On the diffusion behaviour of Os in the binary Ni–Os system

Y. M. Youssef[1], P. D. Lee[1], K. C. Mills[1] and R. C. Reed*[2]

The diffusion of Os in Ni is characterised by measuring interdiffusion coefficients in the binary Ni–Os system, in the temperature range 1200–1350°C. The results are compared with data for Ni–Re. Theoretical calculations indicate that Os should display a diffusion coefficient comparable with Re, among the lowest displayed by elements from the d-block transition elements. The authors' experimental findings confirm these predictions, and suggest that alloying with Os is likely to improve the high temperature properties of the nickel-based superalloys.

Keywords: Nickel-based superalloys, Diffusion, High temperature properties, Microstructural kinetics

Introduction

The nickel-based superalloys have been developed particularly for their resistance to creep and fatigue at elevated temperatures.[1] The alloys are complex; it is not unusual for 10 or more alloying elements to be present, especially in the single crystal superalloys which are used for turbine blade applications. Most of these are taken from the d-block of transition metals, since these show reasonable solubility in Ni. In particular, the second and third generation single crystal superalloys are characterised by substantial additions of Re, and the fourth generation ones are characterised by additions of Ru. However, it seems probable that there are other elemental additions which might possibly improve the high temperature properties still further. Thus, it is unlikely that the compositions of the nickel-based superalloys have been optimised as yet.

One difficulty is that microstructure–property relationships for these materials have yet to be placed on a firm, quantitative basis. To develop these, work is still needed to quantify certain key characteristics, for example, the rates of diffusion of the alloying additions in the nickel matrix which will influence thermally activated mass transport processes. Recently, a number of experimental investigations have been published in which binary interdiffusion coefficients in Ni–X systems (where X=Re, Ta, W, Ir, Pd, Pt, Rd, Ru and Nb) have been reported;[2–6] also available is information for Ni–Al–Ti[7] and other ternary systems Ni–Al–X (where X=Re and W).[8,9] The obtained values for the diffusion coefficients are helping to establish a consolidated database of diffusion data for the Ni based superalloys. This is proving very useful for quantitative predictions of microstructure evolution in these alloys. It also aids in the design of new grades of superalloy and for optimising their properties.

The work reported in the present paper was carried out with the above in mind. Experimental work[5] and theoretical predictions using density functional theory[10,11] have indicated that the interdiffusion coefficients of the d-block of transition metals display a systematic trend with atomic number; elements from the centre of the d-block (e.g. Re and Ru) exhibit values which are several orders of magnitude lower than those from the far west (e.g. Hf) or far east (e.g. Au). Theoretical considerations indicate that this occurs due to large differences in the vacancy/solute exchange energy which varies substantially as one crosses the d-block. Moreover, our theoretical predictions suggest that Os, which sits beside Re and below Ru in the periodic table, is likely to exhibit similarly low rates of diffusion. The authors set out to test this theoretical prediction.

Experimental methods

For the production of diffusion couples, Ni–10Os ingots were prepared using nominally pure Ni and Os (better than 99·99% purity in both cases) using a vacuum induction melting furnace. Since it was of interest to compare the experimental results for Ni–Os with data for the binary Ni–Re system, further binary Ni–10Re ingots were also prepared. After melting, the ingots were homogenised by heating to 1300°C for 7 days under a constant flow of pure argon gas. Tests indicated that this was sufficient to remove any segregation inherited from processing.

The diffusion couples were prepared by joining 14 mm diameter pure Ni bars to the Ni–X alloys via diffusion bonding, using a heating temperature of 1200°C and a bonding pressure of ~3 MPa with a holding time of 3 min. The bonded samples were then machined (using electrical discharge machining) to yield 2 mm diameter × 20 mm length cylindrical specimens for the diffusion experiments. In all cases, the diffusion samples were encapsulated in quartz tubes and the capsules were backfilled with pure argon gas. The diffusion annealing was conducted under continuous flow of pure Ar gas. Subsequently, the quartz tubes were

[1]Department of Materials, Imperial College London, Prince Consort Road, London SW7 2AZ, UK
[2]Department of Metallurgy and Materials, University of Birmingham, Birmingham B15 2TT, UK

*Corresponding author, email R.Reed@bham.ac.uk
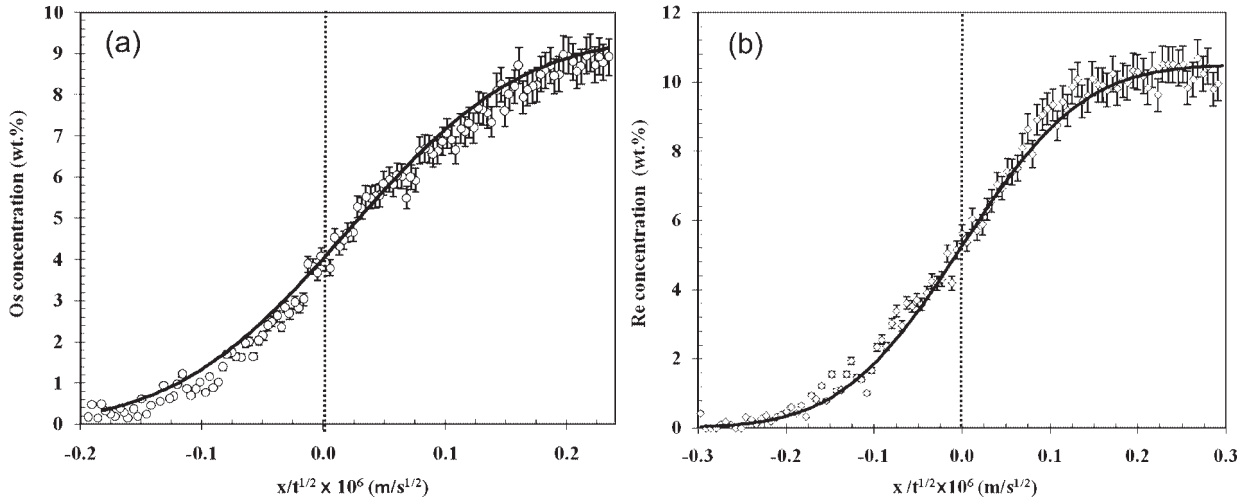
1 Concentration plotted against Matano variable $x/t^{1/2}$ for *a* Os in interdiffusion zone of Ni–10Os couple and *b* Re in interdiffusion zone of Ni–10Re couple: both couples were annealed at 1300°C; zero value of Matano variable denotes position of Matano plane; solid lines are fitted error function profiles

quenched in water and the samples were mounted and polished using conventional metallographic preparation techniques. All samples were polished down to 1 μm finish.

The chemical analysis of the diffusion couples was performed on a SEM JEOL 840 equipped with energy dispersive X-ray spectroscopy. A Co standard specimen was used in the calibration before each measurement and all the measured values were normalised. In each case, the analysis was averaged over four linescans covering the diffusion length across the diffusion interface. The interface of the diffusion bonded samples was checked before the diffusion annealing experiment to ensure that the diffusion length at the bonded interface was negligible.

Results and discussion

Analysis technique

The diffusion behaviour for a binary couple Ni/Ni–X (where X is, for example, Os) can be described by Fick's second law. If Os is taken as the diffusing element, one has

$$\frac{\partial C_{Os}}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial C_{Os}}{\partial x}\right) \tag{1}$$

where the diffusion coefficient for Ni–Os $\tilde{D}$ is considered to be a function of the alloying element concentration C_{Os}. The reaction coordinate x is taken to be normal to the interface and t is time. The solution to equation (1) and thus an estimate of $\tilde{D}$ can be obtained using several analytical techniques. A commonly used method to estimate the diffusion coefficient is the well known one due to Boltzmann–Matano[12,13] for conditions corresponding to a infinite diffusion couple. An equation of the following form can then be used to estimate $\tilde{D}$

$$\int_{C_{Os}^{-}}^{C_{Os}^{*}} (x-x_0)dC_{Os} = -2t\tilde{D}\left(\frac{dC_{Os}}{dx}\right)_{C_{Os}^{*}} \tag{2}$$

where C_{Os}^{-} is the concentration of osmium at one end of the diffusion couple and C_{Os}^{*} is the concentration at which $\tilde{D}$ is to be evaluated. The position of the Matano

interface is given by $x=x_0$ and this must be determined from an equation of the form

$$\int_{C_{Os}^{-}}^{C_{Os}^{+}} (x-x_0)dC_{Os} = 0 \tag{3}$$

using iterative procedures. In practice, the determination of the Matano interface is unnecessary. Instead, a second method can be applied to analyse binary systems (see, for example, Sauer and Freise[14] and den Broeder[15]). This second method was used in the present study to quantify the interdiffusion coefficient. The interdiffusion coefficient is calculated directly from the concentration profile using the following equation

$$\tilde{D} = \frac{1}{2t}\frac{dx}{dY_{Os}}\left[(1-Y_{Os})\int_{-\infty}^{x} Y_{Os}dx + Y_{Os}\int_{x}^{\infty}(1-Y_{Os})dx\right] \tag{4}$$

where the normalised concentration Y_{Os} is given by

$$Y_{Os} = \frac{C_{Os} - C_{Os}^{-}}{C_{Os}^{+} - C_{Os}^{-}} \tag{5}$$

As with the Boltzmann–Matano method, this technique assumes that the concentration can be expressed in terms of the Matano variable $x/t^{1/2}$, and that such concentrations are independent of time.

Finally, it is worth pointing out that if $\tilde{D}$ is considered independent of concentration, the diffusion profile can be modelled using the analytical expression (e.g. Ref. 16)

$$C_{Os} = \frac{C_{Os}^{+} + C_{Os}^{-}}{2} + \frac{C_{Os}^{+} + C_{Os}^{-}}{2}\text{erf}\left[\frac{x-x_0}{2\left(\tilde{D}_{ER}t\right)^{1/2}}\right] \tag{6}$$

Table 1 Diffusion temperatures and annealing times used in experiments

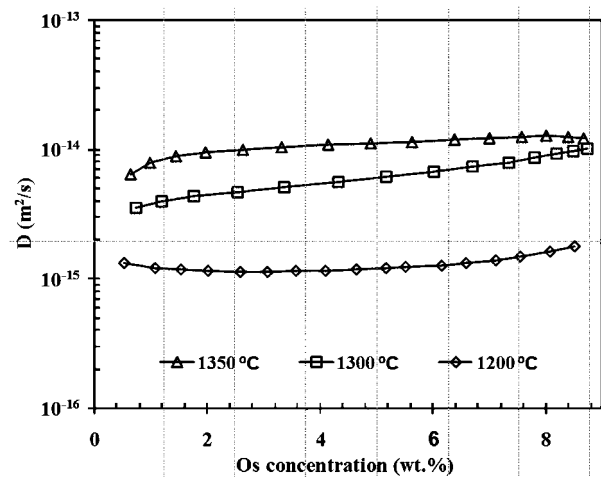| Diffusion couple	Temperature, °C	Time, h
Ni/Ni–10Os	1200	168
	1300	264
	1350	168
Ni/Ni–10Re	1200	336
	1300	282
	1350	144
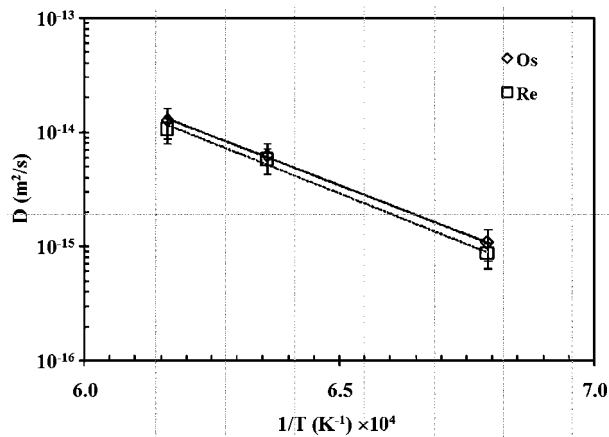
2 Experimentally determined binary interdiffusion coefficients as function of reciprocal temperature for Os in Ni and Re in Ni

3 Interdiffusion coefficient of Os in Ni as function of composition, calculated using Sauer–Freise approach

where erf is the error function. In this expression, the subscript 'ER' indicates an estimate of the interdiffusion coefficient using the error function solution. Knowing the two terminal concentrations C_{Os}^+ and C_{Os}^- and the position of the Matano interface, an average value of the diffusion coefficient $\tilde{D}_{ER}$ can be produced by fitting equation (6) to the experimental diffusion profile.

Data analysis and diffusion coefficient results

The interdiffusion coefficients were estimated for binary Ni/Ni–10Os and for binary Ni/Ni–10Re diffusion couples in the temperature range 1200–1350°C. The various annealing times at different temperatures used in the diffusion experiments are given in Table 1. Typical graphs showing the concentration of Os and Re plotted against the Matano variable for Ni/Ni–10Os and Ni/Ni–10Re diffusion couples annealed at 1300°C are given in Fig. 1. On the same graphs, the fitted diffusion profiles obtained from the error function approximation are shown.

Fitted interdiffusion coefficients for the diffusion of Os in Ni as a function of the reciprocal temperature are given in Fig. 2. The fitted interdiffusion coefficients for Re diffusion in Ni as a function of the reciprocal temperature are also given. The experimentally determined frequency

factors and activation energies are listed in Table 2. The Re data obtained by Karunaratne *et al.*[4,5] are given in Table 2 for the purpose of comparison. The values of the interdiffusion coefficients obtained using the Sauer–Freise method and then used to calculate the pre-exponential terms and activation energies were taken as an average value over the range of compositions studied.

One can see that the activation energy obtained here for Re using the Ni/Ni–10Re diffusion couples is in reasonably good agreement with the value calculated by Karunaratne *et al.* The values obtained for Os are comparable but slightly larger than the values obtained for Re; once the pre-exponential terms are accounted for, the overall effect is that the kinetics of diffusion of Os and Re are comparable.
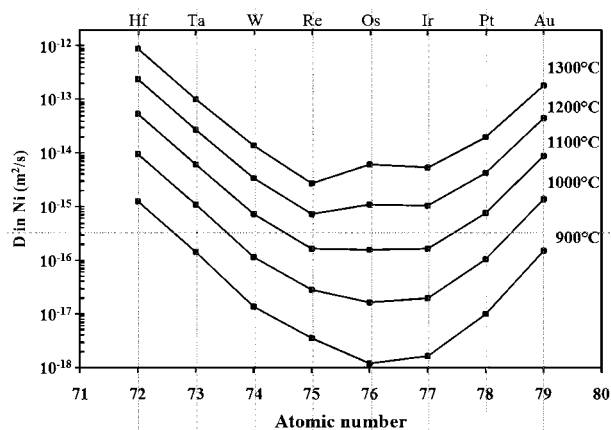
Experimentally determined concentration versus distance data for the couples annealed between 1200 and 1350°C were used to calculate the interdiffusion coefficient as a function of composition using the Sauer–Freise/den Broeder approach (equations (4) and (5)). Calculated interdiffusion coefficients versus composition are plotted for Os in Fig. 3. One can see that for the interdiffusion coefficients in the range of temperatures between 1200 and

Table 2 Experimentally determined frequency factor and activation energy

Diffusion couple	Diffusing element	D_0, $\times 10^{-7}$ m^2 s^{-1}	Q, kJ mol^{-1}	Remarks
Ni/Ni–10Os	Os	4420	327	Error function
		224	289	Sauer–Freise
Ni/Ni–10Re	Re	286	294	Error function
		19·8	259	Sauer–Freise
Ni/Ni–10Re	Re	8·2±3·0	255±8	From Karunaratne *et al.*[4]

Table 3 Comparison between diffusion coefficients obtained using error function fit and Sauer–Freise method

Temperature, °C	$\tilde{D}_{SF}$, $\times 10^{-15}$ m^2 s^{-1}	$\tilde{D}_{ER}$, $\times 10^{-15}$ m^2 s^{-1}	Difference $\left(\tilde{D}_{SF} - \tilde{D}_{ER}\right)/\tilde{D}_{SF} \times 100$, %
Ni–10Os			
1200	1·26	1·07	15·1
1300	6·29	6·13	2·5
1350	10·74	12·50	−16·4
Ni–10Re			
1200	1·36	0·85	37·5
1300	5·19	5·70	−9·8
1350	8·31	10·50	−26·4

4 Variation of interdiffusion coefficients with atomic number for third series of transition elements: points for Os were obtained from present study; points for other elements were taken from published data[4,5]

1350°C, there is only a small variation with composition over the range investigated (up to $\sim 9 \cdot 4$ wt-%Os in Ni). The profile at 1300°C shows a slight increase compared to profiles obtained at other temperatures.

A comparison between the interdiffusion coefficients obtained using the Sauer–Freise method and the error function fit is given in Table 3. The table shows a maximum absolute difference of $\sim 38\%$ between the two approaches which is considered within the accuracy of the measurement.

Finally, it is of interest to compare the values measured for the interdiffusion coefficient in the Ni–Os system with those reported for other Ni–X binary systems in earlier work.[4,5] This is carried out in Fig. 4. One can see that the values determined here for Os are fairly consistent with the trends identified in the earlier papers. The authors' experimental findings are consistent with the theoretical analysis,[10] which has confirmed that the variation of interdiffusion coefficient with atomic number occurs due to a substantial variation with atomic number of the activation energy for solute/vacancy exchange. The authors' work suggests that Os might prove to be a suitable alloying addition for the nickel-based superalloys, since it is expected to retard thermally activated processes such as dislocation creep and rafting.

Summary and conclusions

Interdiffusion coefficients in the Ni–Os system were determined at the temperatures 1200, 1300 and 1350°C in fcc (A1) γ-Ni. Values for the Ni–Re system were also determined for the purposes of comparison. The diffusion annealing experiments were conducted by preparing diffusion couples between pure Ni and Ni-10X (X=Os and Re). Diffusion in these systems gave planar interfaces with no evidence of Kirkendall porosity. A modified form of the Boltzmann–Matano method was used to calculate the concentration dependent diffusion coefficient $\widetilde{D}$, which was found to be only weakly dependent on composition for both Os and Re. It was found that Os displays an interdiffusion coefficient which is comparable to that for Re, at any given temperature in the range examined.

Using the Sauer–Freise approach, it was found that the diffusion coefficients $\widetilde{D}_{SF}$ can be represented by

$$\widetilde{D}_{SF}^{Os}\ (m^2\ s^{-1}) = 2 \cdot 24 \times 10^{-5} \exp\left(-289\ kJ\ mol^{-1}/RT\right)$$

$$\widetilde{D}_{SF}^{Re}\ (m^2\ s^{-1}) = 1 \cdot 98 \times 10^{-6} \exp\left(-259\ kJ\ mol^{-1}/RT\right)$$

Fitting of the concentration profiles with error function profiles yielded the following alternative expressions

$$\widetilde{D}_{ER}^{Os}\ (m^2\ s^{-1}) = 4 \cdot 42 \times 10^{-4} \exp\left(-327\ kJ\ mol^{-1}/RT\right)$$

$$\widetilde{D}_{ER}^{Re}\ (m^2\ s^{-1}) = 2 \cdot 86 \times 10^{-5} \exp\left(-294\ kJ\ mol^{-1}/RT\right)$$

These results confirm previous theoretical predictions[10] that Os diffuses slowly in the Ni matrix, at a rate which is among the slowest of any of the elements in the d-block. It seems likely that Os will retard the rates of thermally activated processes in these materials. It is recommended that experiments be undertaken to determine whether Os improves the high temperature properties of the nickel-based superalloys.

Acknowledgements

References

1. R. C. Reed: 'The superalloys: fundamentals and applications'; 2006, Cambridge, Cambridge University Press.
2. M. Hasaka, T. Morimura, Y. Uchiyama, S. Kondo, T. Watanabe, K. Hisatsune and T. Furuse: *Scr. Metall. Mater.*, 1993, **29**, 959–962.
3. M. S. A. Karunaratne: *Defect Diffus. Forum*, 2005, **237–240**, 420–425.
4. M. S. A. Karunaratne, P. Carter and R. C. Reed: *Mater. Sci. Eng. A*, 2000, **A281**, 229–233.
5. M. S. A. Karunaratne and R. C. Reed: *Acta Mater.*, 2003, **51**, 2905–2919.
6. R. V. Patil and G. B. Kale: *J. Nucl. Mater.*, 1996, **230**, 57–60.
7. M. S. A. Karunaratne, P. Carter and R. C. Reed: *Acta Mater.*, 2001, **49**, 861–875.
8. M. Hattori, N. Goto and Y. Murata: *Mater. Trans.*, 2006, **47**, 331–334.
9. M. Hattori, N. Goto, Y. Murata, T. Koyama and M. Morinaga: *Mater. Trans.*, 2005, **46**, 163–166.
10. A. Janotti, M. Krcmar, C. L. Fu and R. C. Reed: *Phys. Rev. Lett.*, 2004, **92**, 0859011–0859014.
11. M. Krcmar, C. L. Fu, A. Janotti and R. C. Reed: *Acta Mater.*, 2005, **53**, 2369–2376.
12. L. Boltzmann: *Wiedemanns Ann. Phys.*, 1894, **53**, 959–961.
13. C. Matano: *Jpn J. Phys.*, 1933, **8**, 109–113.
14. V. F. Sauer and V. Freise: *Z. Elektrochem.*, 1962, **66**, 353–363.
15. F. J. A. den Broeder: *Scr. Metall.*, 1969, **3**, 321–325.
16. J. S. Kirkaldy and D. J. Young: 'Diffusion in the condensed state'; 1987, London, The Institute of Metals.