

Investigation of diffusion characteristics in a system of alloys on the basis of these two metals is of interest for the purpose of explaining the diffusion mobility of atoms during change over from zirconium, having high diffusion mobility, to niobium, distinguished, judging by its heat resistance, by slow mobility of atoms.

To investigation diffusion of zirconium in zirconium-niobium alloys were melted alloys of the following niobium content (weight %): 1; 2; 3; 7; 20; 35; 70; 90 and 100. In role of basic material for the preparation of alloys was used iodide low-hafnium zirconium and niobium, containing the following admixtures (weight %): Ta-1; C-0.09; Cr-0.1; O-0.05; H - 0.003; N - 0.03.

The alloys were melted in an MIFI-9-3 type arc furnace with tungsten electrode and water cooled crucible in an atmosphere of purified argon. For additional purification of furnace chamber from gases prior to melting the alloys the getter was melted several times. Uniform distribution of elements in the alloys was attained by repeated refounding (8-15 times) without disturbing the hermeticity of the furnace.

Bars of casted alloys containing up to 20% of niobium were subjected to hot forging in open air at a temperature of 900-700°C and to grinding to remove the layer of scales, and then cut into samples with a dimension of 8X8X15 mm. At a more than 20% niobium content in the alloy the samples were prepared from casted alloys.

The obtained samples were subjected to homogenizing annealing at 1200°C for a period of 10 hrs and at 1400°C for a period of 24 hours (alloys containing less than 20% niobium. Annealings at 1200°C were carried out in a quartz tube, pumped out to a pressure of $1 \cdot 10^{-4}$ mm Hg, placing it in a tubular resistance furnace. Alloys with greater niobium content were annealed in a TVV-4 type furnace at a remanent pressure of $1 \cdot 10^{-4}$ mm Hg.

After homogenizing annealing on the samples was applied a layer of radioactive zirconium isotope Zr^{95} in a special vacuum installation. The thickness of the layer was tens of fractions of a micron. The thickness uniformity of the dusted on layer was checked by taking an autoradiogram from samples directly after the dusting on the radioactive isotope.

After the dusting on the samples, placed in pairs with the radioactive surface inward, we bound by a molybdemum wire and subjected to diffusion annealing in vacuum at corresponding temperatures. Together with the samples were wrapped in foil zirconium shavings, serveing as getter. In table 1 are given data on temperature and time of exposure of diffusion annealings of zirconium/niobium alloys.

Table 1. Data on temperature and duration of exposure of diffusion annealings of zirconium/niobium alloys

Alloy	Exposure time (hrs) at a temperature °C												
	900	1000	1100	1200	1300	1350	1400	1500	1600	1750	1900	2000	
Zr	24	11	7	4	-	-	-	-	-	-	-	-	-
Zr + 1% Nb	24	11	7	4	-	-	-	-	-	-	-	-	-
Zr + 2% Nb	24	11	7	4	-	-	-	-	-	-	-	-	-
Zr + 7.3% Nb	24	11	7	4	-	-	-	-	-	-	-	-	-
Zr + 20% Nb	24	15	8	6	-	-	-	-	-	-	-	-	-
Zr + 35% Nb	-	15	8	8	-	-	8	-	-	-	-	-	-
Zr + 50% Nb	-	-	-	8	4	3,5	8	-	2	-	-	-	-
Zr + 70% Nb	-	-	-	6	4	3,5	8	-	2	-	-	-	-
Zr + 90% Nb	-	-	-	-	-	-	-	5	-	6	1	2	
Nb	-	-	-	-	-	-	-	-	-	6	1	2	

After the annealings the diffusion coefficients were determined by the method of removing a layer and measuring the integral radioactivity of the remains of the sample, introduced by P.L.Gruzin [4].

In tables 2-4 are given experimentally found zirconium diffusion coefficients for the investigated alloys. On the basis of temperature dependence of diffusion coefficients were obtained activation energy values for zirconium diffusion and preexponential multiplier values corresponding to them (Table 2-4).

Table 2. Zirconium diffusion parameters for zirconium/niobium alloys

Alloy	Diffusion coefficient ($cm^2 \cdot sec^{-1}$) at temperature, °C						
	900	1000	1100	1200	1450	D_0, $cm^2 \cdot sec^{-1}$	Q, kcal/g atom
Zr	$5 \cdot 10^{-10}$	$9,5 \cdot 10^{-10}$	$3 \cdot 10^{-9}$	$5,6 \cdot 10^{-9}$	—	$1,7 \cdot 10^{-4}$	30,5
Zr + 1% Nb	$4,5 \cdot 10^{-10}$	$6,5 \cdot 10^{-10}$	$2,1 \cdot 10^{-9}$	$3,8 \cdot 10^{-9}$	—	$1,1 \cdot 10^{-4}$	30,0
Zr + 2% Nb	$4,5 \cdot 10^{-10}$	$7 \cdot 10^{-10}$	$1,7 \cdot 10^{-9}$	$4,3 \cdot 10^{-9}$	—	$4,7 \cdot 10^{-5}$	28,0
Zr + 7,5% Nb	$1,5 \cdot 10^{-10}$	$5,6 \cdot 10^{-10}$	$1,1 \cdot 10^{-9}$	$2,6 \cdot 10^{-9}$	—	$4,3 \cdot 10^{-6}$	35,5
Zr + 20% Nb	$3,8 \cdot 10^{-10}$	$1,4 \cdot 10^{-10}$	$2,8 \cdot 10^{-10}$	$10 \cdot 10^{-9}$	—	$7 \cdot 10^{-3}$	42,5
Zr + 35% Nb	—	$0,56 \cdot 10^{-11}$	$1,4 \cdot 10^{-10}$	$5,3 \cdot 10^{-10}$	$8 \cdot 10^{-9}$	$9 \cdot 10^{-3}$	48,5

Table 3. Zirconium diffusion parameters for zirconium/niobium alloys

Alloy	Diffusion coefficients ($cm^2 \cdot sec^{-1}$) at temperature °C						
	1200	1300	1370	1450	1540	D_0, $cm^2 \cdot sec^{-1}$	Q, kcal/g atom
Zr + 50% Nb	$1,9 \cdot 10^{-10}$	$1,5 \cdot 10^{-10}$	$1,0 \cdot 10^{-9}$	$2,1 \cdot 10^{-9}$	$4,7 \cdot 10^{-9}$	$5,9 \cdot 10^{-3}$	52
Zr + 70% Nb	$1,5 \cdot 10^{-11}$	$1,2 \cdot 10^{-10}$	$3,1 \cdot 10^{-10}$	$3,8 \cdot 10^{-10}$	$1 \cdot 10^{-9}$	$2,7 \cdot 10^{-3}$	55

Table 4. Zirconium diffusion parameters in zirconium/niobium alloys

Alloy	Diffusion coefficients ($cm^2 \cdot sec^{-1}$) at temperature °C						
	1500	1600	1730	1900	2000	D_0, $cm^2 \cdot sec^{-1}$	Q, kcal/g atom
Zr + 90% Nb	$3 \cdot 10^{-10}$	—	$2,5 \cdot 10^{-10}$	$8,5 \cdot 10^{-10}$	$1,95 \cdot 10^{-9}$	$1,2 \cdot 10^{-2}$	72
Nb	—	$6,1 \cdot 10^{-12}$	$2 \cdot 10^{-11}$	$1,5 \cdot 10^{-10}$	$2,6 \cdot 10^{-10}$	0,1	90

In fig.1 are given concentrational dependences of zirconium diffusion coefficients in alloys for temperatures of 1000, 1200 and 1600°C. It is evident from the graphs that the diffusion mobility of zirconium alloys changes in dependence upon the niobium concentration in the alloys. Diffusion mobility of zirconium atoms decreases

gradually with a rise in niobium up to 50%, and then follows a sharp drop in the diffusion coefficient magnitude. And so the coefficients of zirconium diffusion at 1200°C decrease by approximately one and one half orders in alloys from pure zirconium to an alloy with 50% zirconium and 50% niobium and by four powers in alloys with an up to 50% niobium content to pure niobium.

The structural diagram of zirconium/niobium alloys has a minimum along the solidus curve in the field of compositions of approximatly 20 to 30% niobium[3]. But on the curve of the concentrational coefficients of diffusion on the side of zirconium a reduction inmelting point of the alloys is not accompanied by a rise in diffusion mobility of zirconium atoms. On the side of niobium with a reduction in the melting point of the alloys the diffusion mobility of zirconium atoms increases.

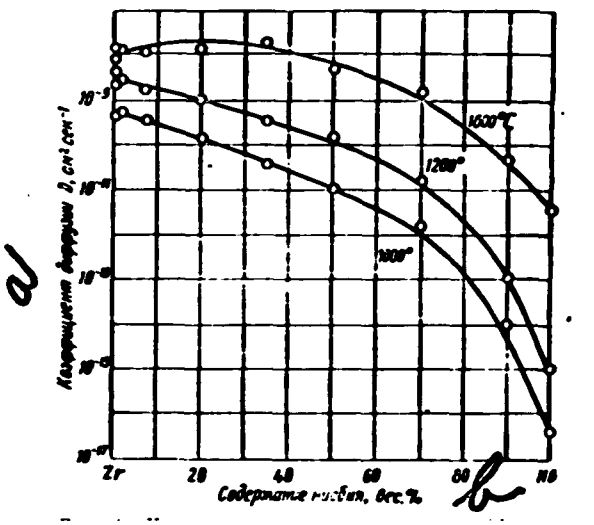

Fig.1.Concentrational dependence of diffusion coefficients of zirconium in zirconium/niobium alloys; a-diffusion coefficient; b-niobium content...

We have obtained results on the diffusion of niobium in zirconium. In connection with the absence of metallic artificial radioactive niobium isotope, Nb^{95}, we used in our experiments a niobium isotope in form of niobium oxalate Nb^{95}. After this solution has been chemically processed on the samples was applied a layer of niobium oxide, containing Nb^{95}. Consequently simultaneously with the diffusion of niobium

in zirconium, apparently, took place diffusion of oxygen, which might have exerted a certain influence on the diffusion of niobium in zirconium. Obtained data are listed in table 5. The coefficients of diffusion of niobium in zirconium are close in magnitude to the coefficients of autodiffusion of zirconium.

Table 5. Parameters of niobium diffusion in zirconium

Alloy	Diffusion coefficients (cm^2/sec) at temperatures, °C			D_0, cm^2/sec	Q, kcal/g-atom
	1000	1100	1200		
Zr	$6.23 \cdot 10^{-11}$	$1.47 \cdot 10^{-9}$	$3.9 \cdot 10^{-9}$	$2.2 \cdot 10^{-4}$	33

By comparing the coefficients of diffusion of zirconium in niobium and niobium in zirconium is evident, that, for example, for a temperature of 1200°C the diffusion coefficients differ by more than 6 magnitudes.

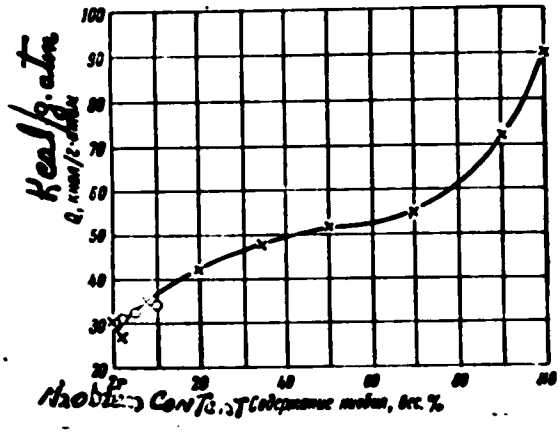

Fig.2. Concentrational dependence of activation energy of zirconium diffusion in zirconium/niobium alloys: x-results of given experiment; ● - results of experiments by [6]

Calculation of zirconium diffusion coefficients for alloys showed, that at melting points all alloys have a diffusion coefficient of the magnitude of 10^{-8} cm^2 sec^{-1}. The melting point of alloys was taken on the basis of the structural diagram of the zirconium/niobium system [5].

The concentrational dependence of activation energy for zirconium diffusion is shown in fig.2. The activation energy of zirconium diffusion rises with the increase in niobium content in the alloys. A rise in diffusion activation energy with simultaneous reduction of diffusion mobility in alloys indicates a strengthening of the interatomic bond in the crystalline lattice of zirconium. This is also confirmed by data about the change in elasticity modulus of the alloys in the zirconium/niobium system, obtained by [5].

In the experiment [6] was examined the diffusion mobility of zirconium in zirconium alloys with a niobium content of 2; 5; 10 percentages by weight. The activation energy values of zirconium diffusion in these alloys are plotted on graph fig.2. and are in conformity with values, obtained in the given experiment.

The magnitude of activation energy of zirconium self-diffusion, obtained in the given experiment, equals 30.5 cal/g.atm. In other experiments [4,7,8] are given activation energy values for self diffusion of zirconium, differing from the previous one. The discrepancy in activation energy values for self-diffusion of zirconium is connected, apparently, with the influence of the structural factor on diffusion mobility of zirconium. As result of alpha → beta-conversion of zirconium when heated in beta-phase crystals is retained a greater amount of intragranular separation surfaces, facilitating the occurrence of diffusion processes. We [8] as well as [7] showed that the elimination of the effect of intragranular separation surfaces leads to a rise in activation energy for self-diffusion of zirconium to 38 [7] and 47 kcal/g.atm [8].

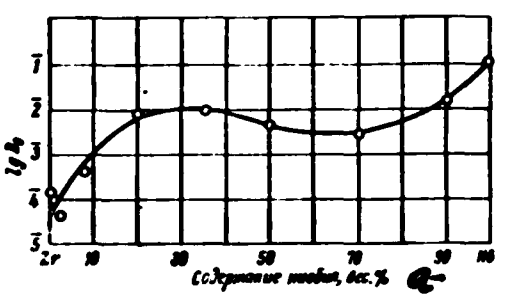

Fig.3. Concentrational dependence lgD_0 for diffusion of zirconium in zirconium/niobium alloys. α - Niobium content.

In fig.3. is shown the concentrational dependence lgD_0, calculated in accordance with experimental data. For diffusion of zirconium in niobium the value $D_0=0.1$ cm^2/sec appears to be conventional for metals. For the diffusion of niobium in zirconium this value equals $2.2 \cdot 10^{-4}$ cm^{2}sec^{-1} as well as for self-diffusion of zirconium ($D_0=10^{-4}$ cm^{2}sec^{-1}), very small. It is evident from fig.3. that with the rise in niobium content in alloys the preexponential multiplier D_0 increases.

The obtained experimental data on the measurement of the diffusion coefficient of zirconium in zirconium-niobium alloys, activation energy of diffusion and preexponential multiplier showed, that all these values depend upon the concentration of elements in the alloys. With a rise in niobium content in zirconium alloys is obser-

ved an increase in activation energy value for the diffusion of zirconium Q and D_o. Simultaneously with these is observed a reduction in diffusion mobility of zirconium atoms.

In this way, in the zone of existence of continuous solid solutions in the zirconium-niobium system is observed a smooth change of all diffusion parameters of zirconium with a rise in niobium content.

Niobium alloying of zirconium hampers the occurrence of diffusion processes in zirconium, strengthens the force of the bond between atoms in the crystalline lattice. With this, apparently, is connected the rise in heat resistance of zirconium in alloys with niobium.

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