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Ternary diffusion and thermodynamic interaction in the β solid solutions of Ti–Al–Fe alloys at 1423 K

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ABSTRACT

The binary interdiffusion coefficients $\tilde{D}_{(Ti-Fe)}$ in β Ti–Fe alloy and $\tilde{D}_{(Ti-Al)}$ in β Ti–Al alloy, Fe impurity diffusion coefficients $D^{*}_{Fe(Ti-Al)}$ in β Ti–Al alloys, and ternary interdiffusion coefficients $\tilde{D}^{Ti}_{AlAl}$, $\tilde{D}^{Ti}_{FeFe}$, $\tilde{D}^{Ti}_{AlFe}$ and $\tilde{D}^{Ti}_{FeAl}$ in Ti-rich β Ti–Al–Fe alloys were determined at 1423 K using binary and ternary diffusion couples by ordinary and extended Matano methods and Hall's one. The $\tilde{D}_{(Ti-Al)}$ values increase with Al concentration, and the $\tilde{D}_{(Ti-Fe)}$ values show almost no concentration dependence. The $D^{*}_{Fe(Ti-Al)}$ values in β Ti–Al alloys steeply decrease with Al concentration up to 7 at.%Al and become almost constant over about 7 at.%Al. In the ternary β Ti–Al–Fe alloys, the $\tilde{D}^{Ti}_{AlAl}$, $\tilde{D}^{Ti}_{FeFe}$, $\tilde{D}^{Ti}_{AlFe}$ and $\tilde{D}^{Ti}_{FeAl}$ values are positive, and the $\tilde{D}^{Ti}_{FeFe}$ and $\tilde{D}^{Ti}_{FeAl}$ values are larger than the $\tilde{D}^{Ti}_{AlAl}$ and $\tilde{D}^{Ti}_{AlFe}$ ones, respectively. They show the complicated dependence on concentrations of Al and Fe elements. The positive ratios of $\tilde{D}^{Ti}_{FeAl}/\tilde{D}^{Ti}_{FeFe}$ and $\tilde{D}^{Ti}_{AlFe}/\tilde{D}^{Ti}_{AlAl}$ indicate that the repulsive interactions exist between Al and Fe atoms in the ternary alloys, but the negative ratios of converted interdiffusion coefficients $\tilde{D}^{Al}_{FeTi}/\tilde{D}^{Al}_{FeFe}$ show the attractive interactions between Ti and Al and between Ti and Fe atoms in this alloy. These diffusion coefficients and data suggest that Al diffusion occur by vacancy diffusion mechanisms and Fe diffusion takes place by some kind of interstitial diffusion mechanism in β Ti–Al–Fe alloys.

1. Introduction

Various kinds of titanium and its alloys have been used as the aerospace materials and newly developed functional materials etc., because they have the high specific strength, excellent corrosion resistance and heat resistance when compared with steels. Most practical β-titanium alloys contain some β-stabilizing elements such as chromium, vanadium, niobium and molybdenum, and only α-stabilizing element of aluminum up to about 5 mass%Al as substitutional solute elements [1,2]. Unfortunately, the expensive elements such as vanadium and molybdenum are hampering the wide and practical use of these alloys. Moreover, in recent years, a part of Ti–Al–V alloys have been used as a biomaterial substituting of stainless steels, but it is pointed out that the vanadium element included in the Ti–Al–V alloy has a possibility of toxicity in biological body. Therefore the developments of new titanium alloys have been desired. One of the favored candidate for the new alloys is Ti–Al–Fe alloys which are substituted by non-toxic and economical Fe element for V in the Ti–Al–V alloys, so that various kinds of data on properties of the Ti–Al–Fe alloys have being accumulated for materials science and engineering until now.

The properties of alloys are closely related to their materials microstructures, and the development of the optimal microstructures is important for the improvements of performance and properties of alloys. The alloy microstructures are formed by working processes, thermomechanical treatments, heat treatments and so on. Especially, in thermomechanical treatments or heat treatments, the microstructures can be developed mainly by recovery, recrystallization, grain size growth, transformation and precipitation and so on, which are controlled by the diffusion phenomena in alloys. In recent years, a sintered Ti–Al–Fe alloys has been produced in vacuum and in the temperature range from 1273 K to 1573 K [3]. The sintering mechanisms are closely related by diffusion mechanisms of the constituting elements in the Ti–Al–Fe alloys. Therefore, the knowledge for diffusion mechanism and the diffusion coefficients of aluminum and iron elements in binary and ternary Ti alloys are indispensable to understand the some industrial processes and scientific diffusional phenomena during heat treatments and sintering of basic β-titanium alloys containing aluminum and iron [4,5].

Until now, many experimental studies on diffusion in binary titanium-base alloys containing α- or β-stabilizing elements have been performed [4–9], but, quite limited number of investigation have been made in Ti–V–Zr ternary alloys at 1073 K [10] and

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Ti–Al–Co ternary alloys at 1473 K [11] because the ternary diffusion experiments are a laborious and delicate work and the diffusion mechanisms and interaction of solute atoms in ternary alloys are complicated when compared with those of binary diffusion ones. Recently, the authors have reported a study of interdiffusion in Ti–Al–Fe alloys at 1473 K and a temperature dependence of impurity diffusion coefficients of Fe in Ti–Al alloys [12]. However, the interdiffusion coefficients of the Ti–Al–Fe alloys at 1423 K have not been determined. Furthermore, the discussion of the detailed diffusion mechanism have not been performed in the Ti–Al–Fe alloys at 1423 K.

The purposes of the present work are (a) to determine the binary and ternary interdiffusion coefficients in the β-Ti solid solution of the ternary Ti–Al–Fe alloys at 1423 K and the impurity diffusion coefficients of Fe in Ti–Al alloys at 1423 K, and (b) to estimate the thermodynamic interactions between solute–solute atoms (and solvent–solute atoms) in β-Ti–Al–Fe solid solutions at 1423 K.

2. Experimental

2.1. Diffusion couples and their concentration profiles

Eight kinds of binary alloy ingots and four kinds of the ternary alloy ingots were prepared with pure metals of 99.9 mass% sponge Ti, 99.99 mass%Al and 99.9 mass%Fe by an Ar arc melting, as listed in Table 1. It is considered that the composition of the binary and ternary alloys are in the β solid solutions of Ti–Al–Fe system at 1423 K, according to the Ti–Al [13], Ti–Fe [9] and Ti–Al–Fe [14] phase diagrams. These binary and ternary alloys are in the β solid solutions of Ti–Al–Fe system at 1423 K, according to the Ti–Al [13], Ti–Fe [9] and Ti–Al–Fe [14] phase diagrams.

The alloy bars were cut from the ingots and sealed into quartz capsules with argon gas about 20 kPa. They were annealed at 1473 K for 86.4 ks for homogenization, and then quenched into ice water. These homogenized alloy bars were cut into alloy plates of $10 \times 10 \times 3$ mm^3 in size, and then the surfaces of alloy plates were metallographically polished by SiC papers and 0.3 μm alumina powder. Immediately after the polishing, ternary and binary diffusion couples were assembled from these polished plates by means of stainless steel clamps according to twelve kinds of combinations of alloys as listed in Table 1, and then these assembled diffusion couples were sealed into a quartz capsule with argon gas about 20 kPa and a small amount of sponge titanium enclosed a tungsten foil for an oxygen getter. They were annealed for diffusion treatments in the temperature range at 1423 K for 23.95 ks, and then quenched in ice water after the annealing. The annealed diffusion couples were mounted in synthetic resin, and cut in half parallel to the diffusion direction in order to expose sections which suffered no oxidation and evaporation of elements. The sections of diffusion couples were metallographically polished. The characteristic X-ray intensities of Al and Fe parallel to the diffusion direction were measured on the polished surface of these diffusion couples by a JEOL JXA-8900 electron microanalyzer (EPMA), and they were converted to solute concentration profiles of Al and Fe elements by correction for atomic number, absorption and fluorescence effects, using the bulk alloy compositions at the ends of the couples as standards [15,16].

2.2. Diffusion coefficients

The binary interdiffusion coefficients $\widetilde{D}_{(\text{Ti-Al})}$ in Ti–Al alloys and $\widetilde{D}_{(\text{Ti-Fe})}$ in Ti–Fe alloys were determined from the concentration profiles in binary diffusion couples (J1 and J2) by using ordinary Matano method [17]. The binary interdiffusion coefficients $\widetilde{D}_{(\text{Ti-Al})}$ and $\widetilde{D}_{(\text{Ti-Fe})}$ were determined by the following equations.

Table 1
Terminal compositions of diffusion couples in Ti–Al–Fe alloys (at.%).

Ternary diffusion couples	
G1	Ti/Ti–3.5Al–13.5Fe
G2	Ti/Ti–7.0Al–10.5Fe
G3	Ti/Ti–10.5Al–7.0Fe
G4	Ti/Ti–13.5Al–3.5Fe
H1	Ti–3.5Al/Ti–3.5Fe
H2	Ti–7.0Al/Ti–7.0Fe
H3	Ti–10.5Al/Ti–10.5Fe
H4	Ti–13.5Al/Ti–13.5Fe
Binary diffusion couples	
J1	Ti/Ti–13.5Al
J2	Ti/Ti–13.5Fe

$$\widetilde{D}_{(\text{Ti-Al})} = -(1/2t)(\partial x/\partial C_{Al}) \int_{C_{Al}^{(-\infty)}}^{C_{Al}} x dC_{Al} \quad (1)$$

$$\widetilde{D}_{(\text{Ti-Fe})} = -(1/2t)(\partial x/\partial C_{Fe}) \int_{C_{Fe}^{(-\infty)}}^{C_{Fe}} x dC_{Fe} \quad (2)$$

On the other hand, the ternary interdiffusion coefficients in the Ti–Al–Fe alloys were evaluated from the concentration profiles in ternary diffusion couples (G1, G2, G3, G4, H1, H2, H3 and H4) by using the extended the Matano–Kirkaldy method [18,19].

$$\int_{C_i^{(-\infty)}}^{C_i} x dC_i = -2t \sum_{k=1}^{2} \widetilde{D}_{ik}^3 \partial C_k / \partial x \quad (i = 1, 2) \quad (3)$$

where C_i is the concentration of solute i (i = 1, 2), $C_i^{(-\infty)}$ and $C_i^{(+\infty)}$ the terminal compositions at the ends of the diffusion couples, $\widetilde{D}_{ii}^3$ the main interdiffusion coefficients, $\widetilde{D}_{ik}^3$ the cross interdiffusion coefficients (the superscript 3 is denoted as the solvent, Ti), t the diffusion time, and x the distance from the Matano interface located at x = 0. This Matano interface can be determined for concentration profile from the following relation:

$$\int_{C_i^{(-\infty)}}^{C_i^{(+\infty)}} x dC_i = 0 \quad (i = 1, 2). \quad (4)$$

The four interdiffusion coefficients in Eq. (3) are evaluated at the common compositions of intersection (C_1 and C_2) of the diffusion paths in two independent diffusion couples.

In addition, the impurity diffusion coefficients of Fe, $D^*_{Fe(\text{Ti-Al})}$, in Ti–Al alloys were determined from the Fe concentration profiles in ternary diffusion couples (H1, H2, H3 and H4) by the Hall's method [20,21]. At the concentration extremes, the impurity diffusion coefficients of Fe in Ti–Al alloys can be evaluated by the Hall's method. The following relationship between the limiting value of $\widetilde{D}_{ii}^k$ on the j–k side and impurity diffusion coefficient $D^*_{i(j-k)}$ in a binary j–k alloy has been derived by Shuck and Tool [22] as follows.

$$\lim_{C_i \to 0} \widetilde{D}_{ii}^k = D^*_{i(j-k)} \quad (5)$$

Eq. (5) indicates that the limiting main coefficient $\widetilde{D}_{ii}^k$ at $C_{Fe} \approx 0$ is equal to the $D^*_{Fe(\text{Ti-Al})}$. The application of Hall's method enable us to obtain the accurate values of limiting main coefficient $\widetilde{D}_{ii}^k$ at $C_{Fe} \approx 0$ from the Fe concentration extremes of the profiles obtained from the Ti–Al sides of the diffusion couples H1–H4 in this work. This application of the Hall's method to the analysis for these impurity diffusion coefficients, that is, $D^*_{Fe(\text{Ti-Al})}$ in a binary Ti–Al alloy, has already been described elsewhere [23].

3. Results

3.1. Microstructures of diffusion couples

Fig. 1 shows scanning electron micrograph of the diffusion zone of the diffusion couple (G2) annealed at 1423 K for 23.95 ks which is eched by hydrochloric, nitric and hydrofluoric acids in order to exposure clearly the original interface and microstructure. In Fig. 1, small voids formed by eching which are arrayed in straight

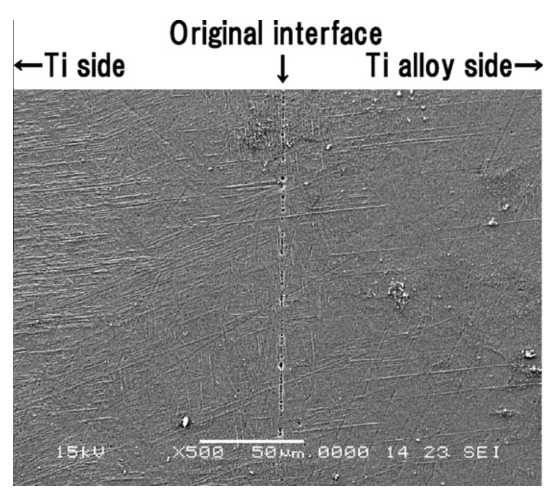

Fig. 1. Scanning electron micrograph of diffusion couple G2 at 1423 K for 23.95 ks.