INTERDIFFUSION IN TITANIUM-IRON SYSTEM

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Synopsis

The present paper reports interdiffusion studies in titanium-iron system using pure metal and incremental couples in the temperature range of 850-1050°C. The diffusion zone exhibits a very steep concentration gradient between 20-80at% of titanium in the temperature range of γ-phase. The steep concentration gradient is also associated with the absence of either of the phases - FeTi as well as Fe_2Ti - present in the phase diagram of the system. Incremental couples with pure iron and FeTi exhibits the formation of Fe_2Ti phase in the diffusion zone when annealed in the temperature range of α-phase but no compound in the temperature of γ-phase. Diffusion coefficients in this system are characterized by high values of frequency factor and activation energies.

An analysis of thermodynamic as well as kinetic factors affecting the occurrence of the phases in the diffusion zone has been made. It has been concluded that kinetic considerations are more significant in controlloing the microstructure of the diffusion zone. The variation of interdiffusion coefficients with composition is discussed on the basis of solidus temperature. Inter-relationship between interdiffusion parameters is also discussed on the basis of Zener relationship.

Introduction

It is well known that chemical diffusion in homogeneous binary systems results in diffusion zones which can be analysed following Darken's hypothesis[1]. A rigorous analysis is possible in these cases as several simplifying assumptions in the original treatment have been removed by subsequent workers [2] . The situation regarding diffusion in heterogeneous binary systems is rather markedly different. In these cases, the diffusion zone may or may not exhibit layer growth of intermetallic phases. It is, however, not possible to predict the same as no acceptable selection rule for occurrence of phases in diffusion zone are known. On the basis of phase diagrams also, multiphase composition in the diffusion zone can only be visualized without any certainity of its being true.

Iron-titanium is a heterogeneous binary alloy system exhibiting two intermetallic phases namely FeTi and Fe_2Ti. Interdiffusion studies in FeTi system by Hirano et al [3] and Tsuji [4] have, however, shown quite contradictory results. Whereas, the formation of both the phases in the diffusion zone is reported by Tsuji [4] , Hirano et al [3] did not observe these features. Present studies were undertaken to resolve the anomaly of these earlier investigations. For this purpose, diffusion couples were annealed in both α - and γ - temperature range of iron and examined by both microscopic techniques and electron probe microanalyser. The thermodynamic and kinetic considerations which determine the microstructure of diffusion zone and also composition dependence of interdiffusivity $\tilde{D}$ for this system is presented here.

Experimental Procedure

The studies involved several steps like preparations of 'sandwich' type couples, diffusion annealing and determination of concentration-penetration profiles. Diffusion couples prepared from 99.99% pure iron and electron beam melted iodide grade titanium and incremental couples with pure iron & FeTi were diffusion annealed in vacuum (better than 19^{-5} mm Hg) in 850-1060°C temperature range for durations varying from 5 to 1000 hrs. The diffusion couples were polished to a metallographic grade and analysed with the help of geoscan electronprobe microanalyser operating at 25 KeV, to establish the concentration-penetration profiles of iron and titanium across the diffusion zone. Intensities of Ti K_α (λ=2.749A°) diffracted by a quartz crystal and Fe K_α (λ= 1.937 A°) by a LiF crystal were recorded both on chart as also by a step counting method. The same were converted into respective atomic fractions and employed to establish concentration-penetration profiles. The latter were analysed in accordance with Boltzmann-Matano equation:

$$\tilde{D} = -\frac{1}{2t}\frac{dx}{dc}\int_0^c x\,dc \tag{1}$$

to yield diffusivity values. For this purpose the Matano interface for the diffusion was established and designated as the origin (x = o). The slope (dx/dc) and values of integral $\int_{o}^{c} x\,dc$ were evaluated graphically at various concentrations and substituted in equation 1 for calculating $\tilde{D}$. To obtain reproducibility of diffusion data, six concentration profiles were examined for each temperature.

Results

a) Microstructure and Concentration Profiles

Despite the presence of compounds FeTi and Fe_2Ti in the phase diagram, none of these phases appear in the diffusion zone of couples with pure Fe & Ti or incremental couple of Fe and FeTi annealed in temperature range of γ-Fe (above 900°C). The fact was confirmed with the help of EPMA and optical microscopy. The typical concentration penetration profile for titanium and iron for the diffusion couple annealed at 959°C for 18 hours is shown in Fig.1. The absence of phases is accompanied by the very steep concentration gradient from 20-80 at%Ti.

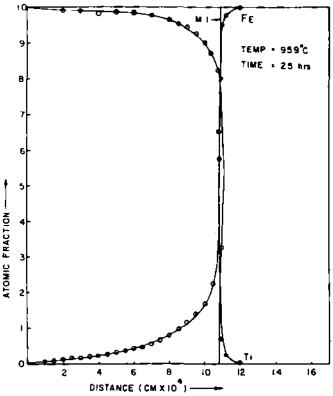

Fig.1 : Concentration profile for Ti & Fe in γFe-Ti couple.

Microstructure of diffusion couple of Fe & FeTi annealed in temperature range of α-Fe shows the occurrence of intermetallic compound in the zone. (Fig.2). The concentration-penetration profiles also show the formation of Fe_2Ti compound by a step of constant concentration (Fig.3).

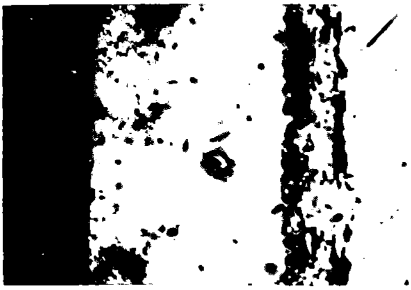

Fig.2: Photomicrograph of the α-Fe - FeTi couple annealed at 860°C for 1056 hrs. (120 X)

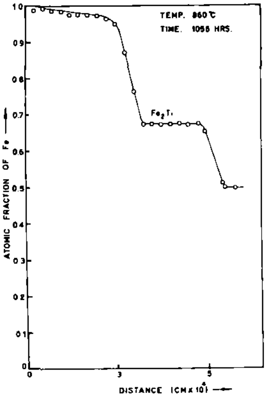

Fig.3 : Concentration profile for Fe in α-Fe-FeTi couple.

b) Temperature and Composition Dependence of $\tilde{D}$

Concentration penetration profiles obtained from γ-Fe-Ti diffusion couples were typical of a solid solution and hence interdiffusion coefficients were evaluated by employing Boltzmann-Matano method at various compositions (Table 1).

Table 1

The Values of Interdiffusion Coefficients at various temperatures and concentrations for γ-Fe-Ti system

Temperature	892°C	916°C	959°C	982°C	1023°C
Composition at pct.Ti	Interdiffusion coefficient $\tilde{D}$ cm^2/sec.				
	$X10^{12}$	$X10^{12}$	$X10^{12}$	$X\ 10^{11}$	$X10^{10}$
20	2.9	6.92	7.94	4.27	1.51
40	4.79	10.5	13.8	6.61	1.86
60	5.75	14.1	18.6	8.71	2.04
80	7.59	17.0	19.5	10.7	2.04
90	672.0	1910.0	3390.0	151.0	229.0

The temperature dependence of these diffusion coefficients can be described by Arrhenius expression of the type $\tilde{D} = \tilde{D}_0 \exp(-Q/RT)$. The values of activation energy (Q) and frequency factor ($\tilde{D}_0$) have been evaluated from the slopes and intercepts by linearly fitting log $\tilde{D}$ vs 1/T using least mean square method and listed in Table 2.

Table 2

Activation energy and frequency factor at various compositions for γ-Fe-Ti system

Composition of Ti (at%)	$\tilde{D}_0$ (cm^2/sec.)	$\tilde{Q}$ (Kcal/mole)
20	1.9×10^5	93.48 ± 16.1
40	1.35×10^4	82.63 ± 13.8
60	7.48×10^3	80.69 ± 12.8
80	1.06×10^3	75.58 ± 14.6
90	1.71×10^6	81.85 ± 11.4

Discussions

1. Formation of intermetallics in the diffusion zone

These studies show that diffusion zone of couples annealed in the temperature range of γ-Fe do not reveal any intermetallic phase whereas diffusion zone of couples annealed in α-Fe temperature range exhibits the occurrence of Fe_2Ti phase. In principle, thermodynamics and kinetics are the two considerations responsible for formation or absence of any phase in diffusion zone.

a) Thermodynamic Considerations

Whether a particular composition will exist as a solid solution on a compound depends upon its free energy. The solid solutions are formed at higher energies whereas the ordered structure as obtained in the compound formations is realized at lower energies. Even when the constituent elements are present in the correct proportions, the nucleation of a phase in the diffusion zone may be inhibited due to the fact that the considerations of equilibrium thermodynamics which govern the occurrence of phases in the phase diagram are modified in the diffusion zone. Concentration gradient, elastic strain energy, interfacial energy, vacancy supersaturation and dislocation multiplication modify the free energies of alloy in the diffusion zone.

Estimation of free energy rise of FeTi in the diffusion zone of γ-Fe-Ti couple at 959°C shows that contribution from vacancy supersaturation is significant and total increase in the free energy is around 16 Kcal/mole. This increase in the free energy of the alloy in the diffusion zone is large enough to compensate for decrease expected on account of compound formation, ($\Delta H = 4.85$ Kcal/mole). Hence, thermodynamically possibility of compound formation during diffusion in γ-Fe-Ti does not exist. Eventhough the thermodynamic conditions are made slightly favourable by using incremental couples of γ-Fe and FeTi compound, these couples do not reveal the occurrence of Fe_2Ti phase. This shows that thermodynamic conditions have a very little influence on the occurrence of phases in the diffusion zone.

b) Kinetic Considerations

The viable nucleus of any phase occurring in the phase diagram could be formed at the corresponding compositions, in the diffusion zone provided it is allowed by the free energy considerations discussed in the previous section. However, the phase will grow only if the flux of species leaving the phase is smaller than the flux entering the phase. For example, in case multiphase diffusion had led to the formation of intermetallic phases in zone, the schematic concentration profile would have been as shown in Fig.4. Further in such cases, the flux of species at a phase boundary (P) would be given by the equation

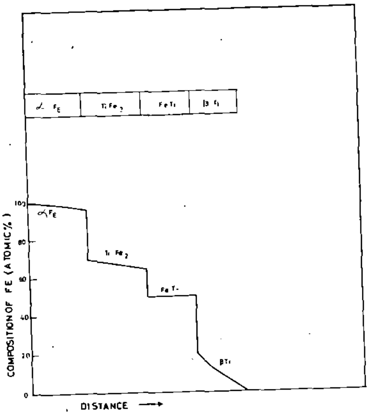

Fig.4

$$J_P = -D_P \left(\frac{\partial c}{\partial x}\right)_P \qquad \ldots (2)$$

where J_P is the flux of atoms, D_P is intrinsic diffusion coefficient and dc/dx is the concentration gradient at the phase boundary.

Flux of Fe atoms has been calculated in the γ-Fe-Ti couple annealed at 959°C using equation 2. In the absence of thermodynamic data on activities in this system and due to the fact that thermodynamic factor α is of the order of unity, tracer diffusion data was used instead of intrinsic diffusivities. Diffusion coefficients of Fe^{59} by Shinayev [5], extrapolated Tomlin's [6] data for diffusion of Fe^{59} in Fe-20 Ti% alloy and actual concentration gradients from profile (Fig.1) were employed for the purpose. Table 3 lists the flux of Fe atoms.

Table 3

Flux of Fe atoms in γ-Fe-Ti couple at 959°C

Phase	D_{Fe} $cm^2/sec.$	dc/dx atomic fraction/cm	Flux No. of $atom/cm^2/sec.$	
			Entering the phase	Leaving the phase
α -Fe	6.49×10^{-13}	666.67	4.68×10^{12}	-
	5.7×10^{-10}	1.35×10^{5}	-	8.4×10^{14}
Fe_2Ti	5.79×10^{-13}	-do-	8.4×10^{14}	-
	9.61×10^{-12}	-do-	-	1.39×10^{16}
FeTi	9.61×10^{-12}	-do-	1.39×10^{16}	-
	1.38×10^{-9}	-do-	-	2×10^{18}

The table shows that flux of Fe atoms entering the phases α-Fe, Fe_2Ti and FeTi would be smaller by two orders of magnitude than the flux leaving these phases. Hence the phases could not have grown in the diffusion zone even after nucleation.

Similarly, the values for Fe atoms in incremental couple of α-Fe and Fe-Ti compound, annealed at 860°C, have been evaluated (Table 4).

Table 4

Flux of Fe atoms in α-Fe - Fe-Ti couple at 860°C

Phase	D_{Fe} $cm^2/sec.$	dc/dx atomic fraction/cm	flux No. of $atoms/cm^2/sec.$	
			entering the phase	leaving the phase
	1.98×10^{-11}	666.67	1.43×10^{14}	
Fe_2Ti	3.98×10^{-14}	-do-	-	2.86×10^{11}

Table 4 shows the flux of Fe atoms entering the Fe_2Ti phase is greater than that leaving the phase and as such the phase grows in the diffusion zone.

Thus, it may be concluded that kinetic considerations are more significant in controlling microstructure of the diffusion zone.

2. Concentration Dependence of $\tilde{D}$

Interdiffusion coefficients for γ-Fe-Ti couples at various temperatures and concentrations have been tabulated in Table 1. It shows that $\tilde{D}$ increases gradually with increase in Ti content in Fe rich side up to 80at%Ti. In Ti rich side $\tilde{D}$ increases with decrease in Fe content beyond 80 at%Ti.

According to Birchenall [7] and LeClaire [8] the variation of diffusion coefficient and solidus temperature with composition are complementary to each other in many binary systems. In the present case, this rationalization is obeyed in Fe-rich side so that diffusion rates increase with increase in Ti content as solidus follows a downward trend with composition. However, reverse is true for Ti rich side, whereas despite the decrease of solidus temperature $\tilde{D}$ is found to be decreased. In the present case, however, the attempt to correlate the diffusion coefficients with solidus temperature is not justified. This is because the solidus temperatures are established under equilibrium conditions whereas the absence of FeTi and Fe_2Ti from the diffusion zone shows that the complete equilibrium has not been attained during diffusion. Hence, the discrepaccy observed in variation of solidus temperature and diffusion coefficient in Fe-Ti system does not permit us to draw any inference regarding their inter-relationship.

3. Interdiffusion parameters

Interdiffusion parameters as frequency factor $\tilde{D}o$ and activation energy for various compositions have been presented in table 3. An important feature of present data is the incidence of very high values of $\tilde{D}o$ and $\tilde{Q}$ as compared to those reported by other workers over a full range of composition. These high values could be due to non-attainment of complete equilibrium during diffusion as is shown by the absence of expected intermetallic compounds from the diffusion zone.

International consistency of diffusion parameters is depicted by the linear relationship between ln $\tilde{D}o$ and Q of the type

$$\ln Do = aQ + b \qquad \ldots (3)$$

This relation was discussed by Zener 9 and LeClaire [10] for self diffusion in pure metals. The relation was also found to be true for tracer diffusion in alloys of different compositions in Fe-Ti system [6]. This behaviour can be extended to interdiffusion from the similar relations for self diffusion in alloys. Validity of this relationship for interdiffusion was observed in many system [11] . This trend is seen in the present case also as shown in Fig. 5.

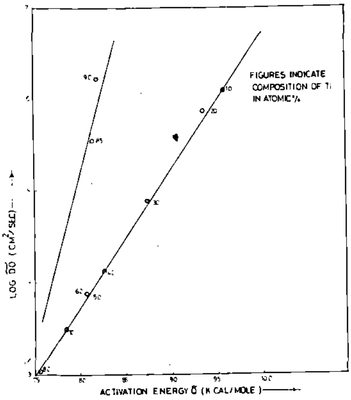

Fig.5 : Log Do vs Q for Fe-Ti system.

Theoretically, according to Zener's elastic model values of a and b in equation 3 are given as

$$a = \frac{\lambda}{RT_m} \frac{d(\mu/\mu_0)}{d(T/T_m)} \qquad \ldots (4)$$

and

$$b = \ln(r^2 \nu) \qquad \ldots (5)$$

Here, μ and μ_0 represent the appropriate elastic modulii of the alloy at temperature T and OK. Tm is the melting point and λ is constant. 'r' is the length of unit diffusion jump and ν is Debye frequency.

As the relevant data (elastic modulii) for Fe-Ti system are not available a direct comparison between the calculated and experimental values of a & b is not possible. However, experimental values are compared with those for interdiffusion in other binary systems in Table 5.

Table 5

Linear Relationship between $\ln \tilde{D}o$ and $\tilde{Q}$ for interdiffusion

$$\ln \tilde{D}o\ (cm^2/sec.) = a\tilde{Q}\ (Kcal/mole) + b$$

System	a	b	Reference
Ti-V	0.30	-17.09	11
Fe-V	0.39	-21.0	12
Fe-Al	0.39	-18.0	13
Fe-Si	0.37	-18.0	14
Fe-Co	0.35	-18.0	11
Fe-Ti (upto 80at%Ti)	0.37	-19.4	Present work
Fe-Ti (beyond 80at%Ti)	0.44	-22.04	-do-

It is seen that there is good agreement between the values for other systems and Fe-Ti system. This serves to underline the internal consistency of diffusion parameter though they have high values.

Conclusions

The present results show that.-
(i) Kinetic factors are more responsible than thermodynamic factors for the presence of phases in diffusion zone; (ii) Interdiffusion coefficient D does not show regular behaviour with solidus temperature; (iii) Zener's theory of Do is in accord with interdiffusion behaviour in Fe-Ti system.

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