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Interdiffusion and atomic mobility in bcc Ti–rich Ti–Nb–Zr system

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ABSTRACT

Accurate interdiffusion information is the necessity for the control of the production of homogeneous biomedical alloys. Ternary interdiffusivities in bcc Ti–rich Ti–Nb–Zr alloys at 1273 K were determined by using the combination of the diffusion couple technique and the Matano–Kirkaldy method. Subsequently, on the basis of the presently obtained interdiffusivities together with the diffusivity and mobility parameters of sub–binary Ti–Nb–Zr system and the thermodynamic descriptions for bcc Ti–Nb–Zr system, the atomic mobilities of Ti, Nb and Zr in bcc Ti–Nb–Zr alloys were assessed by means of DICTRA (DIffusion Controlled TRAnsformation) software package. Moreover, the comprehensive comparisons between the experimental diffusion properties (i.e., interdiffusivities, composition profiles, interdiffusion fluxes and diffusion paths) and the calculated/model–predicted data due to the present atomic mobilities were conducted in order to verify the reliability of the mobilities. The present atomic mobilities for bcc Ti–Nb–Zr system can provide the accurate interdiffusivity matrix over the wide composition range.

1. Introduction

With the increasing population of aged people who are at higher risk of hard–tissue failure, the demand for metallic biomaterials is increasing rapidly to improve the quality of life [1]. Metallic titanium and its alloys are biologically safe, bio–compatible and high mechanical strength [2]. In particular, β–phase (body centered cubic, bcc) titanium alloys are currently attractive metals for biomedical applications since that β–phase titanium alloys have lower Young's modulus than those of α–phase (hexagonal close packed, hcp) and two–phase titanium alloys [3]. Due to several considerations including non–toxicity and lower Young's modulus, the elements Nb and Zr are often added into titanium alloys to develop novel β–phase titanium alloys [3,4]. Therefore, Ti–Nb–Zr system are one of the most important system in metallic biomaterials and attracted more and more attentions [4,5].

Interdiffusion is an omnipresent but important phenomenon in materials science and engineering processes [6–11]. The production of a homogeneous β–phase titanium alloy with super–plastic behavior, which needs the high diffusivity information for determining the heat treatment schedule, is a key procedure for obtaining the biomedical alloys with excellent properties [12]. Thus, accurate interdiffusivity is one extremely important transport parameter for preparing and designing of the Ti–Nb–Zr biomedical materials. Moreover, the reliable interdiffusivity matrices are the essential input for various quantitative theoretical modeling on phase transformation processes of titanium alloys [13]. To the knowledge of the author, there exist no reports on the experimental determinations of the ternary interdiffusivities in bcc Ti–Nb–Zr system available in the literature, which largely restrict the optimization of the Ti–alloy composition design.

Except for the experimental determinations, a phenomenological kinetic technique based on CALPHAD (CALculation of Phase Diagrams) method can also provide reliable diffusion information and is very helpful for materials scientists in alloy design [14,15]. With the aid of the thermodynamic parameters, the atomic mobilities can be adopted in the framework of CALPHAD method to predict diffusion characteristics in Ti–Nb–Zr alloys. Although the atomic mobilities in bcc Ti–Nb, Ti–Zr and Nb–Zr alloys have been assessed by Liu et al. [16–18], accurate atomic mobilities for bcc Ti–Nb–Zr alloys are still absent in the literature. In addition, the thermodynamic descriptions adopted in Refs. [16–18], which are taken from three different research groups, can calculate the accurate phase diagram of sub–binary Ti–Nb–Zr system, but may not be self-consistent and suitable to the ternary Ti–Nb–Zr system and high–order systems. Recently, a self-consistent thermodynamic database for multicomponent Ti–Nb–Zr–Cr–Ta–W–Co system has been developed by Peng et al. [19], which can provide the accurate thermodynamic parameters for bcc Ti–Nb–Zr–based system. It should be noted that the thermodynamic parameters of Nb–Zr system utilized in Ref. [18] are the same as the values in Ref. [19] while the thermodynamic parameters of Ti–Nb and Ti–Zr systems adopted in Refs. [16,17] are different from those in Ref. [19]. Thus, the atomic mobilities of bcc Ti–Nb and Ti–Zr systems [16,17] cannot be directly utilized to establish the atomic mobility parameters of bcc Ti–Nb–Zr system

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Table 1
List of the nominal alloy compositions for the diffusion couples prepared in the present work.

Diffusion couple	Composition (at%)
Couple 1/C1	Ti/Ti–17.7Nb–29.5Zr
Couple 2/C2	Ti/Ti–26.0Nb–20.0Zr
Couple 3/C3	Ti/Ti–36.5Nb–10.4Zr
Couple 4/C4	Ti–9.2Nb/Ti–9.5Zr
Couple 5/C5	Ti–27.5Nb/Ti–27.5Zr

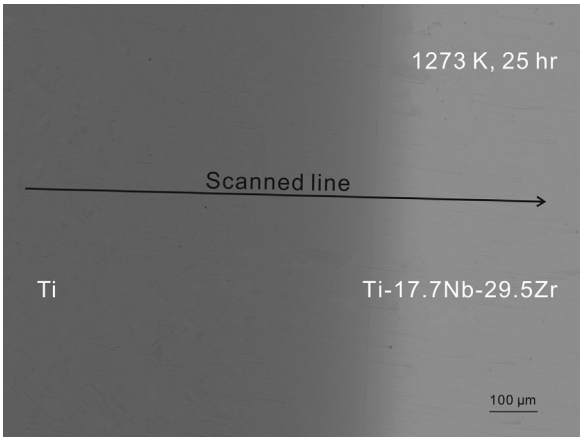

Fig. 1. Backscattered electron image of the microstructure of Couple 1 (C1, Ti/Ti–17.7Nb–29.5Zr) after annealing at 1273 K for 25 h.

corresponding to the thermodynamic descriptions [19]. However, the tracer and inter–diffusivities in bcc Ti–Nb and Ti–Zr alloys have been carefully reviewed by Liu et al. [16,17]. According to the literature review of Liu et al. [16,17], the experimental data in bcc Ti–Nb [20–24] and Ti–Zr [25,26] alloys can be adopted as the reliable data in the assessments of the atomic mobility parameters in bcc Ti–Nb and Ti–Zr systems.

Consequently, the objective of this study was to establish the reliable atomic mobility database in targeted bcc Ti–Nb–Zr system. Firstly, 5 solid diffusion couples of bcc Ti–rich Ti–Nb–Zr system at 1273 K were experimentally prepared and measured by using the electron probe micro analysis (EPMA). And then, the ternary interdiffusivities in bcc Ti–Nb–Zr alloys at 1273 K were efficiently determined by the Matano–Kirkaldy method [27]. Subsequently, the atomic mobility parameters for bcc Ti–Nb–Zr system were evaluated with the aid of the available thermodynamic descriptions [19], the mobilities of Ti–Nb [16], Ti–Zr [17] and Nb–Zr [18], the presently obtained ternary interdiffusivities in bcc Ti–Nb–Zr alloys and the carefully literature–reviewed experimental diffusion data in Ti–Nb [20–24] and Ti–Zr [25,26] sub–binary systems. Finally, the comprehensive comparisons between the experimental diffusion properties, including interdiffusivities, composition profiles and diffusion paths, and the calculated/model–predicted data were conducted to verify the reliability of the present mobilities.

2. Experimental method

Niobium (purity: 99.95 wt%), titanium (purity: 99.995 wt%) and zirconium (purity: 99.95 wt%) slugs purchased from Alfa Aesar (China) Chemicals Co., Ltd. were used as starting materials. The binary and ternary alloys in Ti–rich Ti–Nb–Zr system and pure Ti were prepared by arc melting under an Ar atmosphere using a non–reactive Welectrode (WKDHL–1, Opto–electronics Co., Ltd., Beijing, China). The buttons were re–melted for at least five times to improve their homogeneities. No chemical analysis for the alloys was conducted since the weight loss of each alloy during arc melting was less than 0.5 wt%. The buttons were linearly cut into blocks with the size of 5 × 5 × 2 mm^3. These blocks were ground by using SiC papers (120, 600, 1000, 1500 and 2000 grit), then sealed into an evacuated quartz tubes, and homogenized at 1273 ± 2 K for 7 days. All the samples were ground on SiC paper to remove surface contamination. Five diffusion couples of bcc Ti–rich Ti–Nb–Zr system prepared by Mo clamps in Table 1 were sealed into an evacuated quartz tubes, and annealed at 1273 ± 2 K for 25 h in an ELF1106–type furnace (Carbolite Gero Co., Ltd., United Kingdom). After standard metallographic treatment, the composition profiles of five diffusion couples were determined by using electron probe micro analysis (EPMA, JXA–8230, JEOL, Japan) with an accelerating voltage of 20 kV. Here, variations in alloy compositions were determined to be within ± 0.5 at% for each component.

3. Theoretical methodology

3.1. Matano–Kirkaldy method for ternary interdiffusivity

The interdiffusion flux of component k in a hypothetical 1–2–3 ternary system can be expressed in terms of two independent composition gradients by,

$$\tilde{J}_k = -\widetilde{D}^3_{k1}\frac{\partial c_1}{\partial x} - \widetilde{D}^3_{k2}\frac{\partial c_2}{\partial x}(k = 1, 2) \quad (1)$$

where element 3 is taken as the dependent solvent, c_k is composition of component k, the coefficients $\widetilde{D}^3_{11}$ and $\widetilde{D}^3_{22}$ are main interdiffusivities, while the coefficients $\widetilde{D}^3_{12}$ and $\widetilde{D}^3_{21}$ are cross interdiffusivities. To obtain the four interdiffusivities, one pair of diffusion couples with the diffusion paths intersecting at one common composition need to be use. Using the normalized composition variable Y ($Y(x) = \frac{c(x)-c_L}{c_R-c_L}$, here c_L and c_R are composition at the left and right far–ends, respectively), interdiffusion flux $\tilde{J}_k$ of element k referred to a fixed laboratory coordinate can also be evaluated at any section x' directly from the calculated composition profiles without a need for interdiffusivities [28]:

$$\tilde{J}_k = \frac{c^L_k - c^R_k}{2t}[Y'_k \cdot \int_{-\infty}^{x'}(1 - Y_k)dx + (1 - Y'_k)\cdot \int_{x'}^{\infty} Y_k dx] \quad (2)$$

where t is the diffusion time, the normalized composition variable Y'_k of element k at section x' is the value of $\frac{c(x')-c^L_k}{c^R_k-c^L_k}$, c^L_k and c^R_k are composition of component k at the left and right far–ends, respectively. By combining Eqs. (1) and (2), the four main and cross interdiffusivities at the common composition of the two diffusion couples can be determined by using the Matano–Kirkaldy method [27]. The corresponding standard deviation (SD) can be calculated by using the scientific statistical method [29,30].

3.2. CALPHAD method for atomic mobility

According to Andersson and Ågren [15], the atomic mobility for an element k in simple phases (i.e., disordered substitutional and substitutional–interstitial crystalline phases and disordered liquids), M_k, can be expressed as

$$M_k = \frac{1}{RT}\exp\left(\frac{\Phi_k}{RT}\right)^{mg}\Gamma \quad (3)$$

where R is the gas constant, T is the absolute temperature, and $\Phi_k = -Q_k + RTlnM^0_k$, with Q_k as the activation enthalpy and M^0_k as a frequency factor. Φ_k is generally dependent on the composition, temperature and pressure. $^{mg}\Gamma$ is a factor considering the ferromagnetic contribution to the diffusivity. Due to the low magnetic susceptibility, the ferromagnetic effect on the diffusivity in bcc Ti–Nb–Zr phase is neglected in the present work. In the spirit of the CALPHAD approach [31], the composition dependency of Φ_k can be represented by a linear combination of the values at each end–point of the composition space in a Redlich–Kister expansion as