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Interdiffusion studies in titanium–304 stainless steel system

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Abstract

The interdiffusion characteristics of various elements in Ti–304SS system have been investigated in the temperature range between 976 and 1123 K by employing metallographic and electron probe microanalysis techniques. The diffusion zone of the couple has been found to be of solid solution type and the layer growth can be presented by two linear lines with change of slope lying in the region of Curie temperatures of the alloys. The layer growth kinetics (in the temperature range of 1023–1123 K) can be expressed by the following Arrhenius relationship: $X = 2.3 \times 10^5 \exp(-73.96\ \text{kJ/mol}/RT)t^{1/2}$, m. The concentration and temperature dependence of effective interdiffusion coefficients are evaluated and the diffusion parameters are established. It is observed that the minimum activation energy value for interdiffusion of Ti (78.05 kJ/mol at 60 at.% Ti) and Fe (74.05 kJ/mol at 20 at.% Fe) and the activation energy for layer growth (73.96 kJ/mol) are in good agreement, suggesting that growth kinetics is controlled by the migration of the plane having the composition of ~60% Ti, ~20% Fe, ~10% Ni and ~10% Cr. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Titanium and titanium composites are being considered for the structural applications in the fields like nuclear power generation plants, desalination plants, petrochemical industries, offshore structures, etc. Titanium clad with stainless steel, being a composite material, has the combined properties of both titanium and stainless steel [1]. However, these type of bonded composites while in service give rise to the formation of intermetallic layers [2,3], which are sometimes detrimental to the mechanical and electrical properties of the components [4]. Therefore, the investigation of interdiffusion characteristics of such multicomponent systems becomes technologically important.

The studies on reactive diffusion and layer growth kinetics in Ti–Ni, Ti–Fe, Ti–SS and many other systems containing titanium as one of the components have been reported earlier in the literature [5–14]. Ranzetta and Pearson [6] and Liason and Stelzer [8] have studied the bonding of titanium with 18/8-stainless steel at 1223 K and reported the formation of intermetallic phases in the diffusion zone. However, Bhanumurthy and Kale [10] did not observe any intermetallic phase in the diffusion zone of the samples heat treated at temperatures of 1073 and 1177 K for 2 h. Instead they have reported the enrichment of chromium at the interface of diffusion zone, attributing this observation to the uphill diffusion of chromium due to the presence of titanium in the system. On the other hand, at similar temperatures, the diffusion reactions of Ti with major components of stainless steel viz. Fe, Cr, Ni, exhibit the presence of intermetallic compounds [11–14]. The formation of such phases in titanium systems is in accordance with the respective binary phase diagrams [15]. Although, no quaternary phase diagram for Ti–Fe–Ni–Cr is available in the literature, the reported isotherms of the ternary phase diagrams for Ti–Fe–Ni and Ti–Fe–Cr system [16] in the temperature range of the investigations, do not show any intermetallic phase in the composition region of the 304-stainless steel which has been employed in these experiments. Considering all these observations we have undertaken the programme to investigate in detail the diffusion reactions in titanium–stainless steel systems. This paper reports the inter-diffusion behaviour in titanium–304 stainless steel in the temperature region below 1123 K.

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2. Experimental

The sandwich type diffusion couples are prepared by employing preannealed (1100 K for 7 days) coarse grained (SS – 500 μm and Ti – 2000 μm) rectangular pieces ($10 \times 5 \times 3$ mm^3) of high purity titanium (>99.98%) and commercial grade 304SS (72% Fe–17% Cr–11% Ni). Two pieces with metallographically polished surfaces in contact are kept together in a die under pressure (1000 psi). The whole assembly is then heated for 30 min at a temperature of 1153 K in a vacuum ($>10^{-5}$ mm of Hg). The diffusion couples so formed are wrapped in a tantalum foil and are encapsulated in a quartz tube under helium atmosphere (1 atm). The diffusion annealing runs are carried out in a preheated resistance furnace in the temperature range between 976 and 1123 K for 96 h. One such couple is also annealed for 2 h at 1023 K. The temperature of furnace is controlled within ∓ 1 K. After every diffusion run the capsules are air quenched. These annealed couples are then cut across the diffusion zone and are prepared for metallographic observations and electron probe microanalysis.

The CAMEBAX (WDS), electron probe microanalyser (EPMA) has been employed to get elemental compositions as well as the concentration profiles across the diffusion zones. The K_α emission lines (FeK_α, NiK_α, CrK_α and TiK_α) are generated by employing stabilised beam current of 100 nA with accelerating voltage of 15 keV. The LiF crystal is used to diffract the respective characteristic X-ray radiations. The corrected compositions from these intensities are obtained by using ZAF method [17] of corrections for atomic number effect, the absorption effect and the fluorescence enhancement.

3. Results and discussion

3.1. Metallographic observations and layer growth kinetics

The polished surfaces of these couples are etched by using 1 part HF + 1 part HNO_3 + 2 parts glycerol solution. The metallographic examinations have revealed only two intermediate layers A and B (Fig. 1) in the diffusion zones. First layer, A is a solid solution of Ni, Cr and Ti in iron on the 304SS side of the diffusion couple. The second layer, B is a solid solution of alloying elements of 304SS (Fe, Ni, Cr) in titanium on titanium side of the couple. The migration of these elements through the grain boundaries is also revealed in the titanium side of the diffusion couple. It is further noticed that the width of diffusion zone towards titanium side (B layer) is much larger than that of steel side (A layer). The ratio of these widths measured with respect to Matano interface [18] ranges between 9.43 and 10.76. Such higher rates of growth on titanium side has also been observed earlier in the diffusion couples of titanium with various metals [11–14]. Both these phases (A and B layers) are solid solution phases (Section 3.2). It should be mentioned here that for the couples annealed at 976 and 998 K, metallographic examinations revealed only two phases. However, EPMA profiles in B layer show the presence of third region, α-Ti solid solution along with concentration gap corresponding to the α + β solid solutions (Fig. 3). For Ti–Fe and Ti–Ni binary systems it is reported earlier that while Ti–Fe diffusion couple does not show any intermetallic phase [19], three phases (Ti_2Ni, TiNi and Ti_3Ni) are observed along with the solid solution of titanium in nickel [12]. The structure of 304 stainless steel being austenite the absence of phase containing iron is understandable. The non-observance of intermetallic phases containing nickel in Ti–304SS couple, however, could be due to the fact that the total available quantity of nickel (11% Ni) in the system may not be sufficient for the phase to form.

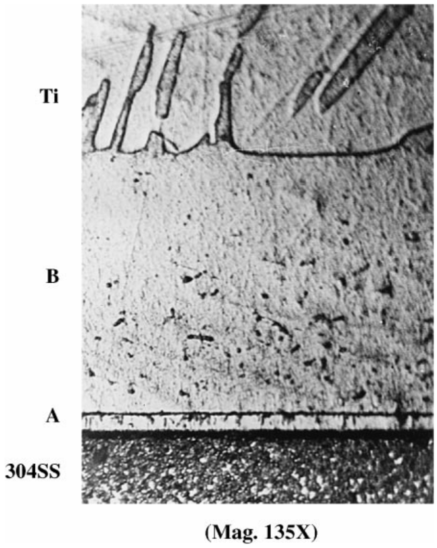

Fig. 1. Micrograph showing the diffusion zone in the Ti–304SS couple annealed at 1073 K for 96 h. A – solid solution of Ni, Cr, Ti in iron and B – solid solution of Fe, Ni, Cr in titanium.

3.2. Temperature dependence of layer growth

The temperature dependence of the total diffusion zone width (*X*), (Table 1 and Fig. 2) can be represented by the following relation,

$$X = K_o t^{1/n} e^{-(Q_p/RT)}, \qquad (1)$$

where $K_o = K e^{(Q_p/RT)}$ m/s$^{1/2}$, the interdiffusion rate constant, t, time of diffusion anneal in seconds, Q_p, kJ/mol, the activation energy for layer growth, and $n = 2$.

Table 1
Diffusion zone width measurements in Ti–304SS couples annealed for 96 h

Temperature (K)	976	998	1023	1073	1123
Width ($\times 10^6$ m)	85.1	366	991	1524	2147

Eq. (1) is plotted in Fig. 2. It is seen that there is a deviation from the linearity in the Arrhenius plot and the data can be presented by two sets of lines. The thicknesses of inter-diffusion zones in low temperature region (<1023 K) are found to be smaller than those from extrapolated values in the high temperature region. Generally it is observed that the diffusion rates get affected because of the phase/magnetic transformations occurred during diffusion processes. It is also known that the binary phase diagrams of iron with body centred cubic (bcc) metals (Ti, Mo, Cr, V, etc.) dictate the formation of stable bcc ferritic phase [15]. Thus during inter-diffusion in the titanium–stainless steel system in the region where the concentration of titanium exceeds ~0.8 at.%, the face centred cubic austenitic stainless steel gets transformed into bcc ferritic steel, which is magnetic (Phase A). The formation of ferritic phase in the joints of austenitic steels through gallium bond has earlier been reported by Batra et al. in their electron microscopic studies on diffusion bonded components [20]. Thus the phase 'A' in diffusion zone of Ti–304SS couples undergoes paramagnetic–ferromagnetic transformations on diffusion annealing. It is well known that the ferromagnetic ordering [21] as well as the change in elastic parameters due to the magnetic transformation [22] affect the diffusion rates. Hence the change in slope of layer growth data on Arrhenius plot at the temperature around 1023 K (Fig. 2) is a manifestation of magnetic transformations occurring during diffusion. It should be noted here that the Curie temperature in Ti–Fe and Ti–Ni system lies between 920 and 1043 K [15,23]. The similar deviation from linearity in ln D vs. $1/T$ plot for self-diffusion in iron has already been reported and discussed thoroughly in the literature when iron goes through the paramagnetic–ferromagnetic transformation at 1043 K [24,25].

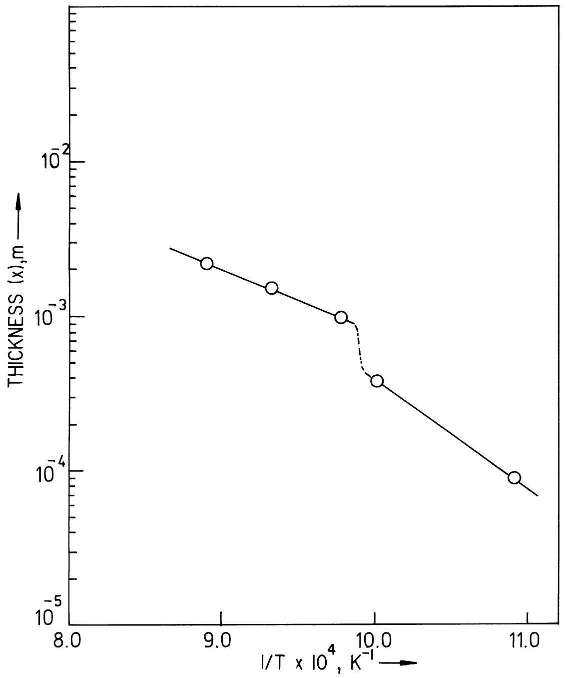

Fig. 2. Arrhenius plot for layer growth (X), in Ti–304SS system.

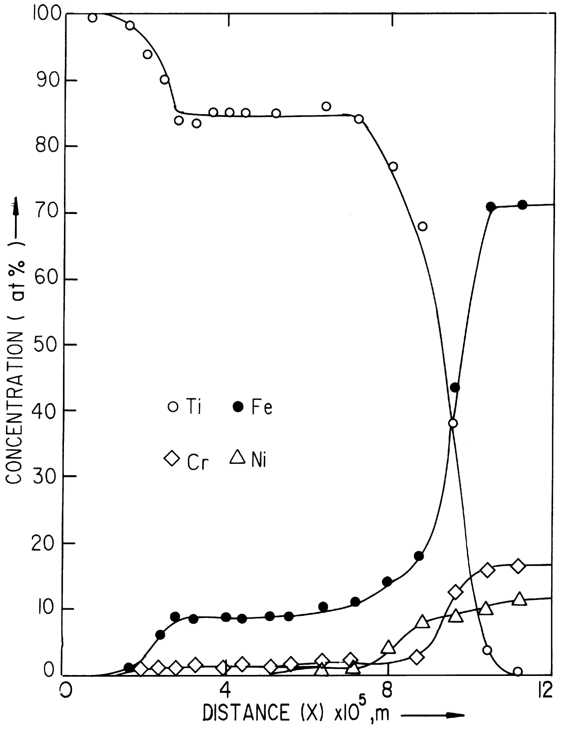

Fig. 3. Concentration profiles of Ti, Fe, Ni and Cr in Ti–304SS diffusion couple (Temp. 976 K, 96 h).

The layer growth parameters (Q_p and K_o) are evaluated by using high temperature data (>1023 K) by linear least mean square analysis. The temperature dependence of the layer growth kinetics in this temperature region can be described by the activation energy, Q_p, of 73.96 kJ/mol, with reaction rate constant K_o, equal to 2.3×10^5 m/s$^{1/2}$.

3.3. Concentration-profiles and interdiffusion coefficients

Figs. 3 and 4 show the typical concentration-penetration profiles obtained by EPMA for all the elements

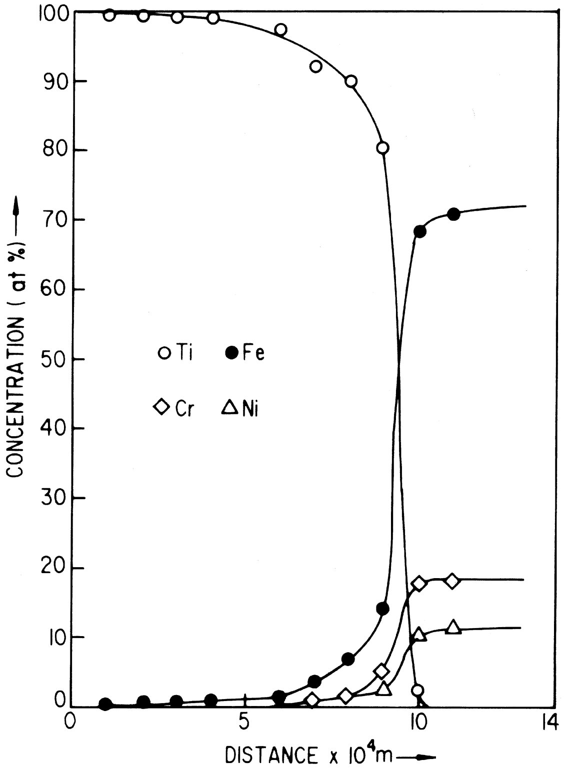

Fig. 4. Concentration profiles of Ti, Fe, Ni and Cr in Ti–340SS diffusion couple (Temp. 1023 K, 96 h).

(Ti, Fe, Ni, Cr) taking part in the diffusion process. The concentration profiles for the couples annealed at 976 K (Fig. 3) and 998 K show step of concentration gap at a composition of around 85% Ti. At higher temperatures, however, a continuous variation of elemental composition across the diffusion zone is observed (Fig. 4). This may be due to the fact that at higher temperatures the concentration gap becomes smaller and could not be resolved by EPMA. Such smooth nature of profiles indicates the absence of intermetallic compound in the diffusion zone. As mentioned earlier, Bhanumurthy and Kale [10] observed the enrichment of chromium at diffusion interface. However, present studies have not shown any enrichment of the said specie even in the sample which has been heat treated at 1023 K for 2 h. It is well known that the surface oxidation of stainless steels shows the enrichment of chromium on the surface. Therefore, the reported chromium enrichment at the interface might have been caused due to the surface oxidation of the stainless steel at the time of preparation of the diffusion couple.

The four component system of this type, in principle, requires the evaluation of nine different diffusion coefficients. This necessitates the preparation of three independent diffusion couples having common point of intersection in their diffusion paths [26]. In the absence of a quaternary phase diagram the selection of proper alloy compositions for making such diffusion couples becomes difficult. Besides it requires the enormous amount of time consuming experimental work. Therefore by making a simple assumption that there is no influence of the presence of one element on the diffusion of the other in the system, the diffusion profiles of individual element can be analysed for getting effective interdiffusion coefficients by employing following conventional well known Boltzmann–Matano relationship [18],

$$\tilde{D}_{(c)} = -1/2t\,\mathrm{d}x/\mathrm{d}c\int_0^c x\,\mathrm{d}c, \qquad (2)$$

where dc/dx is the concentration gradient, $\int x\,\mathrm{d}c$ is area under the curve up to the matano interface and t is the time of diffusion anneal in seconds.

These effective diffusion coefficients are very useful to generate the concentration profiles at given temperature and time through their concentration dependence. Such data become very handy while designing the advanced composite structural materials.

The effective diffusion coefficients for all the elements at various concentrations are evaluated and are listed in Table 2 (Fig. 5). The diffusion couples annealed at 976 and 998 K are not employed for estimating the diffusivity values as these profiles show the concentration gap and hence Boltzmann–Matano method cannot be applied in such cases.

3.4. Concentration and temperature dependence of effective diffusion coefficients

Fig. 5 shows the concentration dependence plots for the effective interdiffusion coefficients for all the elements in the system at various temperatures. It can be seen that the values of effective interdiffusion coefficients for titanium ($\tilde{D}_{\mathrm{Ti}}$) at all the temperatures, are increasing with increase in the titanium content. Although the initial rise is very slow, a sharp rise in the diffusivity values is seen after 70 at.% Ti. As no quaternary phase diagrams are available for the system in question, we have tried to rationalise the diffusivity data on the basis of binary phase diagrams. Ti–Fe and Ti–Ni phase diagram [15], indicate that the solidus temperature decreases with increase in Fe (or Ni) concentration up to ~30 at.% Fe (or Ni). Afterwards the relative rise in solidus temperature is observed with further additions of respective alloying elements. Hence, according to the Le Claire's hypothesis [27] the diffusivity values should decrease with increase in titanium content (>70 at.% Ti). However, contrary to this the diffusivity values are found to increase even after the eutectic composition. The activation energy values (Table 3) however follow

Table 2
Effective interdiffusion coefficients of Ti, Fe, Ni and Cr in Ti–304SS system

Temp (K)	$\tilde{D} \times 10^{15}$ (m²/s)		
	1023	1073	1123
% elem.			
Cr			
05	4.70	15.8	28.8
10	1.02	2.88	6.02
Ni			
05	3.34	4.40	9.33
7.5	2.95	3.01	7.40
Ti			
10	0.334	0.790	3.23
20	0.560	0.790	1.78
30	0.660	1.07	2.23
40	1.10	1.35	3.46
50	1.82	2.45	4.26
60	2.23	3.98	5.07
70	2.66	4.46	7.41
80	10.2	39.5	66.1
90	72.0	199.0	501.0
Fe			
10	30.00	72.0	117.0
20	7.51	14.4	16.2
30	2.86	3.31	11.5

the solidus temperature trend qualitatively. It is well established fact that titanium like zirconium, belongs to the 'anomalous' group of metals. Therefore, such anomalous diffusion results are not uncommon in these systems [28,29]. The interdiffusivity values for iron ($\tilde{D}_{\mathrm{Fe}}$) are also not with the conformity with the melting point rule [27]. This may be due to the anomolous behaviour of the titanium matrix.

Figs. 6–8 show the typical Arrhenius diffusity plots for Ti, Fe, Ni and Cr. The interdiffusion parameters ($\tilde{Q}$ and $\tilde{D}_0$) are evaluated by using linear least mean square analysis of the data (Table 2) and are listed in Tables 3 and 4. The activation energy of Ti decreases from 215.69 kJ/mol at 10 at.% Ti to 78.85 kJ/mol at 60 at.% Ti. It rises again to a value of 185.22 kJ/mol at 90 at.% of titanium. In case of Fe the variation of $\tilde{Q}$ (74.08–132.88 kJ/mol) is

Table 3
Interdiffusion parameters ($\tilde{D}_0$ and $\tilde{Q}$) for Ti in Ti–304SS system

% Ti	$\tilde{D}_0$ (m²/s)	$\tilde{Q}$ (kJ/mol)
10	$3.09^{+3.54}_{-1.65} \times 10^{-5}$	215.69 ± 4.81
20	$1.89^{+0.92}_{-0.62} \times 10^{-10}$	108.98 ± 2.48
30	$5.13^{+2.59}_{-1.72} \times 10^{-10}$	115.80 ± 2.58
40	$3.28^{+1.65}_{-1.09} \times 10^{-10}$	108.29 ± 2.56
50	$2.31^{+0.77}_{-0.58} \times 10^{-11}$	80.76 ± 1.81
60	$2.47^{+0.81}_{-0.08} \times 10^{-11}$	78.85 ± 1.77
70	$2.58^{+1.05}_{-0.79} \times 10^{-10}$	97.76 ± 2.15
80	$1.67^{+1.51}_{-0.79} \times 10^{-5}$	179.48 ± 4.05
90	$2.06^{+1.80}_{-0.98} \times 10^{-4}$	185.22 ± 4.07

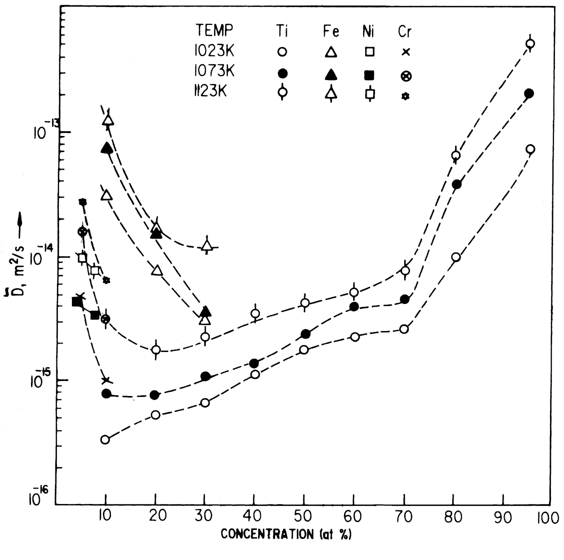

Fig. 5. Concentration dependence of effective diffusion coefficients, $\tilde{D}_{\mathrm{Ti}}$, $\tilde{D}_{\mathrm{Ni}}$, $\tilde{D}_{\mathrm{Cr}}$, $\tilde{D}_{\mathrm{Cr}}$, in Ti–304SS system.

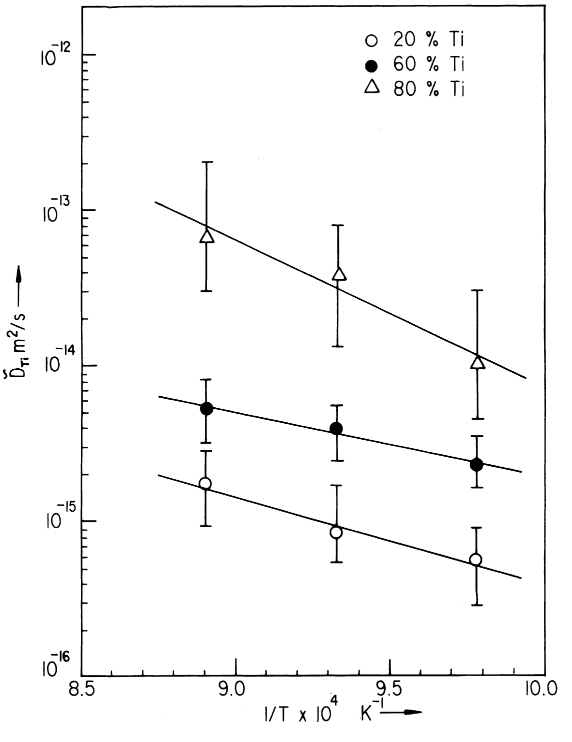

Fig. 6. Temperature dependence of effective diffusion coefficient, $\tilde{D}_{\mathrm{Ti}}$, in Ti–304SS system.

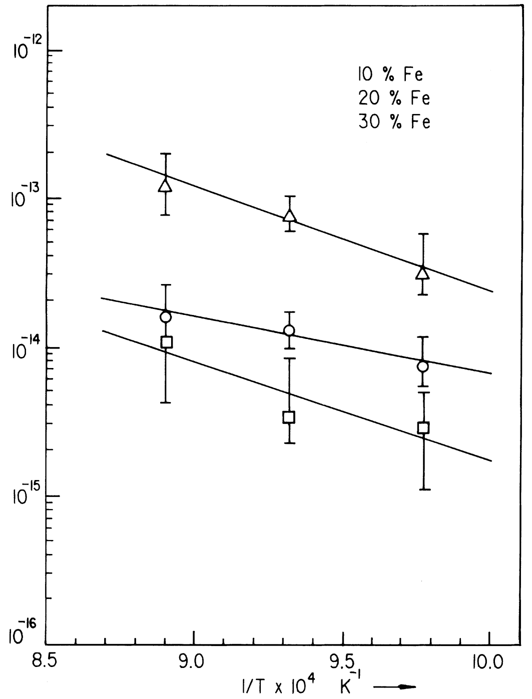

Fig. 7. Temperature dependence of effective diffusion coefficient, $\tilde{D}_{Fe}$ in Ti–304SS system.

also observed with lowest value at 20 at.% Fe. Chromium and nickel show continuous decrease in the activation energy values with increase in concentration of respective element. It may be mentioned here that the minimum activation energy values for major components like iron (74.08 kJ/mol at 20 at.% Fe), titanium (78.85 kJ/mol at 60 at.% Ti) and the activation energy value for layer growth (73.96 kJ/mol) are in good agreement. This suggests that the plane having the composition of ~60% Ti, ~20% Fe, ~10% Cr and ~10% Ni controls the layer growth kinetics in Ti–304SS system.

4. Summary

The present experimental results on the reactive diffusion in Ti and 304SS system, annealed in the temperature range between 976 and 1123 K for 96 h, are summarised below:

1. No intermetallic compounds are formed in the diffusion zone.
2. The minimum activation energy values for interdiffusion of Fe (74.02 kJ/mol), Ti (78.85 kJ/mol) and the activation energy for layer growth (73.96 kJ/mol) in Ti–304SS system, are found to be in good agreement.
3. The migration of plane having the composition of ~60% Ti, ~20% Fe, ~10% Cr and ~10% Ni controls the layer growth kinetics in Ti–304SS system.

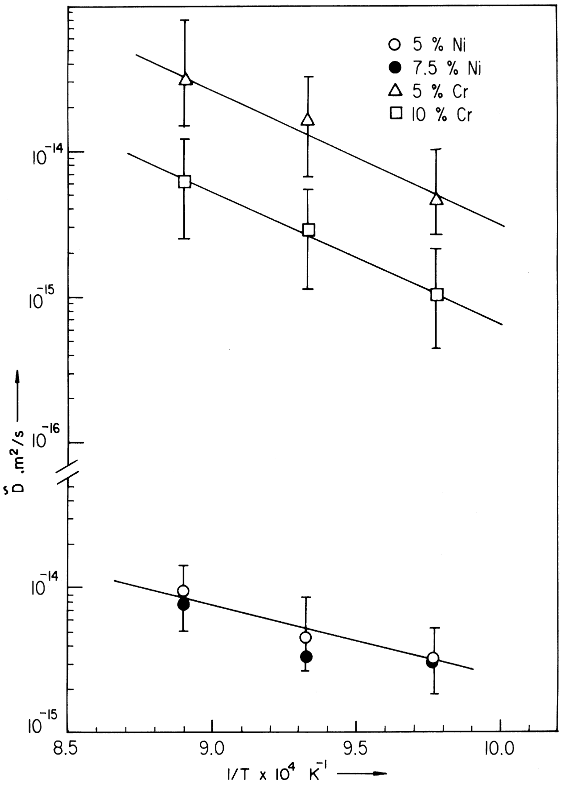

Fig. 8. Temperature dependence of effective diffusion coefficients $\tilde{D}_{Ni}$ and $\tilde{D}_{Cr}$ in Ti–304SS system.

Table 4
Interdiffusion parameters ($\tilde{D}_0$ and $\tilde{Q}$) for Fe, Cr, Ni, in Ti–304SS system

	$\tilde{D}_0$ (m²/s)	$\tilde{Q}$ (kJ/mol)
% Fe		
10	$2.53^{+2.13}_{-1.16} \times 10^{-7}$	132.88 ± 3.85
20	$4.92^{+1.56}_{-1.19} \times 10^{-11}$	74.08 ± 1.74
30	$1.84^{+0.79}_{-0.47} \times 10^{-8}$	131.18 ± 3.21
% Cr		
5	$3.82^{+3.25}_{-1.76} \times 10^{-6}$	173.82 ± 3.88
10	$4.92^{+3.99}_{-2.20} \times 10^{-7}$	169.79 ± 3.74
% Ni		
5	$2.88^{+1.22}_{-0.86} \times 10^{-10}$	97.37 ± 2.22
7.5	$6.63^{+2.28}_{-1.96} \times 10^{-11}$	86.48 ± 2.20

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