

# STUDY OF MUTUAL DIFFUSION IN THE Nb-Zr SYSTEM BY LOCAL X-RAY ANALYSIS

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Mutual diffusion in the Nb-Zr system was studied with a Kameka MS-46 microanalyzer. The  $D_{\mu}$  values were determined as a function of the Nb concentration, and the activation energies for mutual diffusion were calculated.

Several studies have been reported of the state diagram for the Nb-Zr system and of the diffusion characteristics in alloys based on these metals [1-8]. Niobium and zirconium have the same (BCC) crystal lattice, and their atomic dimensions are such that a continuous series of solid solutions is formed with a minimum on the solidus curve which reaches 1740°C at 20 at. % Nb.

Two types states of state diagrams have been described for Nb-Zr system in the literature. Berghaut [8] proposed a state diagram not involving the decomposition of a solid solution for a monotectoid transition.

For the other type of state diagram, involving this decomposition and this transition, there is a difference of opinion regarding the temperature of the monotectoid transition (560-610-800°C), regarding the temperature at which the solid  $\beta$  solution begins to decompose into two solid solutions [ $\beta_{Zr} + \beta_{Nb}$ ] (980-1180°C), and regarding the limiting solubility of  $\alpha$  zirconium and niobium.

We report here a study of mutual diffusion through the use of local x-ray chemical analysis. After their surfaces were carefully cleaned, niobium and zirconium samples were welded under pressure in a special evacuated oven. A good contact was achieved between the metals without any appreciable zone. A diffusion annealing was carried out at 1600°C (45 hr), 1000°C (123, 390 and 483 hr), 900°C (360 hr) or 800°C (500 hr) at a pressure of  $10^{-4}$  torr at temperatures held constant within  $\pm 10^\circ\text{C}$ .

We analyzed the distribution of elements in the diffusion zone with a Kameka MS-46 microanalyzer on the basis of the Nb and Zr  $L_{\alpha}$ -lines with a tube voltage of 15 kV. The uncertainty in the probe position on the surface was a symbol for of the order of  $\sim 1$ . Figure 1 shows the corresponding concentration curves. Some 10-12 curves were recorded at various parts of the diffusion zone for each sample. Curve 1 (Fig. 1) corresponds to a continuous solid solution; its shape shows qualitatively that metals having a relatively low melting point display a relatively high diffusive mobility at a given temperature [5]. Concentration curves numbers 2 and 3 display concentration jumps corresponding to the 2-phase [ $\beta_{Zr} + \beta_{Nb}$ ] region.

Analysis of these curves shows that a  $\beta$  solid solution and a solution based on niobium grow in a layer at these temperatures. Two concentration jumps are clearly evident on the curve corresponding to 800°C. The first jump corresponds to the 2-phase  $\alpha + \beta$  region, while the second to [ $\beta_{Zr} + \beta_{Nb}$ ].

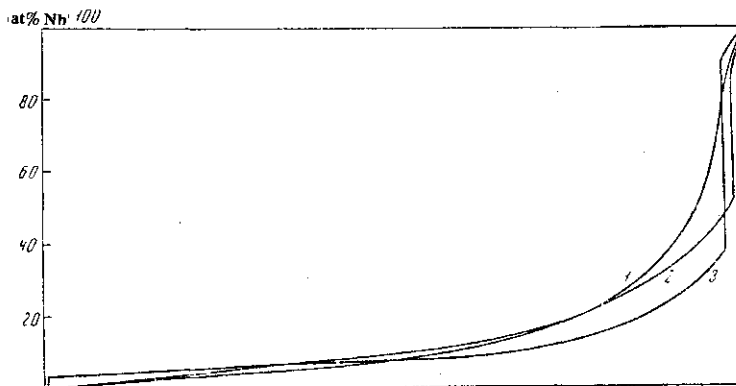


Fig. 1. Concentration curves  $c(x)$  in the Nb-Zr system. 1) Diffusion layer 1942  $\mu$  thick,  $T_{\text{ann}} = 1600^\circ$ ,  $t_{\text{ann}} = 400$  each; 2) 788  $\mu$ , 1000°, 483 hr; 3) 323  $\mu$ , 800°, 500 hr.

The data obtained in our analysis of the layers are shown on the state diagram in Fig. 2, along with the state diagrams constructed from the data of [3, 4, 8]. To illustrate the results most clearly, we calculated the mutual-diffusion coefficients for temperature of 900, 1000 and 1600°C. The Matano method [2]

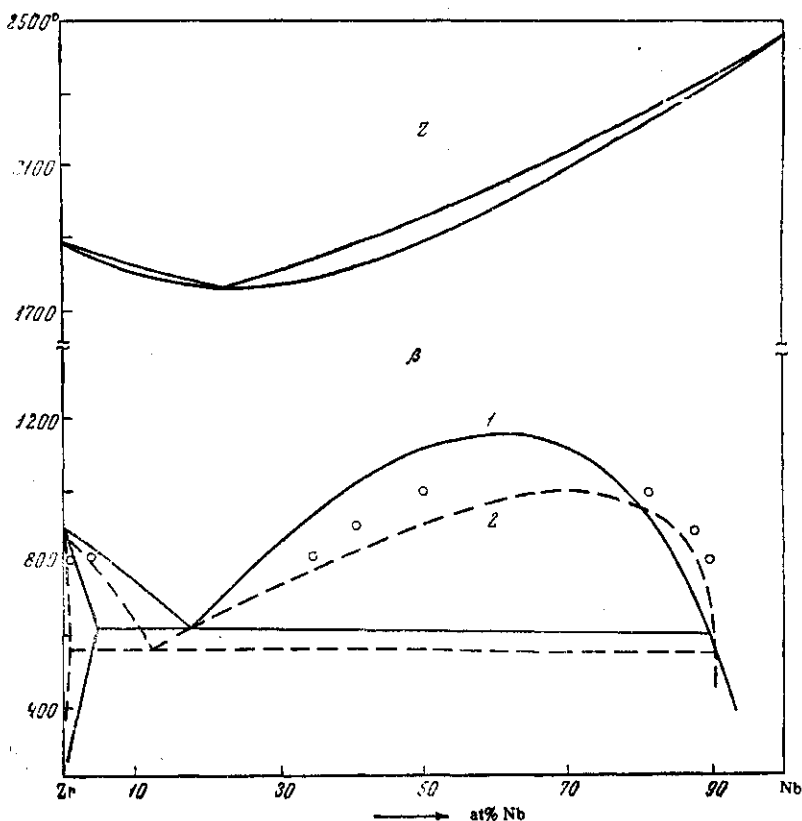


Fig. 2. State diagram for the Nb-Zr system. Solid curves) data of [4]; Dashed curves) data of [3]; Circles) this study.

can be extended to multiphase systems, as was first shown in [10]; this procedure has been used for Cu-Zn and V-Zr systems [11, 12]. In this case we have [13]

$$D_{23} = -\frac{1}{2t} \frac{dx}{dc} \int_0^c xdc. \quad (1)$$

The derivative  $dx/dc$  and the integral  $\int_0^c xdc$  can be found graphically. Use of the Matano method requires that the  $c = f(x)$  concentration curve be determined as accurately as possible. X-ray microanalysis is the most accurate method of those available, yielding compositions within 2-5%.

In addition,  $D_{mu}$  is a function of time and of the annealing temperature  $T$ . The total relative error in  $D_{mu}$  can be evaluated from

$$\eta_D = \eta_t + \eta_T + \eta_c. \quad (2)$$

In our case  $\eta_t$  is negligible. The relative error  $D_{mu}$  due to the temperature is found from  $\eta_T = \frac{Q}{R} \frac{\Delta T}{T^2}$  and amounts to about 7-9%. Determination of the derivative and calculation of the integrals also involves an error,  $\eta_M = 10-15\%$ . The total error in  $D_{mu}$  is thus

$$\eta_D = \eta_T + \eta_c + \eta_M. \quad (2')$$

Some 10-12 concentration curves were constructed by this procedure for each diffusion layer, and then the results were averaged. The over-all error in  $D_{mu}$  is no worse than 20-25%.

Fig. 3 shows the mutual-diffusion coefficient calculated as a function of the concentration for annealing temperatures of 900, 1000 and 1600°C. Comparing these results for  $D_{mu}$  at 1600 and 1000°C with those obtained in [6] by stripping layers and measuring the integral radioactivity of the remaining sample, we see that the  $D_{mu}$  are of the same order of magnitude, but have slightly different dependences on the niobium concentration. The dependence of  $D_{mu}$  on the Nb concentration reported in [6] is less steep in the Zr-ridge region and steeper in the Nb-ridge region. Our data (Fig. 3) show that  $D_{mu}$  decreases toward pure

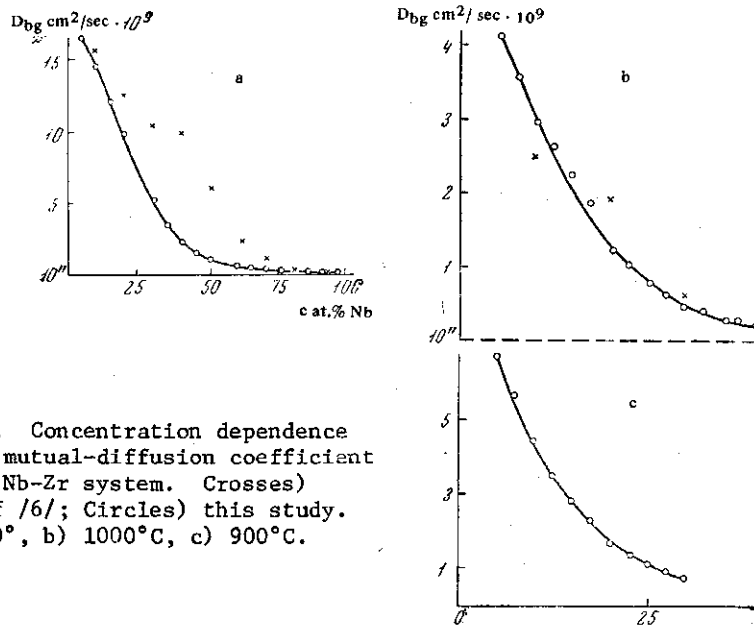


Fig. 3. Concentration dependence of the mutual-diffusion coefficient in the Nb-Zr system. Crosses) data of [6]; Circles) this study. a) 1600°, b) 1000°C, c) 900°C.

Nb, in agreement with the conclusions reached in [7]. Moreover, the  $D_{\mu}$  curve does not reveal an increased diffusive mobility corresponding to the minimum on the solidus curve near 20 at.% Nb.

Figure 3 shows that  $D_{\mu}$  depends strongly on concentration and is much larger in the Zr-ridge than in the Nb-ridge region; this result explains the shape of the curve in Fig. 1. The activation energy was calculated from the diffusion coefficients for 900 and 100°C: it increases from about 52 to about 59 kcal/mole as the Nb concentration is increased to 5 to 30 at.%. At 95 at.% Nb the activation energy is 79.5 kcal/mole. The activation energies we found for the Zr-ridge region agree with those obtained in [7]. The value 79.5 kcal/mole, on the other hand, agrees better with that reported in [6].

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