Diffusion of Cr and Fe in a High-Purity Fe–50 mass%Cr–8 mass%W Alloy

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Volume and grain boundary diffusivities of ⁵¹Cr and ⁵⁹Fe in a high purity Fe–50 mass%Cr–8 mass%W (Fe–50Cr–8W) alloy have been determined in the temperature range between 1023 and 1373 K with the sputter-microsectioning technique. The volume diffusion coefficients of Cr and Fe in the Fe–50Cr–8W alloy are smaller than those in a high-purity Fe–50 mass%Cr (Fe–50Cr) alloy. Linear Arrhenius lines for the volume self-diffusion coefficients of both tracers have been observed in the temperature range examined. The activation energies for the volume diffusion of both components in the Fe–50Cr–8W alloy are somewhat smaller than those in the Fe–50Cr alloy. On the other hand, the grain boundary diffusivities of Cr and Fe in the Fe–50Cr–8W alloy at 1123 K are about two orders of magnitude smaller than those in the Fe–50Cr alloy.

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1. Introduction

Iron-base chromium alloys have been widely used as structural materials, because of their excellent strength at high temperatures and good corrosion resistance. However, in the Fe–Cr alloys with high chromium content, formation of the σ phase causes serious deterioration in mechanical properties such as ductility and impact toughness, which has been well known as the σ embrittlement. Therefore, content of chromium in the ferritic stainless steels has been limited below 30 mass%. Recently, Abiko and coworkers have succeeded in drastic improvement of mechanical properties of iron alloys containing chromium 50 mass% and more by purification.^{1,2)} This research group has challenged further improvement of high purity Fe–Cr alloys by addition of some elements such as tungsten. According to their recent works, Fe–50 mass%Cr–8 mass%W alloy shows much higher yield stress at temperatures above 973 K than that of Fe–50 mass%Cr alloy.^{3,4)}

This remarkable improvement of mechanical properties of the high purity Fe–Cr alloys stimulates us to study the diffusion in the alloys. Diffusion study on the Fe–Cr alloys is important, because diffusion is the basic processes of the atomic transport in materials including phase transformations. As well as the volume self-diffusion, grain boundary diffusion is also important, because diffusion along grain boundaries, which is generally orders of magnitude faster than that in grains, plays a key role especially at lower temperatures in many processes, such as creep, discontinuous precipitation, etc.⁵⁾ Then, we have presented the volume and grain boundary diffusion of ⁵¹Cr and ⁵⁹Fe in a high purity Fe–50 mass%Cr alloy in the temperature range between 923 and 1453 K.^{6,7)} Linear Arrhenius relations for the volume diffusion of both components in the alloy have been observed across the transformation temperature of the σ phase, suggesting that the σ phase was barely formed in the alloy and that it gives negligible influence on the volume diffusion. However, Arrhenius

lines curved downward are observed for the grain boundary diffusivity of both components, which are attributed to the formation of very thin layer of the (Cr,Fe)₂₃C₆ phase at the grain boundary near the surface of the specimens.⁷⁾

The aim of the present work is to determine the tracer diffusion coefficients of ⁵¹Cr and ⁵⁹Fe in a high purity Fe–50 mass%Cr–8 mass%W alloy by use of the serial sputter-microsectioning technique.

2. Experimental Procedure

A high purity Fe–50 mass%Cr–8 mass%W (Fe–50Cr–8W) alloy was made by induction melting high purity electrolytic iron block (99.995%), high purity chromium flake (99.98%) and high purity tungsten flake (99.999%) in a cold copper crucible in a high purity argon atmosphere. The chemical composition of the alloy is shown in Table 1 in comparison with that of the high purity Fe–50Cr alloy used in a previous work.^{6,7)} The ingot was hot-forged and hot-rolled at 1373 K in an argon atmosphere to a rod 14 mm in diameter. Specimens of 12 mm in diameter and 1.5 mm in thickness were machined from the rod. The flat face of the specimens was ground on abrasive papers and was electropolished at 273 K in a solution containing 10 vol% perchloric acid and 90 vol% acetic acid. The specimens were annealed at 1873 K for 43.2 ks in a stream of hydrogen gas purified by permeation through a palladium alloy tube at 700 K and were cooled down at a rate of 5 Kmin^{–1}. The resulting grain size was about 4–5 μ m. After the grain growth, the surface of the specimens was ground on abrasive papers and finally electropolished in the same conditions as above.

The radioisotopes ⁵¹Cr (γ -decay, 0.320 MeV; half-life, 27.7d) in a form of CrCl₃ in 0.5 kmolm^{–3} HCl solution and ⁵⁹Fe (γ -decay, 1.095 and 1.292 MeV; half-life, 44.5d) in a form of FeCl₃ in 0.5 kmolm^{–3} HCl solution were supplied from New England Nuclear Corporation, U.S.A. A few drops of the solutions containing radioisotopes were put onto the mirror-like surface of the specimen and dried under a heating

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Table 1 Chemical composition of Fe–50Cr–8W alloy and Fe–50Cr alloy (Cr, W in mass%, others in mass ppm).

Alloy	Cr	W	C	N	O	S	Si	P	Al	Mn
Fe–50 mass%Cr–8 mass%W	50.1	7.95	12.7	23.7	54.1	3.8	22	4.4	<5	<10
Fe–50 mass%Cr	49.6	—	13.1	5.6	34.1	3.2	25	4.4	1.3	2.4

lamp. A quartz tube with the sample was evacuated dynamically under 1×10^{-4} Pa, and then it was put into an electric furnace controlled within ± 1 K for diffusion annealing at temperatures in the range from 1023 to 1373 K for 1.2 to 241.2 ks.

The serial radio-frequency sputter-microsectioning method was employed to measure the penetration profiles of the radioisotopes in the specimen. The specimen was set on a target in the radio-frequency sputtering apparatus. By applying radio-frequency power with a peak-to-peak voltage of 1.6 kV at 13.56 MHz, the specimen was sputtered in an argon glow discharge. The sputtered-off material was collected on an aluminum foil. The serial sectioning of the whole profile was achieved by moving the collector foil step by step like a roll film in a camera without interrupting the radio-frequency supply. For each specimen 30–40 successive sections were sputtered. The thickness of each section was determined from the individual sputtering time and sputtering rate. In each run the sputtering rate was calculated from the total sputtering time and total reduced thickness, which was estimated by the total weight loss. A constant fraction of more than 60% of the sputtered-off material was collected on an aluminum foil. The intensity of the γ -ray from each section was measured by a well-type Tl-activated NaI scintillation detector in conjunction with a 1024-channel pulse height analyzer.

3. Results and Discussion

3.1 Volume diffusion of Cr and Fe in high-purity Fe–50 mass%Cr–8 mass%W alloy

For one-dimensional volume diffusion of a tracer from an infinitesimally thin surface layer into a sufficiently long rod, the solution of Fick's second law is given by

$$I(X, t) \propto C(X, t) = \frac{M}{\sqrt{\pi D_v t}} \exp\left(-\frac{X^2}{4D_v t}\right), \quad (1)$$

where $I(X, t)$ and $C(X, t)$ are the intensity of radioactivity and the concentration, respectively, of the tracer at a distance X from the original surface after a diffusion time t . D_v is the volume diffusion coefficient of the tracer and M is the total amount of the tracer deposited on the surface before diffusion.

Figures 1 and 2 show the penetration profiles of $\ln I(X, t)$ vs. X^2 for the diffusion of ^{51}Cr and ^{59}Fe in the Fe–50Cr–8W alloy, respectively. Although some deviation from a linearity is observed very near the surface of the profiles in Figs. 1 and 2, the linearity observed in Figs. 1 and 2 proves that eq. (1) holds, and thus it is the volume diffusion that concerned. The deeper tails at 1123 K and 1323 K in Figs. 1 and 2 are due to grain boundary diffusion as discussed later. The diffusion coefficients of ^{51}Cr and ^{59}Fe , D_{Cr} and D_{Fe} , are calculated from the linear slope of the profiles. The Arrhenius plots of the diffusion coefficients are shown in Figs. 3 and 4 in com-

Fig. 1 Penetration profiles of ^{51}Cr in Fe–50Cr–8W alloy.

parison with those in the Fe–50Cr alloy.^{6,7)} The diffusion coefficients of both components in the Fe–50Cr–8W alloy take nearly equal values in the temperature range examined. However, both the values in the alloy are smaller than those in the high purity Fe–50Cr alloy. The difference in the diffusion coefficients of Fe in the two alloys is larger than the difference in the diffusion coefficients of Cr.

The linear Arrhenius lines in Figs. 3 and 4 can be expressed by the following equations.

$$D_{\text{Cr}} = 5 \times 10^{-5} \exp\left[-\frac{(255 \pm 9) \text{ kJmol}^{-1}}{RT}\right] \text{ m}^2\text{s}^{-1} \quad (2)$$

$$D_{\text{Fe}} = 2 \times 10^{-5} \exp\left[-\frac{(247 \pm 7) \text{ kJmol}^{-1}}{RT}\right] \text{ m}^2\text{s}^{-1} \quad (3)$$

The activation energies for the diffusion of Cr and Fe in the Fe–50Cr–8W alloy are smaller than the values of 259 ± 3 and $256 \pm 4 \text{ kJmol}^{-1}$ in the Fe–50Cr alloy, respectively.

3.2 Grain boundary diffusion of Cr and Fe in high-purity Fe–50 mass%Cr–8 mass%W alloy

The grain boundary diffusion behavior in an alloy can be described by the type-B kinetics termed to Harrison,⁸⁾ when the value of $(D_v t)^{1/2}$ is smaller than $d/20$ (d : average diameter of the grains) as is the case of the present experiments; the values of $(D_v t)^{1/2}$ are about 0.01–0.1 μm , and the values of $d/20$ are about 200–250 μm . For the diffusion from an instantaneous source in the type-B kinetics, Suzuoka's solutions^{9,10)}

Fig. 2 Penetration profiles of ^{59}Fe in Fe-50Cr-8W alloy. Fig. 3 Arrhenius plots of D_{Cr} in Fe-50Cr-8W and Fe-50Cr alloys.

are given depending on the value of β ($\beta \equiv \frac{s\delta(D_{\text{gb}}/D_{\text{v}}-1)}{2\sqrt{D_{\text{v}}t}}$, where s : segregation factor, δ : width of grain boundary, D_{gb} : grain boundary diffusion coefficient). The value of β represents the extent of the grain boundary diffusion in comparison with the volume diffusion. For example, the larger the value of β is, the more importantly grain boundary diffusion occurs. In the present experiments, the following equation can be used to analyze the data.

$$s\delta D_{\text{gb}} = 1.084 \left(\frac{D_{\text{v}}^{0.91}}{t^{1.03}} \right)^{\frac{1}{1.94}} \left(\frac{-d \ln C}{dX^{6/5}} \right)^{-\frac{5}{2.91}} \quad \text{for } 10 < \beta < 10^2 \quad (4)$$

The value of β is confirmed to be in the range from 10 to 10^2 .

Fig. 4 Arrhenius plots of D_{Fe} in Fe-50Cr-8W and Fe-50Cr alloys. Fig. 5 Penetration profiles of ^{51}Cr and ^{59}Fe in Fe-50Cr-8W alloy.

Figure 5 shows the penetration profiles of $\ln I(X, t)$ vs. $X^{6/5}$ for the diffusion of ^{51}Cr (at 1123 K and 1173 K) and ^{59}Fe (at 1123 K and 1323 K) in the Fe-50Cr-8W alloy. These profiles are the same as that used to determine the volume diffusion coefficients at the corresponding temperatures. The penetration profiles exhibit two regions: the one is the near surface region and the other the less steep tail of the profile. The former corresponds predominantly to the volume diffusion process, while the latter is due to the diffusion along grain boundaries, because the condition of type-B kinetics is fulfilled. The linear slope of the tail in the profile is used to calculate the grain boundary diffusivity $s\delta D_{\text{gb}}$. The grain boundary diffusivities of chromium are calculated to be $7.9 \times 10^{-22} \text{ m}^3 \text{ s}^{-1}$ at 1123 K and $2.0 \times 10^{-21} \text{ m}^3 \text{ s}^{-1}$ at 1173 K, while those of iron are $2.7 \times 10^{-21} \text{ m}^3 \text{ s}^{-1}$ at 1123 K

Fig. 6 Arrhenius plots of $s\delta D_{gb}$ in Fe–50Cr–8W and Fe–50Cr alloys.

and $1.4 \times 10^{-19} \text{ m}^3 \text{ s}^{-1}$ at 1323 K. The Arrhenius plots for the grain boundary diffusivities of both elements are shown in Fig. 6 in comparison with those in the Fe–50Cr alloy. The grain boundary diffusivity of Fe is about 3 times larger than that of Cr in the Fe–50Cr–8W alloy at 1123 K. Furthermore, grain boundary diffusivities in the Fe–50Cr–8W alloy are two orders of magnitude smaller than those in the Fe–50Cr alloy, suggesting that the addition of tungsten remarkably suppresses the grain boundary diffusion of both components in the Fe–50Cr alloy. Although the data are limited only at two temperatures, the activation energies for grain boundary diffusion of Cr and Fe are tentatively estimated to be 240 kJ mol^{-1} and 200 kJ mol^{-1} , respectively. The activation energies in the Fe–50Cr alloy in the corresponding temperature region⁷⁾ are about 270 kJ mol^{-1} . Further discussion on the grain boundary diffusivities should await more extensive experimental data.

4. Conclusions

(1) Volume diffusion coefficients of Cr and Fe in a high purity Fe–50 mass%Cr–8 mass%W alloy in the temperature

range from 1023 to 1323 K are smaller than those in a high purity Fe–50 mass%Cr alloy.

(2) Grain boundary diffusivities of Cr and Fe in the high purity Fe–50 mass%Cr–8 mass%W alloy are about two orders of magnitude smaller than those in the high purity Fe–50 mass%Cr alloy.

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