Measurement of the Interdiffusion Coefficients in Mo-Ti and Mo-Ti-Zr Beta Phase Alloys from 1273 to 1473 K

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Abstract Accurate interdiffusion information is not only useful to determine alloy stability under long-term service conditions but also valuable in dealing with processing design. The work entailed an initial preparation of four beta phase Mo-Ti diffusion couples, which were used to determine the composition-dependent interdiffusivities at 1273, 1373, 1423 and 1473 K to validate the literature data and provide new experimental data over the whole composition range. Besides, utilizing 18 groups of bulk diffusion couples applied to EPMA technique, the composition dependence of ternary interdiffusion coefficients were obtained by using Whittle–Green method along with the uncertainty analysis for the obtained interdiffusion coefficients. The reliability of the experimental interdiffusivities is validated via thermodynamic constraints. Taking Ti as the solvent element, the present work indicates that in the temperature range between 1273 and 1473 K, the ternary interdiffusion coefficients increase by one order of magnitude per 100 K, and the diffusion of Zr is generally faster than that of Mo. The ternary main interdiffusion coefficients $\tilde{D}_{MoMo}^{Ti}$ with

different compositions of Zr at 1273, 1373, and 1473 K were compared with the values obtained for the boundary binary Mo-Ti system in both present experimental work and the literature. A composition-dependent decreasing-increasing tendency is observed for $\tilde{D}_{MoMo}^{Ti}$.

Keywords β phase · diffusion couples · interdiffusion coefficients · Mo-Ti · Mo-Ti-Zr

1 Introduction

Both Ti and its alloys are biologically safe and bio-compatible in addition to having high mechanical strength.^[1] In particular, β phase (Body Centered Cubic, BCC) titanium alloys are currently attractive for biomedical and uranium applications since the β phase titanium alloys have lower Young's modulus and better radiation resistance than those of α phase (hexagonal close packed, HCP) and two-phase titanium alloys.^[2,3] Besides, in view of several considerations including the stability of the β phase and lower Young's modulus, the elements with BCC crystal structure, such as Mo and Zr, are often added to Ti alloys in order to develop novel β phase Ti alloys.^[4,5]

Most solid-state reactions are largely dependent upon thermodynamic properties and complex diffusion processes. Knowledge of both thermodynamic and kinetic characteristics of Ti alloys is of critical importance in understanding how temperature, time, and compositions affect microstructure during heat treatment.^[6] Such information is not only useful to determine alloy stability under long-term service conditions, but also valuable in dealing with processing design. Interdiffusion is an omnipresent but important phenomenon in materials science and

When the present manuscript was ready for submission, the most recent publication^[36] came into our attention, which has not yet been considered in this work.

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engineering processes.^[7–10] The key aspect in developing Ti-based alloys with excellent mechanical properties is to obtain a homogeneous β phase titanium alloy with superplastic behavior through the heat treatment schedule, which calls for the reliable diffusivity information as a prerequisite.^[11–13] As part of our long-term project aiming at establishing an accurate diffusion database for Mo-Nb-Ti-Zr-based multi-component system, the β phase ternary Mo-Ti-Zr alloys and its boundary binary Mo-Ti alloys were chosen as target systems in the present work.

In the literature, several reports are available about the interdiffusion coefficients in Mo-Ti, Mo-Zr and Ti-Zr alloys.^[14–22] However, most of the measurements focused on the composition range between Ti and Ti-30%Mo, and the experimental data over the whole composition range at 1423 K are missing. Consequently, new experimental interdiffusivities in Mo-Ti alloys should be measured in order to validate the literature data and provide new experimental data. In contrast to binary boundaries, there is no investigation on the interdiffusion coefficients in Mo-Ti-Zr alloys in the literature.

The objective of the present work is thus to: (1) prepare four Mo-Ti binary diffusion couples, and determine the composition-dependent interdiffusivities from 1273 to 1473 K; (2) determine the ternary interdiffusion coefficients of the Ti-rich Mo-Ti-Zr alloys from 1273 to 1473 K by means of electron probe micro-analysis (EPMA) and diffusion couple method; (3) validate the reliability of the measurement and analyze uncertainties of the obtained diffusivities; and (4) investigate the composition-dependent behavior of the ternary diffusion coefficients.

2 Experimental Procedure

The Mo-Ti phase diagram calculated according to the thermodynamic assessment of Shim et al.^[23] is presented in Fig. 1, where the single β phase is stable over the whole composition range from 1200 to 1800 K. Pure Mo (purity: 99.99 wt.%) and Ti (purity: 99.99 wt.%) were individually weighed to prepare the four groups 100Ti/100Mo diffusion couples (as listed in Table 1). Meanwhile, according to the experimental isothermal sections of the Mo-Ti-Zr system at 1273, 1373, and 1473 K,^[24] twelve binary, six ternary alloys in Ti-rich Mo-Ti-Zr system (as listed in Table 2) were individually weighed to prepare the ternary diffusion couples. All the samples were prepared by arc melting using a non-consumable tungsten electrode (WKDHL-1, Opto-electronics Co., Ltd., Beijing, China) under a high-purity argon atmosphere. The buttons were re-melted at least five times to improve their homogeneities.

During the preparation of diffusion couples, the ingots were cut into blocks with the size of $5 \times 5 \times 2 \text{ mm}^3$.

Fig. 1 Calculated Ti-Mo phase diagram according to the thermodynamic assessment of Shim et al.^[23]

After mechanically removing the surface contaminants, all the samples were sealed in the quartz tubes under an argon atmosphere, and then homogenized at $1373 \pm 2 \text{ K}$ for 30 days, such a treatment will obtain a large grain size up to millimeters. With such a large grain size, the effect of grain boundary diffusion could be ignored.

At the next experimental work: (1) four groups of binary Mo-Ti diffusion couples were sealed in the quartz tubes under an argon atmosphere, and separately annealed at 1273 K for 240 h, 1373 K for 63.5 h, 1423 K for 72 h and 1473 K for 96 h, as listed in Table 1; (2) three groups of ternary diffusion couples of Mo-Ti-Zr system assembled with Ta clamps were annealed at 1273, 1373, and 1473 K for 96, 72, and 24 h, respectively, as shown in Table 2. The annealing was performed in a high temperature furnace (GSL-1700X, MTI Co., Ltd., Hefei, China). Subsequently, the annealed twenty-two diffusion couples were quenched in cold water to maintain the composition distribution after diffusion at different temperatures. The annealed diffusion couples were then metallographic polished along planes parallel to the diffusion direction. The solute concentration profiles in all of the 22 diffusion couples were determined by means of the EPMA (electron probe micro-analyzer) technique (JXA-8800R, JEOL, Japan) on the polished section. The uncertainty in alloy compositions was determined to be within $\pm 0.5 \text{ at.}\%$ for each component.

3 Determination of Interdiffusion Coefficients

In the n -component system, according to Onsager,^[25] the mutual diffusion flux of component k , $\tilde{J}_k$ can be expressed by $(n - 1)$ independent concentration gradients, that is:

Table 1 Terminal compositions of the diffusion couples and annealing schedule in the Mo-Ti system

Binary diffusion couples	Composition, at. %	Temperature, K	Time, h
I	100Ti/100Mo	1273	240
II	100Ti/100Mo	1373	63.5
III	100Ti/100Mo	1423	72
IV	100Ti/100Mo	1473	96

Table 2 Terminal compositions of the diffusion couples and annealing schedule in the Mo-Ti-Zr system

Ternary diffusion couples	Composition, at. %	Temperature, K	Time, h
A1	Ti/10Mo-63Ti-27Zr	1273	96
A2	Ti/24.5Mo-65.5Ti-10.5Zr	1273	96
A3	87Ti-13Zr/14Mo-86Ti	1273	96
A4	77.5Ti-22.5Zr/23.5Mo-76.5Ti	1273	96
A5	87Ti-13Zr/23.5Mo-76.5Ti	1273	96
A6	77.5Ti-22.5Zr/14Mo-86Ti	1273	96
B1	Ti/10Mo-61Ti-29Zr	1373	72
B2	Ti/26.5Mo-63Ti-10.5Zr	1373	72
B3	86.5Ti-13.5Zr/13.5Mo-86.5Ti	1373	72
B4	77.5Ti-22.5Zr/23Mo-77Ti	1373	72
B5	86.5Ti-13.5Zr/23Mo-77Ti	1373	72
B6	77.5Ti-22.5Zr/13.5Mo-86.5Ti	1373	72
C1	Ti/10Mo-60Ti-30Zr	1473	24
C2	Ti/27.5Mo-62.5Ti-10Zr	1473	24
C3	85.5Ti-14.5Zr/14Mo-86Ti	1473	24
C4	77.5Ti-22.5Zr/22.5Mo-77.5Ti	1473	24
C5	85.5Ti-14.5Zr/22.5Mo-77.5Ti	1473	24
C6	77.5Ti-22.5Zr/14Mo-86Ti	1473	24

$$\tilde{J}_k = - \sum_{j=1}^{n-1} \tilde{D}_{kj}^n \frac{\partial c_j}{\partial z} \quad (j = 1, 2, \dots, n-1) \quad (\text{Eq 1})$$

where c_j is the concentration of element j with the unit of moles/m³, z is the distance, $\tilde{D}_{kj}^n$ is the interdiffusion coefficient, when $k = j$, $\tilde{D}_{kj}^n$ denotes the main coefficients; when $k \neq j$, $\tilde{D}_{kj}^n$ denotes the cross coefficients. The summations performed over $(n-1)$ independent n concentrations as the dependent component may be taken as the solvent. When $n = 2$, i.e. in a binary system, Eq 1 can be directly used to calculate interdiffusion coefficient with a certain annealing time, and the interdiffusion coefficient can be calculated from the profiles using different methods. In this work, the binary interdiffusion coefficients $\tilde{D}$ was determined by using the Boltzmann–Matano method.^[26] Assuming that the molar volume in the whole diffusion region is constant, the mutual diffusion flux of component k can be expressed as follows:

$$\tilde{J}_k = \frac{1}{2t} \int_{c_k^-}^{c_k^*} (z - z_0) dc_k \quad (\text{Eq 2})$$

where c_k is the concentration of element k , t is the diffusion time, c_k^- is the minimum and c_k^+ is the maximum concentration of the alloying element at the limits of the diffusion couple, z_0 is the position of the Matano plane, which can be determined by the following:

$$\int_{c_k^-}^{c_k^+} (z - z_0) dc_k = 0 \quad (\text{Eq 3})$$

According to the Eq 1 and 2, the binary mutual diffusion coefficient $\tilde{D}(c_k^*)$ can be expressed as follows:

$$\tilde{D}(c_k^*) = \frac{1}{2t} \frac{\partial z}{\partial c_k} \left[\int_{c_k^-}^{c_k^+} (z - z_0) dc_k \right] \quad (\text{Eq 4})$$

The interdiffusion flux of component k ($k = \text{Mo}, \text{Zr}$) in the Mo-Ti-Zr ternary alloy can be expressed in terms of two independent composition gradients:

Fig. 2 The BSE image of Mo/Ti diffusion couple annealed at 1373 K for 72 h

$$\tilde{J}_{Mo} = -\tilde{D}_{MoMo}^{Ti} \frac{\partial c_{Mo}}{\partial z} - \tilde{D}_{MoZr}^{Ti} \frac{\partial c_{Zr}}{\partial z} \quad (\text{Eq 5})$$

$$\tilde{J}_{Zr} = -\tilde{D}_{ZrMo}^{Ti} \frac{\partial c_{Zr}}{\partial z} - \tilde{D}_{ZrZr}^{Ti} \frac{\partial c_{Zr}}{\partial z} \quad (\text{Eq 6})$$

where element Ti is taken as the dependent solvent, c_k ($k = \text{Mo, Zr}$) is composition of component k , $\tilde{J}_k$ is the flux of element k ($k = \text{Mo or Zr}$) and z is distance. The coefficients $\tilde{D}_{MoMo}^{Ti}$ and $\tilde{D}_{ZrZr}^{Ti}$ are main coefficients, which represent the influences of the concentration gradients of elements Mo and Zr on their own fluxes, respectively. While the cross interdiffusion coefficients $\tilde{D}_{MoZr}^{Ti}$ and $\tilde{D}_{ZrMo}^{Ti}$ reflect the influences of the concentration gradients of elements Zr and Mo on the fluxes of elements Mo and Zr, respectively.

To obtain the four interdiffusivities by means of the Matano–Kirkaldy method,^[27,28] one pair of diffusion couples with the diffusion paths intersecting at one common composition are in use. Assuming that the volume change is negligible during diffusion, the position of Matano plane should be the same for concentration profiles of solutes Mo and Zr in theory. However, in actual experimental measurement, due to the influence of instrument error and other factors, the position of Matano plane obtained from the composition–distance curve of different components in the same diffusion couple will not be strictly equal, which will lead to some errors in calculating diffusion flux. To eliminate the need to calculate z_0 , Sauer and Freise^[29] define a new component variable Y :

$$Y_k(z) = \frac{c_k(z) - c_k^-}{c_k^+ - c_k^-} \quad (k = \text{Mo or Zr}) \quad (\text{Eq 7})$$

Combining with the definition of Matano plane, the expression of diffusion flux without z_0 is deduced as follows^[30]:

$$\tilde{J}_{Mo}(z^*) = \frac{c_{Mo}^- - c_{Mo}^+}{2t} \left[(1 - Y_{Mo}^*) \int_{-\infty}^{z^*} Y_{Mo} dz + Y_{Mo}^* \int_{z^*}^{+\infty} (1 - Y_{Mo}) dz \right] \quad (\text{Eq 8})$$

$$\tilde{J}_{Zr}(z^*) = \frac{c_{Zr}^- - c_{Zr}^+}{2t} \left[(1 - Y_{Zr}^*) \int_{-\infty}^{z^*} Y_{Zr} dz + Y_{Zr}^* \int_{z^*}^{+\infty} (1 - Y_{Zr}) dz \right] \quad (\text{Eq 9})$$

where t is the diffusion annealing time, the normalized composition variable Y_k^* of element k ($k = \text{Mo or Zr}$) at section z^* is the value of $\frac{c_k(z^*) - c_k^-}{c_k^+ - c_k^-}$.

4 Results and Discussion

4.1 Experimental Interdiffusivities in Mo–Ti β phase Alloys

One representative back scattered electron (BSE) image of 100Ti/100Mo (at.%, Couple III) annealed at 1423 K for

Fig. 3 Concentration profiles measured in Mo/Ti diffusion couples annealed at: (I) 1273 K for 240 h, (II) 1373 K for 63.5 h, (III) 1423 K for 72 h, (IV) 1473 K for 96 h

Fig. 4 The experimental interdiffusion coefficients for Mo-Ti binary alloys from the present work at 1273, 1373, 1423, and 1473 K, together with literature data^[19–22]

72 h is shown in Fig. 2. Figure 3 shows the measured composition profiles of Mo (denoted in symbols) in the four Mo/Ti diffusion couples annealed at 1273 K for

240 h, 1373 K for 63.5 h, 1423 K for 72 h, and 1473 K for 96 h. As indicated in the figures, the concentration curves determined from the Mo/Ti diffusion couples show an

Fig. 5 The BSE image of Ti/26.5Mo-63Ti-10.5Zr (B2, at.%) diffusion couple annealed at 1373 K for 72 h

extremely steep concentration gradient near the Mo-rich edge, which corresponds to the slow diffusion region. According to the work of Chen and Zhao,^[21] diffusion coefficients extracted from regions with sufficiently steep concentration gradients can be inflated by up to three orders of magnitude due to artificial broadening of the concentration profiles. Hence, only the diffusion coefficients with the composition region of 0 ~ 40 at.% Mo are utilized in the present work since the concentration gradients in this range are shallow enough (less than 1 at.% per micron) to allow reliable diffusion coefficient extraction.

Based on the measured composition profiles, the composition-dependent interdiffusivities in the Mo-Ti alloys can be calculated using the Eq 4, which has been frequently utilized elsewhere^[31,32] in our research group and is therefore not described here. The results of these calculations are presented in Fig. 4, where the experimental interdiffusivities in Mo-Ti alloys at 1273, 1373, 1423, and 1473 K exhibit a noticeable composition-dependence, and the present experimental data agree well with the literature data.

4.2 Concentration Profiles and Diffusion Paths in Mo-Ti-Zr Diffusion Couples

Considering that all the diffusion couples are in single β phase region of Ti-rich Mo-Ti-Zr system, one microstructure of couple B2 was selected as the representative one. Figure 5 shows the backscattered electron image of

microstructure of Couple B2 annealed at 1373 K for 72 h. The composition profile can be experimentally measured along the specific direction of the diffusion couple, as shown in Fig. 5. Meanwhile all the concentration profiles of Mo and Zr in diffusion couples A1-A6, B1-B6, and C1-C6 at 1273, 1373 and 1473 K are presented in Fig. 6, 7 and 8, respectively. According to the EPMA measurement, it is indicated that with the increase of diffusion time, the diffusion distances are almost the same for the alloys annealed at 1273, 1373, and 1473 K, respectively. Besides, the diffusion distance of Zr is generally longer than that of Mo, revealing that Zr diffuses faster than Mo in the Mo-Ti-Zr alloys.

The concentration profiles of Mo and Zr in all the diffusion couples show asymmetric behaviors. The following double iterations of Boltzmann function equation^[33] were used to smooth the experimental data:

$$c(z) = P_7 + P_1 / (1 + \exp((z - P_2)/P_3)) + P_4 / (1 + \exp((z - P_5)/P_6)) \quad (\text{Eq 10})$$

where c is the concentration, z is diffusion distance, and P_i ($i = 1-7$) are the parameters to be fitted. All the parameters are obtained by means of the least-squares fitting method. After that, the fitted functions are employed to determine the ternary interdiffusivities by using Matano-Kirkaldy method.

Fig. 6 The concentration profiles of Mo and Zr in diffusion couples A1, A2, A3, A4, A5, and A6 annealed at 1273 K

The experimental diffusion paths together with Ti-rich isothermal sections at 1273, 1373, and 1473 K are shown in Fig. 9, 10, and 11. In these figures, all the diffusion paths are located in the single β phase region, passing from (β Ti) to the terminal alloy of 26.5Mo-63Ti-10.5Zr (at.%).

4.3 Calculation of Ternary Interdiffusion Coefficients

The interdiffusion coefficients $\tilde{D}_{MoMo}^{Ti}$, $\tilde{D}_{ZrZr}^{Ti}$, $\tilde{D}_{MoZr}^{Ti}$ and $\tilde{D}_{ZrMo}^{Ti}$ extracted at the intersecting compositions of diffusion paths at 1273, 1373, and 1473 K are summarized in Tables 3, 4 and 5, respectively. The population consists of

four values for each interdiffusion coefficient, the main coefficients ($\tilde{D}_{MoMo}^{Ti}$, $\tilde{D}_{ZrZr}^{Ti}$) and the cross one ($\tilde{D}_{MoZr}^{Ti}$, $\tilde{D}_{ZrMo}^{Ti}$). Combining Eq 5, 6, 8, and 9, the four values at the common composition of the two diffusion couples can be determined by using the M–K method.

Experimental errors associated with the measured interdiffusivities were assessed using Lechelle's error propagation method,^[34] in which the uncertainties on the interdiffusion coefficient were estimated by the following function:

$$u(f(A, B, \dots)) = \sqrt{\sum_{\alpha=A, B, \dots} (u(\alpha))^2 \left(\frac{\partial f}{\partial \alpha} \right)^2} \quad (\text{Eq 11})$$

Fig. 7 The concentration profiles of Mo and Zr in diffusion couples B1, B2, B3, B4, B5, and B6 annealed at 1373 K

where $A, B, \dots$ are the correlation quantities of function f , and $u(\alpha)$ is the uncertainty in the measurements of variable α , like concentration. Here, the estimation for the error of main diffusion coefficients $\tilde{D}_{MoMo}^{Ti}$ at the intersection of diffusion couples A1 and A3 is given in detail as an example. According to Matano–Kirkaldy method, $\tilde{D}_{MoMo}^{Ti}$ can be calculated using the following function:

$$\tilde{D}_{MoMo}^{Ti} = \frac{\tilde{J}_{Mo}^{A3} \left(\frac{\partial c_{Zr}}{\partial z} \Big|_{A1} \right) - \tilde{J}_{Mo}^{A1} \left(\frac{\partial c_{Zr}}{\partial z} \Big|_{A3} \right)}{\left(\frac{\partial c_{Mo}}{\partial z} \Big|_{A1} \right) \left(\frac{\partial c_{Zr}}{\partial z} \Big|_{A3} \right) - \left(\frac{\partial c_{Mo}}{\partial z} \Big|_{A3} \right) \left(\frac{\partial c_{Zr}}{\partial z} \Big|_{A1} \right)} \quad (\text{Eq 12})$$

where $\tilde{J}_{Mo}^{A3}$ and $\tilde{J}_{Mo}^{A1}$ are the fluxes of Mo in A3 diffusion couple and A1 diffusion couple at the intersection of diffusion couples A1 and A3, respectively; $\frac{\partial c_{Mo}}{\partial x} \Big|_{A1}$ and $\frac{\partial c_{Zr}}{\partial x} \Big|_{A1}$ are the concentration gradients of Mo and Zr in A1 diffusion couple at the intersection of diffusion couples A1 and A3, respectively; $\frac{\partial c_{Mo}}{\partial x} \Big|_{A3}$ and $\frac{\partial c_{Zr}}{\partial x} \Big|_{A3}$ are the concentration gradient of Mo and Zr element of A3 diffusion couple at the intersection of diffusion couples A1 and A3, respectively. Therefore, the error of the main diffusion coefficient, $u(\tilde{D}_{MoMo}^{Ti})$, contains the contributions of individual variables and could be express as follows:

Fig. 8 The concentration profiles of Mo and Zr in diffusion couples C1, C2, C3, C4, C5, and C6 annealed at 1473 K

$$u(\tilde{D}_{MoMo}^T)^2 = \left\{ \begin{aligned} & \left(\frac{\partial \tilde{D}}{\partial J_{Mo}^{A3}} \right)^2 u(\tilde{J}_{Mo}^{A3})^2 + \left(\frac{\partial \tilde{D}}{\partial J_{Mo}^{A1}} \right)^2 u(\tilde{J}_{Mo}^{A1})^2 + \left[\frac{\partial \tilde{D}}{\left(\frac{\partial c_{Mo}}{\partial z} \right)_{|A1}} \right]^2 u \left(\frac{\partial c_{Mo}}{\partial z} \right)_{|A1}^2 \\ & + \left[\frac{\partial \tilde{D}}{\left(\frac{\partial c_{Zr}}{\partial z} \right)_{|A1}} \right]^2 u \left(\frac{\partial c_{Zr}}{\partial z} \right)_{|A1}^2 + \left[\frac{\partial \tilde{D}}{\left(\frac{\partial c_{Mo}}{\partial z} \right)_{|A3}} \right]^2 u \left(\frac{\partial c_{Mo}}{\partial z} \right)_{|A3}^2 \\ & + \left[\frac{\partial \tilde{D}}{\left(\frac{\partial c_{Zr}}{\partial z} \right)_{|A3}} \right]^2 u \left(\frac{\partial c_{Zr}}{\partial z} \right)_{|A3}^2 \end{aligned} \right\} \quad (\text{Eq 13})$$

where $u(\tilde{J})$ is the uncertainty of flux at the intersection point. According to Eq 8 and 9, $\tilde{J}(z^*)$ and $u(\tilde{J})^2$ can be calculated as follows:

$$\begin{aligned} \tilde{J}(z^*) &= \frac{c^- - c^+}{2t} \left[(1 - Y_k^*) \int_{-\infty}^{z^*} Y_k dz + Y_k^* \int_{z^*}^{+\infty} (1 - Y_k) dz \right] \\ u(\tilde{J})^2 &= \left(\frac{\partial \tilde{J}}{\partial c} \right)^2 u(c)^2 + \left(\frac{\partial \tilde{J}}{\partial t} \right)^2 u(t)^2 + \left(\frac{\partial \tilde{J}}{\partial z} \right)^2 u(z)^2 \end{aligned} \quad (\text{Eq 14})$$

Since the diffusion annealing time t and diffusion distance z can be measured very accurately, the errors for two terms are assumed to be zero (i.e. $u(t) = 0$, $u(z) = 0$). Consequently, $u(\tilde{J})^2$ is estimated as follows:

$$u(\tilde{J})^2 = \left(\frac{\partial \tilde{J}}{\partial c} \right)^2 u(c)^2 \quad (\text{Eq 15})$$

Fig. 9 Experimental diffusion paths together with Ti-rich isothermal section at 1273 K

Fig. 10 Experimental diffusion paths together with Ti-rich isothermal section at 1373 K

Fig. 11 Experimental diffusion paths together with Ti-rich isothermal section at 1473 K

$u(c)$ is the uncertainty of concentration, which is associated with the error in EPMA measurement and fitting function. In this work, the double iterations of Boltzmann function Eq 10 were used to smooth the experimental data, so the error calculation for fitting concentration is given by the following equation:

$$c = c(z, p_1, p_2, \dots, p_n) \quad (\text{Eq 16})$$

$$u(c)^2 = \lambda \cdot \sum_{k=1}^n \left(\frac{\partial c}{\partial p_k} \right)^2 \cdot u(p_k)^2$$

where the parameter λ is estimated as 1.02 in view of composition measurement error (about 0.02) from EPMA. According to present calculations, the uncertainty of calculating the ternary interdiffusion coefficients are estimated as: 60% uncertainty from interdiffusion flux and 40% uncertainty from concentration.

In order to check the reliability of the evaluation, all the 27 series of the determined ternary interdiffusion coefficients $\tilde{D}_{MoMo}^{Ti}$, $\tilde{D}_{ZrZr}^{Ti}$, $\tilde{D}_{MoZr}^{Ti}$ and $\tilde{D}_{ZrMo}^{Ti}$ for Ti-rich Mo-Ti-Zr alloys are subjected to the following thermodynamical constraints, which are defined as^[35]:

$$\tilde{D}_{MoMo}^{Ti} + \tilde{D}_{ZrZr}^{Ti} > 0 \quad (\text{Eq 17})$$

$$\tilde{D}_{MoMo}^{Ti} \tilde{D}_{ZrZr}^{Ti} - \tilde{D}_{MoZr}^{Ti} \tilde{D}_{ZrMo}^{Ti} \geq 0 \quad (\text{Eq 18})$$

$$(\tilde{D}_{MoMo}^{Ti} - \tilde{D}_{ZrZr}^{Ti})^2 + 4\tilde{D}_{MoZr}^{Ti} \tilde{D}_{ZrMo}^{Ti} \geq 0 \quad (\text{Eq 19})$$

Examination shows that all the interdiffusivities determined by using the Matano–Kirkaldy method can satisfactorily fulfill the thermodynamically stable constraints in Eq 17, 18, and 19.

As shown in Tables 3, 4, and 5, the main coefficients are positive at 1273, 1373, and 1473 K, whereas the cross coefficients are positive or negative. As expected, the main coefficients are generally larger than the absolute values of cross ones. Moreover, the values of $\tilde{D}_{ZrZr}^{Ti}$ are much larger than those of $\tilde{D}_{MoMo}^{Ti}$, indicating that the diffusion rate of Zr in the Mo-Ti-Zr alloy is faster than that of Mo. In addition, the magnitude of the ternary interdiffusion coefficients increases from 10^{-15} to 10^{-13} m²/s when the temperature elevates from 1273 to 1473 K, showing that a temperature increase of 100 K would bring a diffusion coefficient increase by one order of magnitude.

In order to show the composition-dependent interdiffusion coefficients in detail, the diffusivities at different contents of Zr at 1273, 1373, and 1473 K are plotted in Fig. 12, together with the experimental data along the boundary binary Mo-Ti system from the present work and the literature data.^[19–22] It can be found that $\tilde{D}_{MoMo}^{Ti}$ decreases with the increase of x_{Mo} or x_{Zr} (x_k is the

Table 3 Experimental interdiffusion coefficients in Mo-Ti-Zr alloys at 1273 K

Composition, at. %		Interdiffusion coefficients, 10^{-15} m ² /s			
Mo	Zr	$\tilde{D}_{MoMo}^{Ti}$	$\tilde{D}_{ZrZr}^{Ti}$	$\tilde{D}_{MoZr}^{Ti}$	$\tilde{D}_{ZrMo}^{Ti}$
5.2	9.1	7 ± 4	35 ± 18	-3 ± 3	5 ± 5
5.8	10.0	4 ± 2	25 ± 12	0.2 ± 0.1	3 ± 3
7.7	12.5	3 ± 1	19 ± 10	-0.5 ± 0.4	2 ± 2
8.5	14.0	3 ± 1	18 ± 9	-0.3 ± 0.2	3 ± 2
12.2	7.0	1 ± 1	14 ± 6	-1 ± 1	1 ± 1
13.6	1.7	2 ± 1	12 ± 6	-2 ± 2	-0.6 ± 0.5
14.2	1.9	2 ± 1	10 ± 5	-2 ± 2	-0.6 ± 0.5
19.8	3.0	0.5 ± 0.2	3 ± 1	-0.3 ± 0.2	-0.3 ± 0.3
21.2	3.8	0.4 ± 0.2	3 ± 1	-0.3 ± 0.3	-0.4 ± 0.3

Table 4 Experimental interdiffusion coefficients in Mo-Ti-Zr alloys at 1373 K

Composition, at. %		Interdiffusion coefficients, 10^{-14} m ² /s			
Mo	Zr	$\tilde{D}_{MoMo}^{Ti}$	$\tilde{D}_{ZrZr}^{Ti}$	$\tilde{D}_{MoZr}^{Ti}$	$\tilde{D}_{ZrMo}^{Ti}$
5.1	9.4	2 ± 1	12 ± 5	-0.9 ± 0.8	0.8 ± 0.7
6.7	11.4	1 ± 1	6 ± 3	-0.3 ± 0.3	0.4 ± 0.3
7.4	12.9	0.9 ± 0.4	6 ± 3	-0.1 ± 0.1	0.03 ± 0.03
8.2	14.8	1 ± 1	5 ± 3	-0.1 ± 0.1	0.3 ± 0.2
10.7	9.5	0.9 ± 0.4	4 ± 2	-0.3 ± 0.3	0.8 ± 0.8
13.1	1.6	0.9 ± 0.5	3 ± 2	-0.5 ± 0.4	-0.7 ± 0.6
14.2	1.8	0.8 ± 0.4	3 ± 2	-0.2 ± 0.2	-0.3 ± 0.3
20.7	3.0	0.3 ± 0.1	0.4 ± 0.2	-0.1 ± 0.1	-0.04 ± 0.03
21.4	3.8	0.2 ± 0.1	0.5 ± 0.5	-0.2 ± 0.1	-0.2 ± 0.1

Table 5 Experimental interdiffusion coefficients in Mo-Ti-Zr alloys at 1473 K

Composition, at. %		Interdiffusion coefficients, 10^{-13} m ² /s			
Mo	Zr	$\tilde{D}_{MoMo}^{Ti}$	$\tilde{D}_{ZrZr}^{Ti}$	$\tilde{D}_{MoZr}^{Ti}$	$\tilde{D}_{ZrMo}^{Ti}$
4.2	10.1	1 ± 1	5 ± 2	0.4 ± 0.3	1 ± 1
6.4	13.2	0.4 ± 0.2	2 ± 1	0.3 ± 0.2	0.4 ± 0.3
6.8	14.0	0.3 ± 0.2	2 ± 1	0.1 ± 0.1	0.4 ± 0.3
7.4	15.9	0.2 ± 0.1	1 ± 1	0.08 ± 0.07	0.2 ± 0.1
7.4	12.8	0.4 ± 0.2	2 ± 1	0.1 ± 0.1	0.3 ± 0.3
13.9	2.0	0.3 ± 0.2	1 ± 1	0.09 ± 0.08	0.2 ± 0.2
14.5	2.1	0.3 ± 0.1	1 ± 1	0.06 ± 0.05	0.2 ± 0.2
20.6	3.0	0.2 ± 0.1	0.6 ± 0.3	0.05 ± 0.04	0.1 ± 0.1
21.5	3.3	0.1 ± 0.1	0.4 ± 0.2	0.07 ± 0.06	0.09 ± 0.08

concentration of element k with the unit of mol.%). However, the decreasing rate varies with different diffusion Mo contents. In general, a large ratio of x_{Mo}/x_{Zr} speeds up the process of decrease. From these phenomena, we can infer that the influence of element Mo on the variations of $\tilde{D}_{MoMo}^{Ti}$ is much larger than that of Zr.

5 Conclusion

In this work, four groups of Mo/Ti binary diffusion couples were chemically prepared to determine their composition-dependent interdiffusion coefficients at 1273, 1373, 1423, and 1473 K, in an attempt to verify the literature data and also provide new experimental data. The present experimental data in the Mo-Ti alloys agree well with the literature data. Moreover, the composition-dependent ternary interdiffusion coefficients of the Ti-rich Mo-Ti-Zr ternary

Fig. 12 The main interdiffusivities of $\tilde{D}_{MoMo}^{Ti}$ vs. mole-fraction of Mo at different compositions of Zr at 1273, 1373, and 1473 K, together with the experimental data for the boundary binary Mo-Ti system in present work and the literature data^[19–22]

system at 1273, 1373, and 1473 K were systematically determined using EPMA technique coupled with the Kirkaldy–Matano method. The reliability of the experimental interdiffusivities is validated via thermodynamic constraints. The uncertainties associated with the measured interdiffusivities were evaluated by considering error propagation. Results show that the values of $\tilde{D}_{ZrZr}^{Ti}$ are generally larger than $\tilde{D}_{MoMo}^{Ti}$, and for both the main and cross interdiffusion coefficients, their magnitude increases from 10^{-15} to 10^{-13} m²/s when the temperature goes from 1273 to 1473 K. In addition, at the same temperature, with the increase of Mo content, the decreasing trend of main interdiffusion coefficient $\tilde{D}_{MoMo}^{Ti}$ is more significant. Furthermore, the presently obtained ternary $\tilde{D}_{MoMo}^{Ti}$ with different compositions of Mo and Zr at 1273, 1373, and 1473 K were compared with the reported values in the boundary binary Mo-Ti systems. A decreasing-increasing tendency was found for $\tilde{D}_{MoMo}^{Ti}$.

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