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DISTRIBUTION OF SOLUTE NEAR THE ALPHA PLATES FORMED IN TITANIUM BINARY ALLOYS

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The partitioning of solute from α plates formed in Ti-5.1at.%Fe, Ti-5.4at.%V and Ti-2.6at.%Fe alloys has been investigated theoretically. These plates grow isothermally from solid solution in titanium binary alloys. The idea was to clarify whether they grow without diffusion or whether the partitioning of solute occurs after transformation. To check whether the latter mechanism is plausible, calculations have been conducted of the diffusion profile of solute and of the time required for the plate to achieve its equilibrium composition. The model based on a finite difference (FD) technique was used for the calculations. The results have been compared with the published experimental data and with that obtained using analytical technique.

Keywords: Titanium alloys, Solute, Partitioning, Transformation, Diffusion

1. Introduction

Pure titanium melts at 1670ºC and has a density of 4.51 g cm^{-3}. It should, therefore, be ideal for use in components which operate at elevated temperatures, especially where large strength to weight ratios are required. The crystal structure of titanium at ambient temperature and pressure is close-packed hexagonal (α) with a c/a ratio of 1.587. At about 890ºC, the titanium undergoes an allotropic transformation to a body-centred cubic β phase which remains stable to the melting temperature. Although "commercially pure" titanium has acceptable mechanical properties and has been used previously for orthopedic and dental implants, for most applications titanium is alloyed with small amounts of aluminum and vanadium etc., typically 3% and 2.5% respectively, by weight [1,2]. Titanium alloys have very high tensile strength and toughness (even at extreme temperatures), light weight, extraordinary corrosion resistance, and ability to withstand extreme temperatures. However, the high cost of both raw materials and processing limit their use to military applications, aircraft, spacecraft, medical devices, and some premium sports equipment and consumer electronics. In titanium alloys, the proeutectoid reaction product often has a plate morphology. Considerable attention has been paid to the mechanism of plate formation by a number of researchers [3-5]. Because of the surface relief effect usually accompanied and other features as well, it was considered that the diffusionless shear is operative mechanism in the formation of such plates [6,7]. This implies that the formation process is essentially the repetition of displasive interfacial motion and for subsequent redistribution of solute in the region swept by interface [8-14]. The kinetics of supersaturated bainite plates of Ag-Cd alloy has been discussed by Mujahid and Bhadeshia [15]. The concentration gradient during the partitioning of solute from plate to neighbouring matrix in Ti-V and Ti-Fe alloys is being investigated in this analysis.

According to the Aziz model [16,17] for solute trapping the partitioning coefficient can be written as:

$$K_p = \frac{c^{\alpha}}{c_l^{\beta}} = \frac{1+\eta K_e}{1+\eta} \qquad (1)$$

where $\eta = D/\lambda V$, c^{α} and c_l^{β} are the solute compositions in α plate and in the matrix at the interface, respectively. D, λ and V are the diffusivity of solute in Ti-V alloys, interatomic spacing and interface velocity, respectively. The equilibrium partitioning coefficient [16, 17] is:

$$K_e = \frac{c^{\alpha\beta}}{c^{\beta\alpha}} = 0.21 \qquad (2)$$

where $c^{\alpha\beta}$ and $c^{\beta\alpha}$ are the equilibrium solute compositions in the plate and matrix respectively for Ti-5.4at.%V alloy at the transformation

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temperature of 680 °C. Using the values of D, interatomic spacing λ, and V as 3.97×10^{-16} m^{2}s^{-1} [18, 19], 0.25 nm [16-17] and 2.27×10^{-7}ms^{-1} [20] respectively, the following value of partitioning coefficient has been calculated :

$K_p = 0.938 \approx 1$

Which means that there is almost no partitioning of vanadium during the growth of α plates. This could support the idea that the plates grow with an excess of solute. The solute may then diffuse to the neighbouring matrix during ageing. In the present work the finite difference (FD) technique is used to examine the partitioning of solute from the plate into the adjacent matrix. The analytical model [21] has also been applied for this analysis. The presence of oxygen in any Ti-based alloy may affect the partitioning behaviour because of V-O and Fe-O affinity. In the present analysis it is assumed that the Ti-alloys (specially Ti-Fe alloys) contains very low level of oxygen. Hence this effect is not included in the calculations.

2. The Diffusion Coefficients

The diffusion coefficient is given by the following Arrhenius equation.

$$D=Ae^{-Q/RT} \tag{3}$$

where A and Q are the frequency factor and activation energy respectively. R is a constant having the value of 8.31451 Jmol^{-1}K^{-1} The values of A, Q and temperature range for Ti-V and Ti-Fe are given in Table 1.

Table 1. Values of A, Q and temperature range.

Diffusion of	A (m^2 s^{-1})	Q (kJmol^{-1})	Temperature (K)
Fe in Ti (α)	1.2×10^{-8}	110.5	973 – 1123 [22]
Fe in Ti (β)	5.6×10^{-7}	131.0	1273 – 1473 [22]
V in Ti (β)	1.25×10^{-6}	173.3	1173 – 1573 [18,19]

2.1. Analytical models

Model by Enomoto and Fujita [23]

In the diffusionless mechanism of plate formation, it is postulated that plates are formed with supersaturation of of solute - in an extreme case with a composition identical to the matrix - and subsequently, some atoms are quickly drained from the plates. It is useful to estimate the time taken for solute atoms to diffuse away to attain the near equilibrium solute concentration in the plate. The diffusion geometry of this model is shown in Fig. 1.

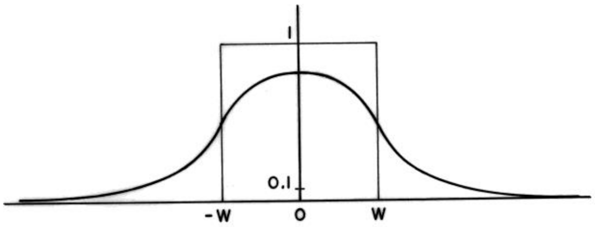

Figure 1. Diffusion geometry taken by M. Enomoto and Fujita [23] for the calculation of time.

Under the assumption that the diffusivity of solute (D) in the plate and the matrix is the same, the concentration of solute at distance *x* from the centre of the plate and at time *t* was given as [24]:

$$c = \frac{c_0}{2}\left[\operatorname{erf}\left(\frac{W+x}{2\sqrt{Dt}}\right) + \operatorname{erf}\left(\frac{W-x}{2\sqrt{Dt}}\right)\right] \tag{4}$$

where c_0 is the height of the initial concentration and erf(ξ) is the error function. *W* is the half width of α plate i.e. $\omega_\alpha/2$. The time at which the concentration at the centre of the plate falls to one-tenth of c_0 may then be estimated from the following equation:

$$\tau_{0.1} \sim \frac{1}{D}\left(\frac{\omega_\alpha}{0.18}\right)^2 \tag{5}$$

This model also assumes that the compositions of alpha and beta are equal at the interface.

Model by Bhadeshia [21]

An analytical approximation [21], has also been applied to the titanium alloy. During β transformation of Ti-V and Ti-Fe alloys, the plates appear to be different in composition from the parent phase. The partitioning of solute from plate into the β matrix occurs after the formation of α plate. For a plate thickness , it is assumed that the flux of solute is one dimensional normal to the a/β interface. The time taken to diffuse all of the excess solute from α plate into the β matrix, t, is given by the following equation [21].

$$t^{0.5} = \frac{\omega_\alpha(\bar{c}-c^{\alpha\beta})\pi}{4(D^\beta)^{0.5}(c^{\beta\alpha}-\bar{c})} \tag{6}$$

where D^β is diffusivity of solute in β matrix, $\bar{c}$ is the average concentration of solute in the alloy, $c^{\alpha\beta}$ and $c^{\beta\alpha}$ are the equilibrium solute concentrations in the α plate and β matrix respectively. In this model, it is assumed that the diffusion coefficient of solute in the plate is much higher than that of the matrix.

2.2. Finite difference model

The escape of solute from the α plate to matrix is examined here using a finite difference as discussed by Crank [25]. The matrix-plate aggregate is treated as a composite diffusion couple in which flat slabs of matrix, each of thickness are welded on either side of a slab of plate of thickness , Fig. 2. The slab dimensions were chosen to compare the results with earlier published work [23]. The model assumes a one dimensional diffusion process ahead of a planar/interface, and is symmetrical about the centerline so that only half the couple needs to be considered in the finite difference analysis [26].

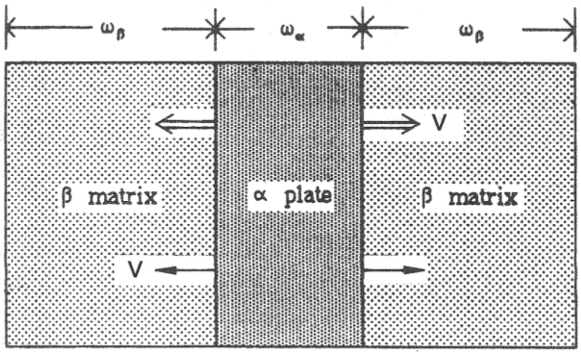

Figure 2. Schematic illustration of the plate/matrix diffusion couple.

The matrix and plate regions were divided into a number of slices n_β and n_α, respectively, with

$$\omega_\beta^s = \omega_\beta / n_\beta \tag{7}$$

$$\omega_\alpha^s = \omega_\alpha / n_\alpha \tag{8}$$

A compromise has to be made between accuracy and computer time in the choice of the number of slices. The larger the number of slices, the greater the accuracy of the method, although the calculations are then more expensive in terms of computing time. The choice of n_β, is initially made arbitrarily, so that can be calculated. This in turn leads to the time t, representing the interval between successive recalculations of the concentration profile of the whole couple:

$$t = r_\beta \frac{\left(\omega_\beta^s\right)^2}{D_V^\beta} \tag{9}$$

where r_β is a grid parameter in the finite difference method, which can be set to a smaller value for higher accuracy. Having thus fixed the interval t, the thickness of the α plate follows as

$$\omega_\alpha^s = \left(t D_V^\alpha / r_\alpha\right)^{0.5} \tag{10}$$

where r_α is another dimensionless grid parameter, this time for a plate, which in the present work is taken to be the same as r_β. The finite difference analysis is carried out using non-dimensional variables, the concentrations *c* and distances ω being normalized with respect to average concentration in the alloy and the thickness of matrix, respectively [25]. The normalized variables are defined as follows

$$\omega' = \omega / \omega_\beta \tag{11}$$

$$c' = c / \bar{c} \tag{12}$$

$$t' = Dt / \left(\omega_\beta\right)^2 \tag{13}$$

where D is the diffusion coefficient. Since the α plate occupies space $0 \leq \omega' \leq (\omega_\alpha / 2\, \omega_\beta)$, the region is covered by a grid of rectangles of sides $\delta\omega'$ and $\delta t'$. The coordinates of a grid point (ω', y') can be written $(j\delta\omega', j\delta t')$, where *i* and *j* are integers. The normalized concentration at that point (for the α plate) is written $c_{i,j}^{\prime\alpha}$

The explicit finite difference formula is then given by Crank [25] :

$$c_{i,j+1}^{\prime\alpha} = c_{i,j}^{\prime\alpha} + r_\alpha \left(c_{i-1,j}^{\prime\alpha} - 2c_{i,j}^{\prime\alpha} + c_{i+1,j}^{\prime\alpha}\right) \tag{14}$$

where $r_\alpha = \delta t' / (\delta\omega')^2$ is a grid parameter for the finite difference method. The normalized concentration c'^{α} in the α/β interface has been taken as $c^{\alpha\beta}/\bar{c}$. Relationship (14) has been used to calculate the value of c at all points along successive time rows of the grid, for the initial concentrations $c_{0,0}^{\prime\alpha} = c'^{\beta}/\bar{c}$ and $c_{i,0}^{\prime\alpha} = 1$ for all $i > 0$.

A similar analysis was carried out for the matrix, and the diffusion processes in the plate and matrix were related by using the mass conservation condition which ensures that the amount of vanadium leaving the plate at any instant is identical to that entering the matrix (i.e. the fluxes to and from the interface must be equal):

$$D_V^{\beta}\left(c_{0,j}^{\prime\beta}-c_{i,j}^{\prime\beta}\right)=D_V^{\alpha}\left(c_{1,j}^{\prime\alpha}-c_{0,j}^{\prime\alpha}\right) \qquad (15)$$

where $c_{i,0}^{\prime\beta}=1$ for all $i>0$. Thus the value of $c_{i,0}^{\prime\beta}=1$ can be obtained by using the above equation.

3. Results and Discussion

The finite difference (FD) technique is employed for the calculation of diffusion equation in order to study the partitioning of solute from the plates to the matrix. These results were compared with that of Enomoto and Fujita [23]. The diffusion profile at the plate interface given by Enomoto and Fujita [23] is based on the experimental data whereas their results of time to escape solute from plate are based on a theoretical model. Therefore, the finite difference results of diffusion profile were compared with the experimental data of Enomoto and Fujita [23]. The FD results of time to escape solute from plate and the results of Bhadeshia analytical model [21] were compared with that of Enomoto and Fujita [23]. The earlier theoretical results of Enomoto and Fujita [23] show that the time at which the concentration at the centre of the plate falls to one – tenth of c_0 ($\tau_{0.1}$) is larger than the time actually needed for each plate to grow to the observed thickness. They regard this as reasonable because the redistribution of solute after the plate formation requires the diffusion of atoms from the interior of the plates and thus, may take a longer time than the diffusion driven by the steep concentration gradient at the advancing interface as postulated by the diffusional mechanism. The semi-infinite model applied by Enomoto and Fujita is based on the simplest set of assumptions. Therefore, this model is not realistic for the compositions across the α/β interface, where interfacial equilibrium is expected so that the compositions of alpha and beta are not equal at the interface. Hence this model may not give precisely accurate results.

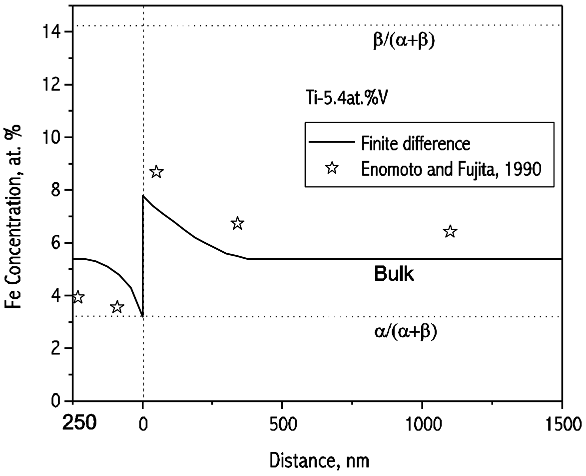

Figure 3. Comparison between calculated and measured profile [23] normal to α/β interface in the Ti-5.4 at.% V alloy reached at 680 °C for 30 s.

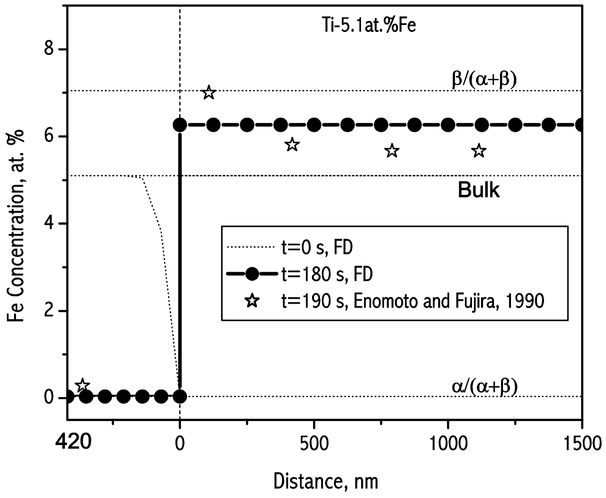

Figure 4. Comparison between calculated and measured profile [23] normal to α/β interface in the Ti-5.1 at.% Fe alloy reached at 730 °C for 180 s.

A rather different approach was used by Bhadeshia [21] in which solute atoms are depleted from the plates. As in case of ferrous alloys [26], the analysis based on this model may not be completely satisfactory given that it does not allow for the coupling of fluxes at the α/β interface. It, therefore, contains nothing about diffusion in the plate. The Bhadeshia model represents a situation where the diffusivity is two orders of magnitude larger in the plate than in the matrix. Therefore, the diffusion with the plate can be ignored so that elemental redistribution is dominated by diffusion through the matrix. This also relaxes the interfacial condition balancing the flux across the interface and the concentration gradients either side of the interface. These conditions do not apply to the Ti-V or Ti-Fe systems. Because of these limitations, this model may not give satisfactory results.

The finite difference (FD) model is able to deal with the interfacial equilibrium and different diffusivities and is cable to give good fit as long as the fluxes are balanced. It takes into account the coupling of fluxes in the β matrix and α plate through equation 15. For Ti-Fe alloys different diffusion coefficients for α and β phases were used whereas for Ti-V alloy the diffusion coefficient of vanadium in α phase is assumed to be same as in β phase. Typical concentration gradients that develop during the partitioning process for a freshly formed plate for Ti-5.4 at.%V of 500 nm projected length and aged for 30 s is illustrated in Fig. 3 and for Ti-5.1 at.%Fe of 840 nm projected length and aged for 180 s is illustrated in Fig. 4. The figures compare the calculated profile with the earlier data of Enomoto and Fujita [23]. The comparison shows the agreement upto certain degree. The trend in both the data is however the same. For Ti-5.4 at.%V alloy, both theoretical and experimental data [23] show that the vanadium concentration in β matrix increases gradually as the interface is approached. In α plate, the experimental concentration decreases more rapidly than the calculated data from the middle of the plate towards the interface. However in FD results no partitioning is observed for Ti-5.1 at. %Fe at an ageing of 180 seconds whereas the data of Enomoto and Fujita shows some partitioning, as shown in Fig. 4.

The time taken to escape solute from plate to matrix at a variety of temperatures has also been calculated. Fig. 5 illustrates the time taken to diffuse all the excess Fe to β matrix versus different transformation temperatures in Ti-5.1 at %Fe alloy. The time taken to diffuse all the excess Fe to β matrix versus transformation temperatures in Ti-2.6 at %Fe alloy is shown in Fig. 6. For both of Ti-Fe alloys, the comparison of the values calculated using the finite difference method with those calculated by the analytical method [21] shows that the analytical model by Bhadeshia [21] underestimates the diffusion time. This is due to the fact that the Bhadeshia model does not take into account the coupling of fluxes at the interface.

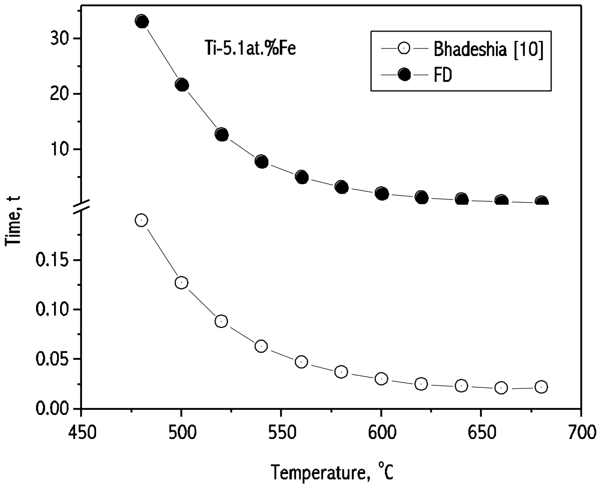

Figure 5. Time taken for excess Fe to diffuse to the neighboring matrix as a function of temperature in Ti-5.1at.%Fe.

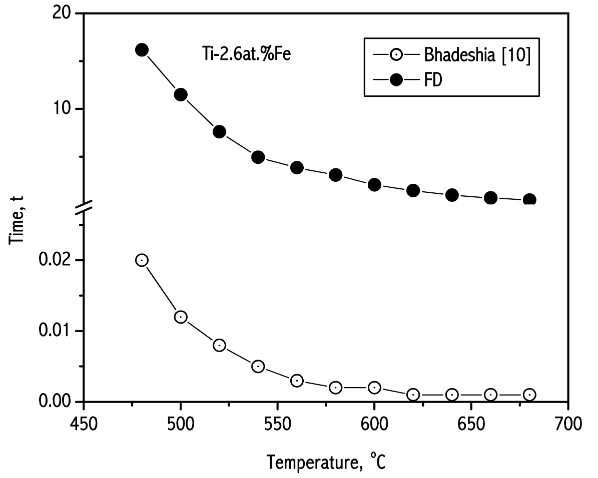

Figure 6: Time taken for excess Fe to diffuse as a function of temperature from the α plates of Ti-2.6at.%Fe.

4. Conclusions

The partitioning of excess solute from a plate in the titanium binary alloys have been examined. For Ti-5.4 at %V alloy, both theoretical and earlier experimental results of Enomoto and Fujita [23] show that the vanadium concentration in β matrix increases gradually as the interface is approached. In case of Ti-5.1 at.%Fe alloy, the FD profile shows that the plate has been depleted before the ageing time of 180 s whereas data of Enomoto and Fujita still show some partitioning. The anlytical data of Bhadeshia model for Ti-5.1 at.%Fe and Ti-2.6 at %Fe alloys underestimates the time to diffuse excess Fe to β matrix at various transformation temperatures because it do not take into account the coupling of fluxes at the α/β interface. However, the trends of both types of results are similar.

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