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A study of Re and Al diffusion in Ni

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ABSTRACT

Alloy couples of Ni–1(wt.%)Re/Ni–4.8(wt.%)Re and Ni–*x*%Re/Ni–*x*%Re–5.3(wt.%)Al with *x* being 1, 2 and 3 were annealed at different temperatures to investigate the diffusion behavior of Re in Ni and the effect of Re on the diffusion behavior of Al in Ni. The composition profiles of these alloys were measured by electron probe microanalysis, and used to calculate the diffusion coefficients and activity energies of Re and Al. The results showed that the diffusion activation energy of Re in Ni was 412 kJ/mol and that of Al increased slightly from 230 kJ/mol to 256 kJ/mol with Re content being varied from 1% to 3% in Ni matrix.

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1. Introduction

The second and third generation single crystal Ni-based superalloys typically contain 3–6 wt.% Re, to enhance the creep performance and fatigue strength of these superalloys [1–3]. It was reported that the coarsening rate of γ'decreases significantly with increase in Re content in superalloys [4,5]. In order to inhabit coarsening of γ' (Ni_3Al) precipitates, it is necessary for Re to diffuse away from the γ–γ'interface. Blavette has revealed that about 80% of the added Re is dissolved in the γ phase and 20% dissolved in the γ' phase in the super alloys [1]. The diffusion behavior of Re and its effect on the diffusion behavior of Al in Ni are the key factors controlling the segregation behavior of Re at the γ–γ' interfaces, formation and coarsening of γ' precipitates in these superalloys, hence possessing a strong effect on the high-temperature mechanical performance of the superalloys. Therefore, a thorough understanding of the diffusion behavior of Re in Ni could help to optimize the design and thermomechanical treatment for these alloys used in critical turbine engine applications. Although diffusion data of many elements in γ phase have been obtained in Ni so far, the diffusion behavior of Re in Ni still needs to be studied.

In this study, Ni–Re and Ni–Re–Al couples were made, and diffusion experiments were conducted on these couples. The diffusion coefficients and activity energies of Re in these Ni alloys were calculated from the composition profile measurement in the diffusion experiments.

2. Experimental details

The four Ni–Re–Al alloy couples used in this study were made with different Re and Al contents, as shown in Table 1. These alloys were prepared from high-purity nickel, aluminum and rhenium in an arc-melting furnace in vacuum. To ensure the homogeneity in chemical composition of these alloys, they were melted three times and then homogenized at 1200 °C for 50 h in a sealed quartz capsule in vacuum of 1×10^{-3} Pa. The average grain size of the homogenized alloys was about 1.5 mm. These alloys were cut into 5 mm × 5 mm × 10 mm blocks and then mechanically polished using a 0.3 μm diamond paste after grinding. These alloy blocks were assembled to form diffusion couples, as shown in Table 1, by clamping each pair in a special holder.

The diffusion couples were placed in a sealed quartz capsule in vacuum of 1×10^{-3} Pa and then diffusion annealed. The diffusion temperatures and times used are listed in Table 2. After the diffusion annealing, the diffusion couples were quenched in water and then cross-sectioned at a series of locations along the diffusion direction. These cross-sections were ground and metallographically polished. The chemical compositions on these polished surfaces were determined by electron probe microanalysis with a step size of 10 μm, and the composition vs. distance curves were obtained in these couples.

3. Results and discussion

Fig. 1(a) and (b), respectively, show the diffusion profiles in the diffusion couples of Ni–Re and Ni–Al with the addition of 1%Re, 2%Re and 3%Re, respectively. The diffusion depth (30 μm) of Re in Ni was much smaller than that (220 μm) of Al in Ni with the addition of Re. In addition, Re showed a small effect on Al diffusion in Ni, since the diffusion depths of Al (230 μm, 220 μm and 210 μm) decreased slightly with increasing Re content in the Ni matrix, as shown in Fig. 1(b). The Boltamann and Matano method was used, in the present work, to calculate the diffusion coefficient, $\tilde{D}$, of Re in Ni, and Al in Ni–Re alloys [6,7]. $\tilde{D}$ is determined from the following

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Table 1
Diffusion couples and their compositions.

Couple designation	Compositions (wt.%)
Re	Ni–1Re/Ni–4.8Re
1Re	Ni–1Re/Ni–1Re–5.3Al
2Re	Ni–2Re/Ni–2Re–5.3Al
3Re	Ni–3Re/Ni–3Re–5.3Al

Table 2
Diffusion temperature (°C) and time (h).

T (°C)	t (h)
1100	50
1150	25
1200	13
1250	7

equation

$$\int_{C^-}^{C^+}(x-x_0)\,\mathrm{d}C_{Re} = -2t\tilde{D}\frac{\mathrm{d}C_{Re}}{\mathrm{d}x}$$

where C^{+}_{Re} is the concentration of rhenium at the one end of the infinite diffusion couple and C^{-}_{Re} is the concentration at the other end, x is the position from the interface of a diffusion couple, x_0 is the coordinate of the Matano interface, and t is time. The Matano interface is the zero point shown in Fig. 1. Since the above equation is for a binary alloy, $\tilde{D}$ calculated from this equation was actually an effective binary diffusion coefficient [8], $\tilde{D}_{\mathrm{EBDC}}$, of Al in Ni–Re–Al ternary systems. However, since the existence of Re did not seem to affect the diffusion of Al in these alloys significantly (Fig. 1(b)), the diffusion coefficients so-calculated could be regarded as the equivalent diffusion coefficients of Al in Ni.

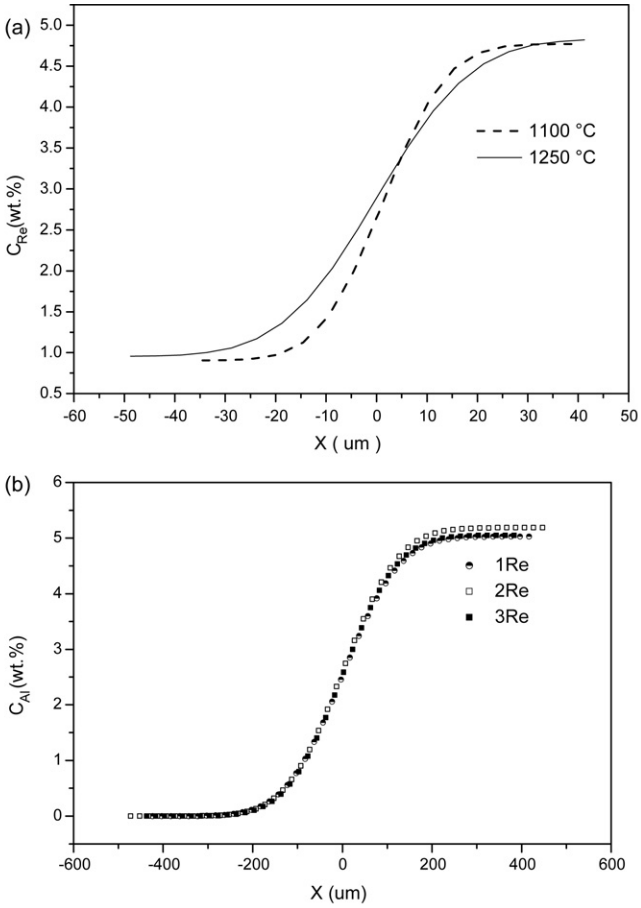

Fig. 1. Diffusion profiles in the diffusion couples: (a) Ni–1Re/Ni–5Re, annealed at 1250 °C for 7 h and 1100 °C for 50 h, and (b) Ni–1Re/Ni–1Re–6Al, Ni–2Re/Ni–2Re–6Al and Ni–3Re/Ni–3Re–6Al, annealed at 1150 °C for 25 h.

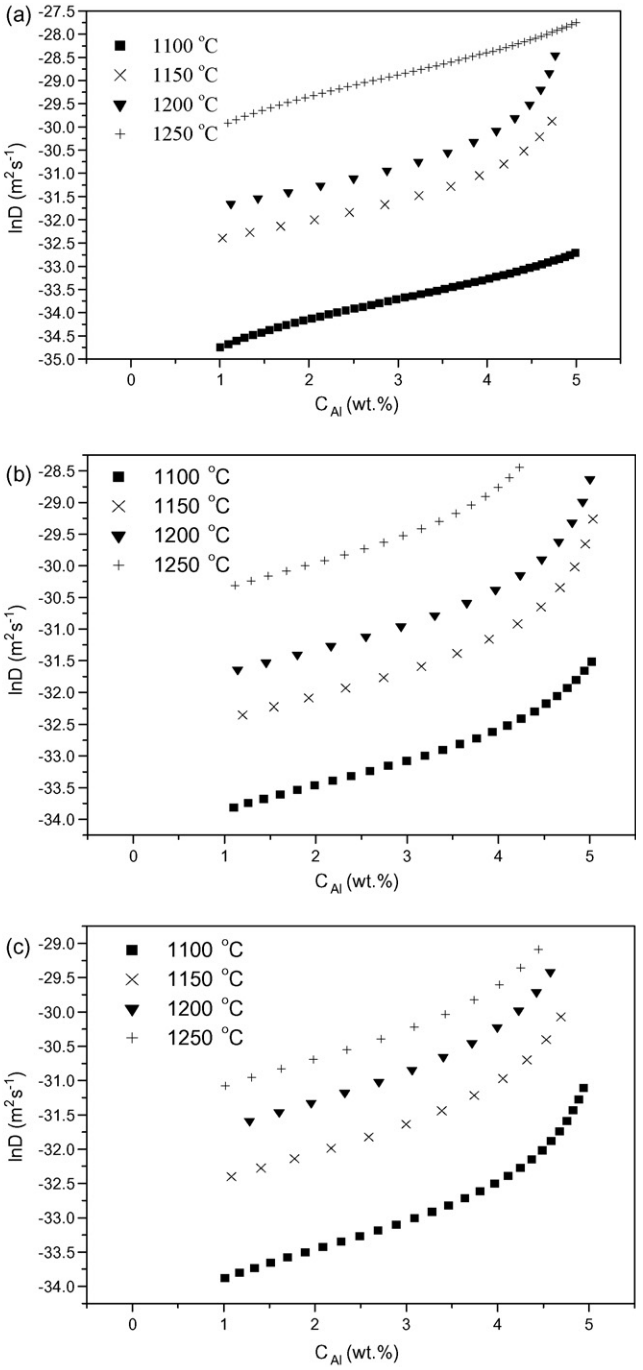

Fig. 2. Diffusion coefficient determined as a function of concentration for the (a) Ni(1Re)–6Al, (b) Ni(2Re)–6Al and (c) Ni(3Re)–6Al systems.

The calculated diffusion coefficients of Al in the diffusion couples containing different Re contents annealed between 1100 °C and 1250 °C are plotted as a function of Al composition in Fig. 2(a)–(c).

The values of diffusion coefficients increased with annealing temperature and the concentration of aluminum in the three Ni–Re–Al alloys. In other words, at the same Al content, with increase in annealing temperature, the diffusion coefficient of Al increased, and, at the same temperature, it also increased with Al content, in these alloys. The temperature effect on diffusion

Table 3
Diffusion activation energy of some elements in Ni or Ni_3Al (kJ/mol).

	Re	Ti	Cr	Co	Mn	V	Hf
Ni	412	275 [10]	273 [11]	271 [12]	–	–	385 [14]
Ni_3Al	–	468 [9]	366 [9]	325 [9]	377 [13]	459 [13]	–

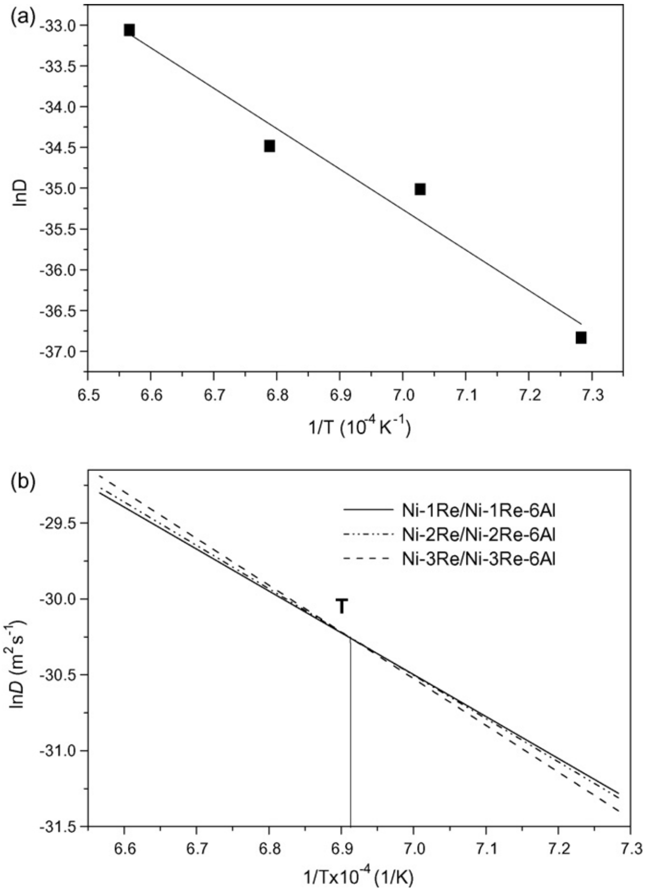

Fig. 3. ln *D* vs. 1/*T* is plotted for the (a) Ni–Re and the (b) Ni(Re)–Al systems.

coefficient is generally expressed in the form of $D = D_0\exp(-Q/RT)$, where Q is the activation energy; D_0 is the frequency factor, T is temperature and R is the gas constant. Fig. 3 shows the plots of logarithmic diffusion coefficient vs. reciprocal of absolute temperature for all the alloys studied in this work. The logarithmic diffusion coefficients of the Ni–Re and Ni–Re–Al systems indeed varied linearly with $1/T$. D_0 and Q were determined by linear regression analysis of the lines shown in Fig. 3.

Therefore, the relationships of diffusion coefficient and temperature in these alloys studied in this work were obtained,

$$\tilde{D}_{Re}(m^2s^{-1}) = 5.96 \times 10^{-1}\exp\left(\frac{-412\,kJ\,mol^{-1}}{RT}\right)$$

$$\tilde{D}_{Al}^{1Re}(m^2s^{-1}) = 1.4 \times 10^{-5}\exp\left(\frac{-230\,kJ\,mol^{-1}}{RT}\right)$$

$$\tilde{D}_{Al}^{2Re}(m^2s^{-1}) = 2.7 \times 10^{-5}\exp\left(\frac{-238\,kJ\,mol^{-1}}{RT}\right)$$

$$\tilde{D}_{Al}^{3Re}(m^2s^{-1}) = 1.4 \times 10^{-4}\exp\left(\frac{-256\,kJ\,mol^{-1}}{RT}\right)$$

Compared with Al, Re showed a much higher value of diffusion activation energy, which was consistent with the shorter depth of Re diffusion found in the Ni–Re alloy than that of Al in Ni–Re–Al alloys. The activation energies and frequency factors for Al in Ni increased slightly with Re content increasing from 1% to 3% in Ni. This minor Re effect on Al diffusion can also be demonstrated in ln *D* vs. 1/*T* plots of the Ni–Re–Al alloys in Fig. 3(b) where the increase rate of *D* with temperature increases with the Re content in the alloys, i.e., the increase rate is the highest in Ni–3Re–5.3Al and the lowest in Ni–1Re–5.3Al. As shown in Fig. 3(b), in a temperature range from 1043 °C to 1193 °C, the values of diffusion coefficients of Al were nearly the same in these Ni–Re–Al alloys. In other words, the Re content had almost no effect on the diffusion behavior of Al in Ni over this temperature range.

The activation energy of Re, together with those of other common alloying elements obtained previously, for diffusion in pure nickel and γ' (Ni_3Al) is shown in Table 3. It was found that the activation energy of Re in Ni was much higher than those of other elements in Ni, even higher than that of Cr, Co and Mn in Ni_3Al which has an ordered $L1_2$-type structure. Due to the requirement for the neighboring atoms being different element in an ordered lattice structure, such as Ni_3Al, diffusion of an element generally becomes more difficult, i.e., the activation energy of the element is higher in Ni_3Al than in a pure metal. Giamei's study showed that the diffusion coefficient of Re was expected to be small and Re substitutions for W increase the activation energy for coarsening, which is attributed to the higher activation energy for diffusion of Re in Ni [4]. The results obtained in the present work were consistent with Giamei's investigation. The higher diffusion activation energy of Re in Ni is related to the short-range ordering of Re atoms in γ phase. Blavette revealed the occurrence of fine Re clusters in the γ matrix of single crystal superalloys by means of atom-probe techniques [1]. These Re enriched regions probably act as more efficient obstacles against jumping motion of other atoms, compared to isolated solute atoms in a γ solid solution.

The high activation energy of Re could help to explain why addition of Re improves the creep properties of Ni-based superalloys, as it enhances the stability of microstructures of the superalloys at elevated temperatures. In the same time, the addition of Re showed a minor effect on the diffusion behavior of Al, indicating that Re should have a very small detrimental effect on the formation of γ' which is the primary strengthening mechanism in Ni-based superalloys. On the other hand, the low diffusion coefficient of Re in Ni may slow down the homogenization process in Re-bearing cast superalloys, since the heavy element Re segregates at the dendrite core preferably. This micro-coring could hardly be eliminated by heat treatment at 1315 °C for 12 h [15–17]. It has been recognized that Re element is a potent TCP, freckle and SRZ former. Some Re-bearing superalloys precipitate the plate shaped TCP phase in dendrites after a long period of exposure to high temperature, e.g., for more than 1000 h, between 900 °C and 1100 °C. As a result, the 10,000 h stress rupture life of a Re-containing superalloy is found to be lower than that of a Re-free alloy [18]. These phases, once formed, are detrimental to mechanical performance of these alloys. For this reason, the single crystal superalloys utilized for industrial gas turbine blades usually contain a low Re content or no Re.

4. Conclusion

1. The diffusion activation energy of Re in Ni was 412 kJ/mol, which was higher than that of other common alloying elements in Ni.
2. The diffusion activation energy of Al increased slightly with increasing Re content in Ni.

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