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Temperature dependence of vacancy wind effect in β–Zr(Al) solid solution

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In a classical experiment, Smigelskas and Kirkendall [1] demonstrated the movement of the lattice induced by the difference in the diffusion rate between two metals diffusing in the opposite direction. Later this phenomenon came to be known as the famous *Kirkendall effect*. The difference in the rate of diffusion in the presence of a chemical concentration gradient is believed to be due to the difference in the intrinsic diffusivity between the two components of a binary system. The difference in the rate of diffusion between the two interdiffusing species leads to a net flow of matter during diffusion. If vacancy exchange mechanism is the dominant mechanism prevailing, the net flow of matter is compensated by a flow of vacancies in the opposite direction. This sets in a *vacancy wind* due to the random motion and the directional flow of the vacancies, which causes an enhancement in the diffusion rate of the faster diffusion species and retardation in the diffusion rate of the slower diffusion species. This *vacancy wind effect* was first considered for the analysis of interdiffusion by Manning [2]. He showed that a better estimation of the intrinsic diffusion coefficients and the interdiffusion coefficients can be made by making suitable corrections for the vacancy wind effect. Efforts to estimate the vacancy wind effect experimentally are reported for binary as well as ternary systems. Carlson [3] had determined the vacancy wind factors in the V–Ti solid solution system. Sohn and Dayananda [4] determined the vacancy wind parameters in the β (B2) and β' (bcc) phases of the Fe–Al system. Determination of these factors in ternary systems such as Ag-Zn-Cd were reported by Carlson *et al.* [5]. Recently, Belova and Murch evaluated, using computer simulations, the vacancy wind factors in intermetallic compounds with DO_3 and A15 structures [6].

The Zr–Al system has gained importance recently as Zr_3Al based alloys are being considered as potential structural materials for thermal nuclear reactors. A recent work reported the marker movement indicating the difference in diffusion rate between Zr and Al in the β-Zr(Al) solid solution system [7]. The present investigation is focussed upon the evaluation of the vacancy wind effect in the β-Zr(Al) phase. The nature of temperature dependence of the vacancy wind factors is also discussed.

Darken, in a landmark paper [8] deduced equations that interrelate intrinsic, interdiffusion and tracer diffusivities. For a simple binary system involving diffusion species A and B, these relations are

$$D_A = D_A^* \Phi; \quad D_B = D_B^* \Phi \tag{1}$$

$$\tilde{D} = (D_A^* N_B + D_B^* N_A)\, \Phi \tag{2}$$

where D_A, D_A^* and D_B, D_B^* are the intrinsic and tracer diffusion coefficients respectively and $\tilde{D}$ is the interdiffusion coefficients respectively, N_A and N_B are the mole fractions of A and B; Φ is the thermodynamic factor, expressed by the relation

$$\Phi = \frac{\partial \ln a_A}{\partial \ln N_A} \tag{3}$$

where a_A and N_A are the thermodynamic activity and mole fraction of component A respectively. The above two relations were deduced by some simplifying assumptions to the phenomenological equations for diffusion. Manning [9] pointed out that the presence of vacancy wind in a direction opposite to that of the faster moving species results in a perturbation in the intrinsic diffusion flow of the either species. On the basis of a random alloy model, Manning [2, 9] modified Equation 1 by introducing an additional term which accounts for the vacancy wind effect. The modified equations are:

$$D_A = D_A^* \Phi r_A; \quad D_B = D_B^* \Phi r_B \tag{4}$$

where r_A and r_B are the vacancy wind factors. If $D_A > D_B$ then r_A and r_B are expressed as [2, 10]

$$r_A = 1 + \frac{(1 - f_0) N_A (D_A^* - D_B^*)}{f_0 (N_A D_A^* - N_B D_B^*)} \tag{5a}$$

$$r_B = 1 - \frac{(1 - f_0) N_B (D_A^* - D_B^*)}{f_0 (N_A D_A^* - N_B D_B^*)} \tag{5b}$$

where f_0 is the geometrical tracer correlation factor for self diffusion in a pure crystal of the structure under consideration. The limits for the values of r_A and r_B are

$$1 \le r_A \le \frac{1}{f_0}; \quad 0 \le r_B \le 1 \tag{6}$$

Equation 2 was also modified to include corrections for the vacancy wind effect [2]:

$$\tilde{D} = (D^*_{\mathrm{A}} N_{\mathrm{B}} + D^*_{\mathrm{B}} N_{\mathrm{A}})\, \Phi\, S \tag{7}$$

where

$$S = 1 + \frac{(1 - f_0) N_{\mathrm{A}} N_{\mathrm{B}} (D^*_{\mathrm{A}} - D^*_{\mathrm{B}})^2}{f_0 (N_{\mathrm{A}} D^*_{\mathrm{A}} - N_{\mathrm{B}} D^*_{\mathrm{B}})(N_{\mathrm{A}} D^*_{\mathrm{B}} - N_{\mathrm{B}} D^*_{\mathrm{A}})} \tag{8}$$

The vacancy wind parameter S is always greater than unity, hence interdiffusion coefficient values predicted by Manning's formalism are always greater than those predicted by Darken's model, where S is assumed to be 1.

The Manning expressions, Equations 5 and 8, have been extensively used for the last three decades to determine the vacancy wind factors. The accuracy of these relations appear to be very good as indicated by number of computer simulation studies of tracer and vacancy correlation factors [11]. Therefore, these equations were used in the present analysis.

Single phase diffusion couples of pure Zr and Zr-2.8wt% Al alloy were prepared using inert markers of tungsten between them. The couples were annealed isothermally at various temperatures between 1203 and 1323 K for 72 hr each under inert atmosphere. The concentration profiles established across the interface in each couple due to the diffusion annealing were determined using a CAMECA SX100 electron microprobe. The details of the experimental procedure is discussed elsewhere [7].

The intrinsic diffusion coefficients, D_{Al} and D_{Zr}, of Al and Zr respectively were calculated from the interdiffusion coefficient at the marker location and the velocity of the markers using Darken's equations [8]. The tungsten markers were found to be located at almost the same composition, i.e. 2 at.% Al in all the diffusion couples after annealing. The tracer diffusion coefficients, D^*_{Al} and D^*_{Zr}, of Al and Zr respectively were evaluated from the intrinsic diffusion coefficients of Al and Zr using the Darken–Dehlinger relation [12]. The values of D^*_{Al} and D^*_{Zr} were reported in Ref. [7] and are tabulated in Table I.

The values of the vacancy wind factors r_{Al}, r_{Zr} and S in the β–Zr(Al) solid solution were evaluated from the tracer diffusion coefficients, D^*_{Al} and D^*_{Zr} at various temperatures using Equations 5 and 8. Here β–Zr(Al) has a bcc lattice hence f_0 is taken as 0.727. The values of r_{Al}, r_{Zr} and S are presented in Table II. The direction of migration of the markers showed that the intrinsic diffusion coefficient of Zr is greater than that of Al in β–Zr(Al) phase [7]. The values of r_{Al} are less than unity and range from 0.9961 to 0.9982. This indicates that the intrinsic diffusion coefficient of Al is reduced by the presence of the vacancy wind in the diffusion zone; whereas for Zr, it is just the reverse. The values of the vacancy wind factor ranges from 1.0884 to 1.1922 and therefore, Zr being faster diffusing species, its diffusion rate is enhanced in the presence of vacancy wind. The values of r_{Zr} and r_{Al} follow the limits in Equation 6.

TABLE I The values of the tracer diffusion coefficients D^*_{Al} and D^*_{Zr} at various temperature [7]

Temperature (K)	$D^*_{\mathrm{Al}} \times 10^{15}$ ($\mathrm{m^2/s}$)	$D^*_{\mathrm{Zr}} \times 10^{15}$ ($\mathrm{m^2/s}$)
1203	1.4	2.9
1233	2.01	3.99
1263	3.51	5.81
1293	6.56	9.34
1323	9.64	12.67

TABLE II The values of the vacancy wind factors r_{Al}, r_{Zr} and S at various temperatures evaluated by Equations 5a and 8

Temperature (K)	r_{Al}	r_{Zr}	S
1203	0.9961	1.1922	1.0040
1233	0.9962	1.1843	1.0036
1263	0.9970	1.1467	1.0019
1293	0.9978	1.1101	1.0009
1323	0.9982	1.0884	1.0006

Both the factor r_{Zr} and r_{Al} were plotted against temperature as shown in Fig. 1. It was found that both of them show linear variation with temperature. The values of r_{Al} increases with increase in temperature though very marginally. Whereas the values of r_{Zr} shows a decreasing trend with increase in temperature but the variation is large in the present temperature range. Both the factors tend to approach unity at high temperatures. Straight lines were fitted to the data points using the least square technique. The temperature dependence of the factors can be represented by

$$r_{\mathrm{Zr}} = 2.3310 - 9.3958 \times 10^{-4} T \tag{9a}$$

$$r_{\mathrm{Al}} = 0.9728 + 1.9175 \times 10^{-5} T \tag{9b}$$

The values of the vacancy wind factor, S, which accounts for the change in the interdiffusion coefficient ranges from 1.004 to 1.0006 in the present temperature range. On plotting these data points against temperature, also shows a linear variation (Fig. 2). The temperature dependence of the values of S is given by the equation of the straight line fitted by least square

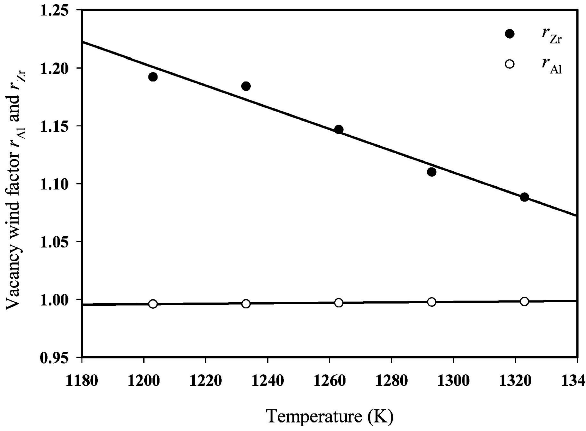

Figure 1 Temperature dependence of the vacancy wind factors r_{Zr} and r_{Al}.

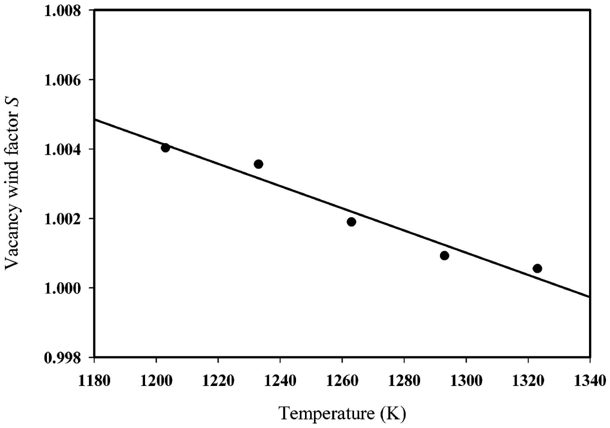

Figure 2 Temperature dependence of the vacancy wind factor S.

method

$$S = 1.0426 - 3.1987 \times 10^{-5} T \qquad (10)$$

The decrease in S with increase in temperature suggests that the vacancy wind effect becomes feeble at higher temperatures. The vacancy flux in a system can be accounted for by two contributions (a) random motion of vacancies and (b) directional flow of vacancies. It is the later contribution, which is manifested in the form of vacancy wind effect in the diffusion zone. Therefore, the vacancy wind factor S serves as an indirect measure of the contribution from the directional flow of vacancies. As the temperature increases, the contribution from the random motion of vacancies increases and hence the contribution from the directional motion decreases. This results in decrease in the value of S. Whereas the values of r_{Al} and r_{Zr} serve as a measure of the effect of the presence of the vacancy wind on the intrinsic diffusion of the individual elements, the values of the factor S quantifies its effect on the overall rate of interdiffusion.

In a recent work, the present authors have examined the temperature dependence of the correlation factors of Zr and Al (f_{Zr} and f_{Al}) in the β–Zr(Al) phase [13]. It was shown that the values of $f_{\text{Zr}} < f_{\text{Al}}$ throughout the temperature range. But f_{Al} and f_{Zr} approaches the value of the correlation factor for diffusion in bcc lattice, i.e. 0.727, with increase in temperature. This indicates that the alloy tends to behave as nearly random alloy at high temperature. It is worth noting here that the relative difference in the tracer diffusion coefficients between Zr and Al decreases as the temperature increases (see Table I). This hints upon the diminishing effect of the presence of vacancy wind as the temperature increases, which is supported by the findings that the value of S decreases with increase in temperature. The values of r_{Al} and r_{Zr} also tends to unity as the temperature increases. Therefore, the results of the present study seems consistent with the conclusions made from examination of the behavior of the correlation factors.

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