JOURNAL OF MATERIALS SCIENCE 25 (1990) 1640–1644

Mass transport of cobalt and nickel in Incoloy–800

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Lattice diffusion of cobalt and nickel in Incoloy–800 has been studied in the temperature range 1070 to 1500 K by serial sectioning and residual activity techniques using radioactive tracers ^{60}Co and ^{63}Ni. The lattice diffusion coefficient can be expressed by the relation:

$$D_{Co/Incoloy\text{-}800} = 2.54 \times 10^{-5} \exp\left(-\frac{249.5\,kJ\,mol^{-1}}{RT}\right) m^2\,sec^{-1}$$

$$D_{Ni/Incoloy\text{-}800} = 8.62 \times 10^{-5} \exp\left(-\frac{255.9\,kJ\,mol^{-1}}{RT}\right) m^2\,sec^{-1}$$

Segregation and mass transport studies of these tracers along the grain boundary in Incoloy–800 have also been carried out in the temperature range 750 to 1080 K. The grain boundary diffusion coefficients are evaluated by Whipple and Suzuoka methods and are found to be in good agreement. Grain boundary diffusivity D_{gb} can be expressed by the equation

$$D_{gb\,Co/Incoloy\text{-}800} = 1.06 \times 10^{-5} \exp\left(-\frac{152.72\,kJ\,mol^{-1}}{RT}\right) m^2\,sec^{-1}$$

$$D_{gb\,Ni/Incoloy\text{-}800} = 3.82 \times 10^{-5} \exp\left(-\frac{156.40\,kJ\,mol^{-1}}{RT}\right) m^2\,sec^{-1}$$

Segregation of these tracers along the grain boundary in Incoloy–800 has been studied by autoradiographic technique. The results have been discussed and presented in this paper.

1. Introduction

Incoloy–800 is one of the important materials used as tubes in nuclear steam generators. Although investigations on the corrosion behaviour of this alloy have been carried out, the diffusion of various corrosion products that could be picked up by the material from high temperature water is meagre. In addition, very little work has been conducted on the mass transport studies of its constituents in it. In the earlier investigation, the authors have studied [1, 2] the diffusion of iron, cobalt, nickel and copper in Monel–400 (a steam generator tube material). The present work is an extension of the earlier work and deals with the segregation and mass transport of nickel and cobalt in bulk and along the grain boundaries in Incoloy–800.

2. Experimental procedure

For the present study specimens in the form of circular discs of ~ 12 mm dia. and 3 mm thickness were used. The chemical analysis of the material is given in Table I. For volume diffusion these were annealed in high vacuum at 1450 K for seven days. This yielded the average grain of about 1 mm dia. For grain boundary diffusion, the specimens were annealed at 1350 K for three days. This yielded the grains of about 300 μm diameter. One end face of each specimen was polished following the usual procedure of polishing for metals and alloys. The cold worked materials from the polished surface were removed by careful etching in suitable etchant.

Radioactive ^{60}Co was deposited on the polished and slightly etched surface in metallic form by vacuum deposition technique. While depositing the active material, the entire surface except the polished face was covered with tantalum foil. Prior to the vacuum deposition, the specimen was heated at 500 K to remove the adsorbed water vapour from the surface. The thickness of the radioactive cobalt layer on the polished surface was about 10 nm. For the grain boundary diffusion studies by Whipple's method [3], a thick layer (~ 2 μm) was deposited on the polished surface of a few samples. For the diffusion studies of nickel, radioactive ^{63}Ni was deposited on the polished surface by electroplating method. Thickness of the deposition was about the same as that of ^{60}Co deposited layer by vacuum evaporation technique.

0022–2461/90 $03.00 + .12

TABLE I Chemical composition of Incoloy-800

Element	Wt %
Fe	45.02
Ni	32.34
Cr	20.58
Mn	0.79
Al	0.37
Ti	0.35
Cu	0.19
Si	0.31
C	0.05

For the diffusion annealing below 1273 K, the specimen was put in well-baked quartz ampoules filled with ultra purified helium gas at precalculated pressure of about one atmosphere at diffusion annealing temperature. For mass transport studies above 1273 K, the specimens were annealed in a recrystallized alumina tube in inert atmosphere by passing helium gas through the tube. The temperature of the furnace was maintained within ± 0.2 K for diffusion annealing below 1200 K whereas above this temperature up to highest temperature of annealing (1500 K) it was controlled within 1 K. The volume and the grain boundary diffusion of ^{60}Co and ^{63}Ni were carried out in the temperature ranges 1050 to 1470 K and 750 to 1080 K, respectively. The time of annealing varied from a few hours to several days depending upon the temperature of annealing. Metallographic investigations were made on a few specimens before and after diffusion annealing to check the size and geometry of the grain. No noticeable change was observed in the specimen.

In order to eliminate the surface diffusion effect from the sides, the diameter of each annealed specimen was reduced by about 2 mm. For diffusion study of ^{60}Co in Incoloy-800, the serial sectioning technique was used. The specimen was ground on carborundum paper and the removed material was dissolved carefully in concentrated nitric acid. Each time an approximately equal weight of the material was dissolved to correct the self-absorption effect. 1.33 MeV γ-radiation of ^{60}Co was selectively counted using a scintillation counter having well defined 2π geometry. For ^{63}Ni diffusion residual activity technique was employed. 0.067 MeV β activity of ^{63}Ni was measured by a windowless proportional counter.

3. Results and discussion

3.1. Volume diffusion

Under the present boundary conditions the volume diffusion coefficient D could be evaluated following the expression [4]

$$C(X) = \text{Const. exp}\left(-\frac{X^2}{4Dt}\right) \quad (1)$$

where $C(X)$ is concentration of diffusant at a distance X into the specimen and t is the time of annealing. Thus the diffusion coefficients D could be evaluated from the plot log C against X^2.

A few characteristic plots of log C against X^2 for the diffusion of ^{60}Co and ^{63}Ni in Incoloy-800 is shown in Fig. 1. It has been observed that the curves in the plot are linear over the entire range of penetration profile (order of magnitude about two). Thus the effect of grain boundaries towards the diffusivity is negligibly small and the results show the lattice diffusivity satisfying the boundary conditions.

The diffusion coefficients were evaluated from the slopes of these linear curves and the values are given in Table II. The error estimated in the values of diffusivity was less than 12%. The temperature dependence of diffusivity is found to obey Arrhenius' relation. The corresponding plot of log D against T^{-1} is shown in Fig. 2. The diffusivity of ^{60}Co and ^{63}Ni in Incoloy-800 in the range of temperature 1070 to

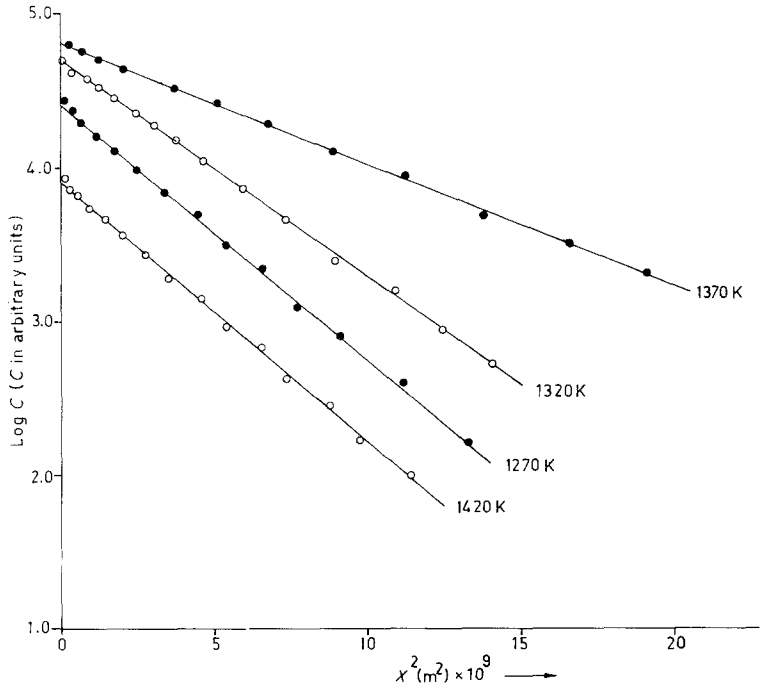

Figure 1 Characteristic plots of log C versus X^2 for the diffusion of ^{60}Co and ^{63}Ni in Incoloy-800 (C is the specific activity and residual activity for ^{60}Co and ^{63}Ni, respectively in arbitrary units). o – ^{60}Co, • – ^{63}Ni.

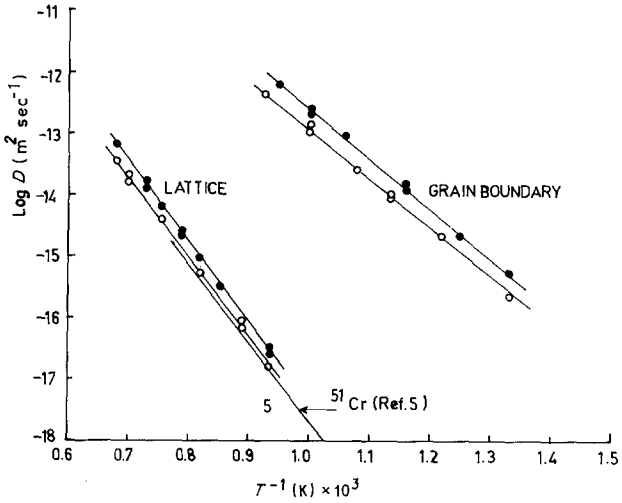

Figure 2 Temperature dependence of lattice and grain boundary diffusion of ^{60}Co and ^{63}Ni in Incoloy–800. ○ – ^{60}Co, ● – ^{63}Ni.

1500 K could be expressed by the relation

$$D_{\text{Co/Incoloy-800}} = 2.54 \times 10^{-5} \times \exp\left(-\frac{249.5\,\text{kJ mol}^{-1}}{RT}\right)\text{m}^2\,\text{sec}^{-1}$$

$$D_{\text{Ni/Incoloy-800}} = 8.62 \times 10^{-5} \times \exp\left(-\frac{255.9\,\text{kJ mol}^{-1}}{RT}\right)\text{m}^2\,\text{sec}^{-1}$$

The frequency factors and activation energies were evaluated by the least square method.

It is difficult to draw a definite conclusion about the impurity diffusion in a multicomponent alloy system like Incoloy–800. Nevertheless it is better to compare the values of activation energies in this system with those of impurity diffusion in iron, chromium and nickel alloy (major components of alloy). The D_0 and Q values of diffusion of ^{60}Co and ^{63}Ni in Incoloy–800 are 2.54×10^{-5} m^2 sec^{-1}, 249.5 kJ mol^{-1} and 8.62×10^{-5} m^2 sec^{-1}, 255.9 kJ mol^{-1}, respectively. These values are comparable with the diffusion of ^{51}Cr in the alloy [5] having composition 33 wt % nickel, 19.8 wt % chromium, 46 wt % iron and 0.66 wt % aluminium. The frequency factor and activation energy for ^{51}Cr diffusion in the above alloy is 10^{-5} m^2 sec^{-1} and 245.45 kJ mol^{-1}. There is no relation that can predict the value of activation energy for the impurity diffusion in a multicomponent alloy. It is usually believed that for a vacancy mechanism to be operative as in the case of self-diffusion in pure metals, the activation energy for diffusion would be about $34T_m$ (T_m is the melting point). The Q values obtained for the diffusion of ^{60}Co and ^{63}Ni in Incoloy–800 are found to obey this relation quite satisfactorily. The values of frequency factor yield positive entropy of activation when analysed on Zener's theory [6]. This supports the vacancy mechanism of mass transport of cobalt and nickel in Incoloy–800.

TABLE II Lattice diffusivities of cobalt and nickel in Incoloy–800

Diffusing species	Temperature (K)	Time of anneal (sec)	Diffusion coefficients (m^2 sec^{-1})
^{60}Co	1070	5.18×10^5	1.50×10^{-17}
	1120	3.06×10^5	6.52×10^{-17}
	1120	3.06×10^5	5.98×10^{-17}
	1220	5.18×10^5	5.00×10^{-16}
	1320	1.98×10^5	3.94×10^{-15}
	1420	4.32×10^4	1.47×10^{-14}
	1420	4.32×10^4	1.78×10^{-14}
	1470	3.60×10^4	3.11×10^{-14}
^{63}Ni	1070	4.32×10^5	2.48×10^{-17}
	1070	4.32×10^5	2.87×10^{-17}
	1170	3.46×10^5	3.12×10^{-16}
	1220	3.46×10^5	9.68×10^{-16}
	1270	2.59×10^5	2.54×10^{-15}
	1270	2.59×10^5	2.23×10^{-15}
	1320	1.73×10^5	6.52×10^{-15}
	1370	8.64×10^4	1.26×10^{-14}
	1370	8.64×10^4	1.59×10^{-14}
	1470	3.60×10^4	6.62×10^{-14}

3.2. Grain boundary diffusion

Segregation and mass transport problems along the grain boundaries have been investigated by several workers and the subject has been discussed and reviewed [7–10]. In the present investigation, Whipple [3] and Suzuoka [11, 12] methods have been employed to evaluate the diffusion along the grain boundaries. An exact solution to the grain boundary diffusion problem for a constant source by Whipple's method is a complicated one and cannot be used directly to evaluate diffusion coefficients from experimentally determined concentration as a function of penetration depth. At larger penetration depths, where the mass transport by volume diffusion is negligibly small (at a

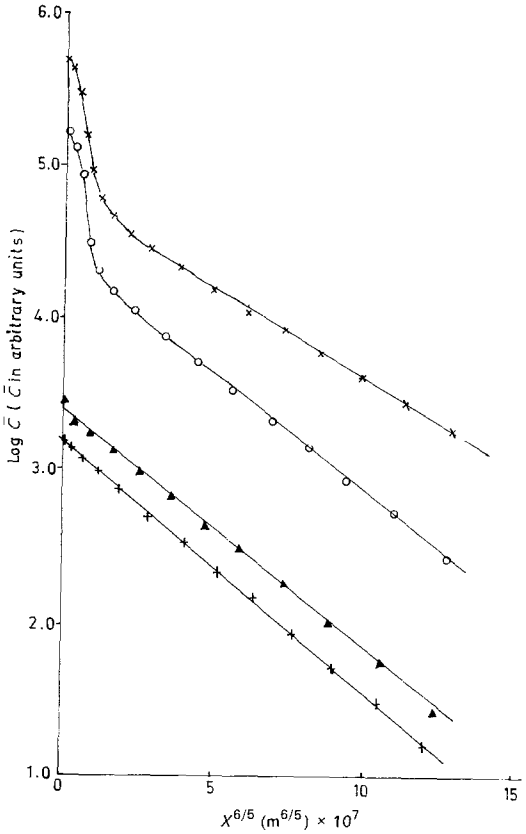

Figure 3 Characteristic plots of log $\bar{C}$ against $X^{6/5}$ for the grain boundary diffusion of ^{60}Co and ^{63}Ni in Incoloy–800. ○ Co 1000 K for 30 h Suzuoka method; x Ni 1000 K for 30 h, Suzuoka method; + Co 880 K for 100 h, Whipple method; ▲ Ni 800 K for 100 h, Whipple method.

TABLE III Grain boundary diffusion coefficients of cobalt and nickel in Incoloy-800

Diffusing species	Temperature (K)	Time of anneal (sec)	Diffusion coefficients ($m^2\ sec^{-1}$)
^{60}Co	750	3.60×10^5	2.29×10^{-16}
	820	3.60×10^5	2.34×10^{-15}
	880	3.60×10^5	9.77×10^{-15}
	880	3.60×10^5	9.55×10^{-15}*
	920	3.60×10^5	2.63×10^{-14}
	1000	1.08×10^5	1.38×10^{-13}*
	1000	1.08×10^5	1.16×10^{-13}
	1080	1.08×10^5	4.57×10^{-13}
^{63}Ni	750	3.60×10^5	5.62×10^{-16}
	800	3.60×10^5	2.10×10^{-15}
	860	3.60×10^5	1.45×10^{-14}
	860	3.60×10^5	1.26×10^{-14}*
	940	3.60×10^5	9.55×10^{-14}
	1000	1.08×10^5	2.63×10^{-13}*
	1000	1.08×10^5	2.34×10^{-13}
	1050	1.08×10^5	6.17×10^{-13}

*Calculated from Equation 3 and the rest from Equation 2.

lower temperature of annealing) Whipple's equation reduces to:

$$D_{gb}\delta = \left(\frac{\partial \ln \bar{C}}{\partial X^{6/5}}\right)^{-5/3}\left(\frac{4D}{t}\right)^{1/2}(0.78)^{5/3} \quad (2)$$

where δ is the grain boundary width usually taken as twice the atomic spacing in the lattice and assumed to be 0.5 nm for most of the elements [13, 14], D is the volume diffusion coefficient, $\bar{C}$ is the average concentration of diffusing atoms at a distance X from the surface and t is the annealing time.

Suzuoka's instantaneous source solution [11, 12] may be written in simple form [8, 9, 15]:

$$D_{gb}\delta = (\partial \ln \bar{C}/\partial X^{6/5})^{-5/3}(4D/t)^{1/2}\beta^{0.013}(0.578) \quad (3)$$

where

$$\beta = (D_{gb} \cdot \delta)/(2D\sqrt{Dt})$$

At larger penetration distances where mass transport of impurity is mainly along the grain boundaries log $\bar{C}$ plotted against $X^{6/5}$ should be linear in both cases. A few characteristic plots of log $\bar{C}$ against $X^{6/5}$ for the diffusion of ^{60}Co and ^{63}Ni in small grained specimens of Incoloy-800 are shown in Fig. 3 where it is seen that at lower temperatures of annealing most of the diffusing atoms are confined to within a short distance. As the temperature increases an upward bend of the concentration profile in the plot of log $\bar{C}$ against $X^{6/5}$ is observed. This is the region where the mass transport of the tracer is through the volume diffusion process. As the penetration distance increases both the processes of diffusion take place. At larger penetration distances a linear relation in the plot of log $\bar{C}$ against $X^{6/5}$ is observed which clearly indicates that most of the activity is transferred along the grain boundaries. Several autoradiographic pictures have been taken after sectioning which showed that at shorter penetration distances from the initial surface, volume diffusion is predominant whereas at larger distances diffusion along the grain boundaries is solely operative. Fig. 4 shows such a typical autoradiograph for diffusion of ^{63}Ni along the grain boundaries at a penetration distance 6.5 μm from the surface of a specimen annealed at 900 K for 120 hours.

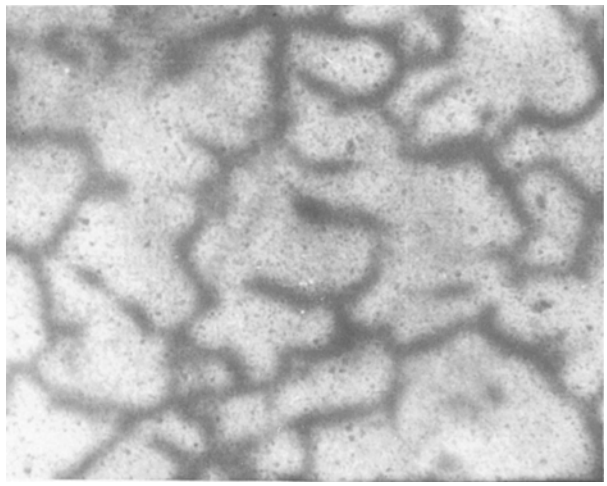

Figure 4 Autoradiograph showing the ^{63}Ni activity along the grain boundaries. The specimen was annealed at 900 K for 120 hrs. Abrasion distance 6.5 μm. Magnification: × 50.

From the linear part of the curve log $\bar{C}$ against $X^{6/5}$ diffusion coefficients along the grain boundaries D_{gb} were evaluated (Table III). Whipple's method (from initial thick deposit ~ 2 μm) and Suzuoka's method of instantaneous source solution gave D_{gb} values which were in good agreement within experimental limits (error ~ 12%). The diffusivity could be represented by equations:

$$D_{gb\,Co/Incoloy\text{-}800} = 1.06 \times 10^{-5} \times \exp\left(-\frac{152.74\,kJ\,mol^{-1}}{RT}\right) m^2\,sec^{-1}$$

$$D_{gb\,Ni/Incoloy\text{-}800} = 3.82 \times 10^{-5} \times \exp\left(-\frac{156.40\,kJ\,mol^{-1}}{RT}\right) m^2\,sec^{-1}$$

The ratio of D_{gb}/D for the diffusion of ^{60}Co and ^{63}Ni at 1000 K is ~ 10^5. Q_{gb}/Q (0.61) is similar to the values for most of the face centered cubic metals and alloys where a general trend of $0.4 < Q_{gb}/Q < 0.7$ is observed and a vacancy mechanism of grain boundary diffusion is considered probable.

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Received 22 November 1988
and accepted 8 May 1989