Impurity Diffusion of Al in β-Zr

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Abstract

The impurity diffusion of Al in β-Zr has been investigated in the temperature range of 1203K to 1323K. The interdiffusion coefficients have been determined by Hall's analytical method. The interdiffusion coefficients bear a linear relation with Al concentration of the type $\tilde{D}$=a+b C_{Al} in the range $0 \leq C_{Al} \leq 2$at%. The impurity diffusion coefficients have been established by extrapolation of interdiffusion coefficients to limiting concentration of $C_{Al} \rightarrow 0$.The impurity diffusion coefficients show an Arrhenius type of temperature dependence and can be described by: $D_{Al\ (c_{Al}=0)}^{\beta Zr} = 5.567_{-1.80}^{+2.65}$ X10^{-6}exp[(-220.08±3.33)kJmol^{-1}/RT] m^2/s. The difference between the activation energies of impurity diffusivity of Al and self-diffusivity of Zr in β-Zr is 104.3kJmol^{-1}. This positive difference in the activation energies indicates very low impurity-vacancy binding energy. The interrelation between the activation energy Q and the pre-exponential factor D_0 of impurity diffusivity is discussed in perspective of Swalin's and Beke's theories. The values of the impurity diffusion parameters are in conformation with these theories. A co-relation between the impurity diffusion coefficients $D_{imp}^{\beta Zr}$ of various elements in β-Zr and their atomic radii (r) has been established and can be presented by the relation: $\log D_{imp}^{\beta Zr}(m^2 s^{-1}) = -14.57 \pm 1.22 + \exp[(4.84 \pm 2.83) - (30.22 \pm 2.66) r(nm)]$. The impurity diffusion coefficient value of Al in is in conformation to this relation.

Keywords: Diffusion, impurity diffusion coefficient, interdiffusion, activation energy, atomic radius.

1.Introduction

Alloys based on Zr_3Al intermetallics are considered as potential structural materials for thermal nuclear reactors due to their low thermal neutron absorption cross-section, high melting point and high strength[1,2]. But only limited diffusion data[3] on the Zr-Al system is available in the literature and these were determined using multi phase diffusion couples. No data for tracer diffusivity of aluminium (D_{Al}^{*}) in β–Zr exist in the literature. This is mainly due to non-availability of suitable radioactive isotope of Al that can be used as tracer. The only isotope suited for such experiments is ^{26}Al, which has low activity. In the present study the impurity diffusion coefficient of Al in β-Zr is determined by extrapolation of interdiffusion coefficients to infinite dilution.

2.Experimental Procedure

Dilute alloy of Al in Zr with nominal composition Zr-2.8wt%Al was prepared by arc melting proportionate mixture of pure (99.9%) Zr and pure (99.95%) Al under high purity argon atmosphere. Samples of size 10 X 8 X 3 mm^3 were cut from the rolled alloy and pure Zr and annealed in He atmosphere at 1250K for 72 hrs to form stable coarse grained structure, which reduces the contribution of grain boundary diffusion in the diffusion annealing stage. The surfaces of the samples were metallographically polished to 0.25μm finish. The diffusion couples were made of pure Zr and Zr-2.8wt%Al pieces under 5 MPa pressure and 10^{-5} mbar vacuum for 1 hour, at a temperature at which it will subsequently be diffusion annealed. The couples were sealed in quartz capsules in He atmosphere and diffusion annealed in a furnace in the temperature range 1203K to 1323K for 72 hours, the temperature being controlled within ± 1K, and were quenched in water. The annealed couples were sectioned perpendicular to the bond interface. The polished sections of the diffusion couples were analysed by CAMECA SX100 Electron Probe Micro-Analyser (EPMA) at an operating voltage and beam current of 20kV and 20nA respectively. Quantitative analysis on point-to-point basis was done at a regular interval of 1-2μm across the bond interface to determine the concentration profile. For each sample, at least three scans were taken at different locations to confirm the consistency of the concentration profiles.

3. Analytical Procedure

The most widely used method to determine the concentration dependent interdiffusion coefficient is Boltzmann-Matano method[4,5]. But as the method incorporates a lot of error in calculation of the slope at the extreme ends of the concentration profile, where we are presently interested in. Hall's analytical method [6,7] has been used instead to evaluate the interdiffusion coefficients.

In this method, a variable λ is defined in such a way that,

$$\frac{C^*}{C_0} = \frac{1}{2}(1 + erf(\lambda)) \tag{1}$$

where C^* is the solute concentration at time t and position x with respect to the Matano Interface, $C_0 = | C^{+\infty} - C^{-\infty} |$ and $erf(\lambda)$ is the error function of λ. λ is found to bear a linear relationship with the variable $\eta (= x/\sqrt{t})$,as:

$$\lambda = h\eta + k \tag{2}$$

The concentration dependent interdiffusion coefficient $\tilde{D}(C)$ can be determined from the values of h and k by the following relation[6]:

$$\tilde{D}(C^*) = \frac{1}{4h^2} + \frac{k\sqrt{\pi}}{4h^2}(1 + erf(\lambda))\exp(\lambda^2) \tag{3}$$

4. Results and Discussions

4.1 Impurity Diffusion Of Al In β–Zr

A typical concentration profile across the diffusion zone obtained after annealing a diffusion couple for 72 hours at 1293K is shown in Fig.1. This is a typical solid solution type of concentration profile asymmetric with respect to the Matano-Interface (MI). The values of slope h and intercept k (of Eqn. 2) were determined for the concentration profiles of Al at each temperature by least square fit. These values are used in the Eqn.3 to calculate the interdiffusion coefficient $\tilde{D}$ by Hall's method. According to the Darken [8], the interdiffusion coefficient in infinitely dilute solid solution corresponds to the impurity diffusion coefficient of the solute in the solvent matrix. In the narrow composition range $0 \le C_{Al} \le 2$at%, $\tilde{D}_{ZrAl}$ bears a linear relationship with C_{Al} of the type $\tilde{D}_{ZrAl} = a + bC_{Al}$. The impurity diffusion coefficient of Al in β-Zr is evaluated by extrapolating $\tilde{D}_{ZrAl}$ to $C_{Al} \to 0$. Here we shall denote impurity diffusion of Al in βZr as $D_{Al\ (C_{Al}=0)}^{\beta Zr}$. The temperature dependence of $D_{Al\ (C_{Al}=0)}^{\beta Zr}$ was determined and is expressed by an Arrhenius type of relation:

$$D_{Al\ (c_{Al}=0)}^{\beta Zr} = 5.567_{-1.80}^{+2.65}\ X10^{-6}\exp[(-220.08\pm3.33)kJ/RT]\ m^2/s.$$

The activation energy of self-diffusion of Zr in β-Zr is 115.78kJ/mol[9] as compared to 220.08kJ/mol for the impurity diffusion of Al in β-Zr. The difference between the activation energy values, ΔQ (Q^{Al}-Q^{self}) is 104.3 kJ/mol. Such a positive value suggests a rather low impurity-vacancy binding energy according to the theory of vacancy diffusion[10,11].

4.2 Interrelation Between Impurity Diffusion Parameters

The diffusion parameters of impurity diffusion of Al in β−Zr i.e. activation energy Q^{Al} and the pre-exponential factor D_0^{Al} are compared with those of its counterparts in other βZr-X systems (X=Co, Mn, Sn, V, Be, Fe, Ag and Ta)[9]. Both the values were found to be on the higher side. According to Swalin[12] a quantity ($\frac{d\log D_0}{dQ}$) should remain constant for different impurity elements in a particular solvent. The values of $\log D_0$ and Q for impurity diffusion of various elements in β−Zr are plotted in Fig.2. Data for Al impurity diffusion falls close to the straight line of least square fit. The value of the slope of the straight line 4.52X10^{-3} mol/kJ, is comparable with that for impurity diffusion in other metals viz. Ni[13] and Ag and Cu[14].

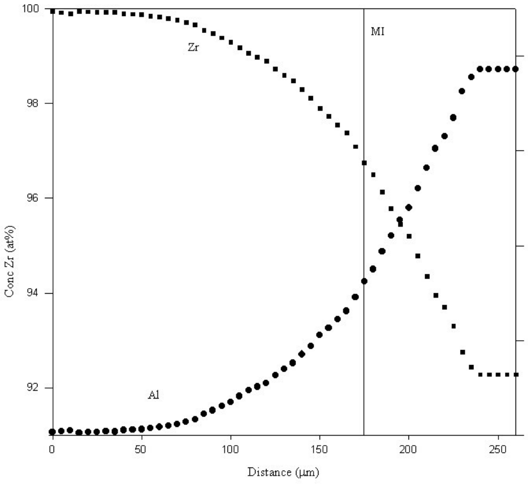

Fig. 1 Concentration profile of Zr/Zr-2.8wt%Al couple annealed at 1203K for 72 hrs.

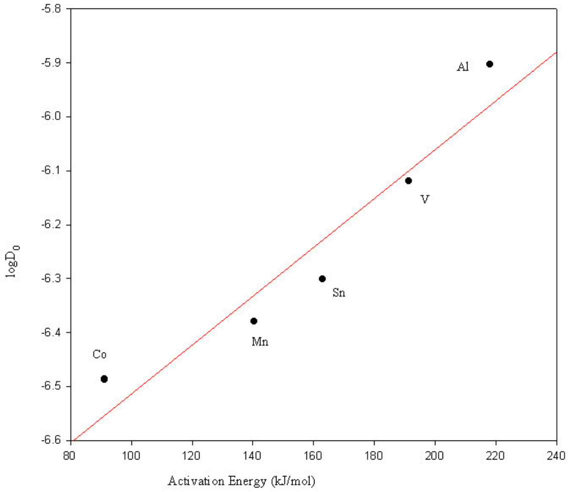

Fig.2 Log D_0 versus Q for impurity diffusivity in β-Zr.

Beke et al[15] proposed a general expression for impurity diffusion. They showed that in a plot of $\ln(D_0^{imp}/D_0^{self})$ versus $\Delta Q/T_m$, the data points for various impurity elements should fall in a straight line. Such a plot for impurity diffusion in β−Zr is shown in Fig. 3. A straight line is drawn by least square method and has a slope of 1.0126X10^{-2} molK/kJ. The value of the slope is in excellent agreement with similar values reported earlier[15] for impurities in Al ((9.3±0.7) X10^{-2} molK/kJ), Ag ((6.7±0.4) X10^{-2} molK/kJ) and Cu ((4.3±0.9) X 10^{-2} molK/kJ). The impurity diffusion coefficient value of Al, therefore, is consistent with the related theories of Swalin[12] and Beke[15].

4.3 Impurity Diffusion And Atomic Size

Hood[16] showed that a close correlation exists between impurity diffusivity and the atomic size and the two can be related by an expression of the type:

$$\log D = A + \exp(B - Cr) \qquad (4)$$

where A, B and C are constants for the host metal and *r* is the atomic radius of the impurity atom. Such expressions were derived for Pb, αZr and Cu[16]. Fig. 4 shows a plot of log D for impurity diffusivities of various elements in β-Zr against *r*, their atomic radii. The data points are fitted to an expression of the type Eqn. (4) by least square fit to produce a relation:

$$\log D_{imp}^{\beta Zr}(m^2 s^{-1}) = -14.57 \pm 1.22 + \exp[(4.84 \pm 2.83) - (30.22 \pm 2.66) r(nm)] .$$

Al occupies a position very close to the curve. This shows good correlation between the impurity diffusivity of Al with that of other elements in βZr.

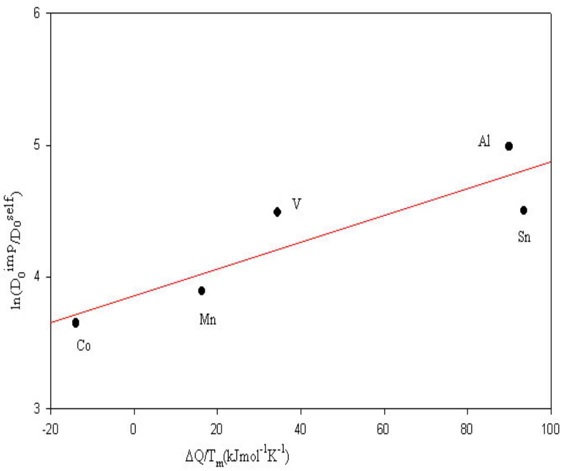

Fig. 3 The $\ln(D_0^{imp}/D_0^{self})$ versus $\Delta Q/T_m$ plot for impurity diffusion in β-Zr.

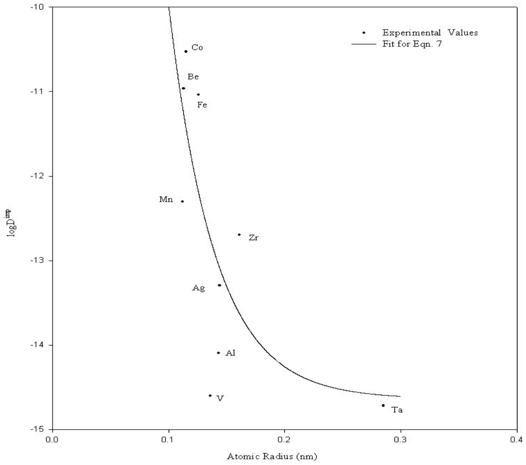

Fig. 4 Variation of impurity diffusivity in β-Zr with atomic radius of impurity atoms.

5. Conclusions

1. The interdiffusion coefficient $\tilde{D}$ continuously increases with concentration.
2. The temperature dependence of impurity diffusivity of Al in βZr is $D_{Al\ (c_{Al}=0)}^{\beta Zr} = 5.56_{-1.80}^{+2.65} \mathrm{X}10^{-6} \exp[(-220.08 \pm 3.33)\mathrm{kJ/RT}]\ \mathrm{m}^2/\mathrm{s}$.
3. The positive difference in the activation energies ($Q^{imp} - Q^{self}$), indicates very low impurity- vacancy binding energy.
4. The impurity diffusivity parameters are found to be consistent with Swalin's and Beke's theories.
5. A relation between impurity diffusivity in β–Zr and atomic radii can be represented by the equation:

$$\log D_{imp}^{\beta Zr}(m^2 s^{-1}) = -14.57 \pm 1.22 + \exp[(4.84 \pm 2.83) - (30.22 \pm 2.66) r(nm)] .$$

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