Diffusion of niobium in α-iron

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Diffusion coefficient of 95\textsuperscript{Nb} in α-iron has been determined in the temperature range between 823 and 1163 K by use of a serial sputter-microsectioning technique. The diffusion coefficient of niobium is about two times as large as the self-diffusion coefficient in α-iron. The temperature dependence of the diffusion coefficient, D, in the whole temperature range of α-iron across the Curie temperature (TC = 1043 K) can be expressed by $D = (1.40 \pm 0.17) \times 10^{-11} \exp\left[-\frac{299.7 \pm 12.3 \text{kJmol}^{-1}}{RT} + 0.96(\pm 0.07)\right] \text{m}^2\text{s}^{-1}$ where $s$ is the ratio of the spontaneous magnetization at 7 K to that at 0 K. The factor 0.061 in the equation is smaller than 0.156 for the self-diffusion, showing that the magnetic effect on the diffusion of niobium in α-iron is smaller than that on the self-diffusion. The activation energy 299.7 kJmol$^{-1}$ for niobium diffusion in the paramagnetic iron is much higher than 250.6 kJmol$^{-1}$ for the self-diffusion. Atomic size effect is predominant in the activation energies for the diffusion of transition metal solutes in the paramagnetic α-iron.

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1. Introduction

Diffusion data on iron-base alloys are very important in evaluating the behavior for high temperature creep, oxidation, grain boundary corrosion, etc. of the materials in operation. Addition of niobium improves generally the heat resistance and creep strength of steels.\(^1\) Niobium is also used for the stabilization of carbon in stainless steels and for gain size control and precipitation hardening in high strength low alloy steels.\(^2\) A knowledge of the diffusion behavior of niobium in iron and steels is therefore important for a full understanding of these processes.

In the past, diffusion of niobium in iron has been studied by Geise and Herzig\(^3\) and by Herzig et al.\(^4\) using radioactive tracer 95\textsuperscript{Nb} and the serial sectioning technique with precision grinding and microtome. However, the diffusion coefficient of niobium in α-iron obtained by these authors\(^3,4\) is about one order of magnitude larger than the self-diffusion coefficient.\(^5,6\) It seems that their values are anomalously high in comparison with the diffusion coefficients of transition metal solutes in α-iron.\(^7\) In the studies on self-diffusion in α-iron,\(^5,6\) it has been noted that the diffusion coefficient obtained by use of conventional mechanical sectioning methods is larger than that obtained by the sputter-microsectioning technique. In the experiments with mechanical sectioning methods, the average diffusion distance, $2\sqrt{D_0t}$ ($D_0$: diffusion coefficient, $t$: diffusion time), is usually in the range 30-100 μm which is greater than normal inter-dislocation spacing in α-iron. As a result, the measured diffusion coefficients in α-iron obtained by the conventional mechanical sectioning techniques are affected by the enhancement effect due to the diffusion along the dislocation networks. In particular, the influence of short circuit paths on diffusion is more serious at low temperatures; i.e. the γ-α transformation temperature of iron corresponds to 0.65$T_m$ ($T_m$: melting temperature). In the previous experiments of the diffusion of niobium in α-iron,\(^5,4\) the average diffusion distance in the paramagnetic α-iron was in the range from 33 to 90 μm. Therefore, the large diffusion coefficient of niobium in α-iron\(^3,4\) was probably caused by the enhanced diffusion along short-circuit paths.

The activation energy for diffusion of niobium in iron is also interesting. A linear relationship between the atomic radius and the activation energy for the diffusion of transition metal solutes in the paramagnetic α-iron has been observed.\(^8\) The atomic radius of niobium is about 15% larger than that of iron,\(^9\) which is, in the view of Hume Rothery’s rule, nearly the upper limit to form a solid solution with iron, and thereby the solid solubility of niobium in α-iron and γ-iron is very low.\(^10\)

Below the Curie temperature, the Arrhenius plot of diffusion coefficients of solute as well as solvent atom in iron of the ferromagnetic state deviates downwards from the Arrhenius relationship extrapolated from the paramagnetic state.\(^11\) The temperature dependence of the diffusion coefficient in the whole temperature range across the Curie temperature has been well described by\(^12\)

$$D = D_0^p \exp\left[-Q^p(1 + \alpha s^2)/RT\right].$$

Here $D_0^p$ and $Q^p$ are respectively the preexponential factor and the activation energy for the diffusion in the paramagnetic state. The value of $s$, the ratio of the spontaneous magnetization at $T$ K to that at 0 K, has been experimentally determined by Potter\(^13\) and by Crangle and Goodman.\(^14\) The constant $\alpha$ expressing the extent of the influence of the magnetic transformation on diffusion, is given by

$$\alpha = \frac{\alpha_f + \alpha_m}{Q^p},$$

where $\alpha_f$ and $\alpha_m$ are the increments of formation energy and migration energy, respectively, of a vacancy by the magnetic transformation.

The purpose of this work is to study the diffusion behavior of niobium in high purity α-iron in a wide range of temperature by use of a sputter-microsectioning technique and radioactive tracer 95\textsuperscript{Nb}.

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Table 1 Chemical analysis of iron rod (mass ppm).

<table>
<thead>
<tr>
<th>C</th>
<th>N</th>
<th>O</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>37</td>
<td>2</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>7</td>
<td>3</td>
</tr>
</tbody>
</table>

2. Experimental Procedure

High purity iron rod was supplied by Mitsubishi Heavy Industries, Ltd. The rod was prepared as follows; high purity electrolytic iron, “Miron HP” made by Toho Zinc Co., was induction-melted in a cold-copper crucible under 2 x 10^{-7} Pa after evacuation of the chamber to a base pressure of 10^{-7} Pa. The ingot was hot-forged and machined in the form of a rod 12 mm in diameter. The chemical analysis of the rod is shown in Table 1. The rod was cut to make the disc specimen 1 mm in thickness. The flat face of the specimen was ground on abrasive papers and electro-polished in an aqueous solution containing 77 vol% acetic acid and 18 vol% perchloric acid at 273 K. To induce grain growth and to reduce the contents of carbon, nitrogen and oxygen, the specimen was annealed at 1123 K for 7.2 ks in the stream of purified hydrogen gas. To obtain a stress-free surface, the specimen was electropolished under the same conditions as mentioned above. To make the gaseous contents would be less than 1 mass ppm. The resultant grain size was about 3-5 mm.

The radioisotope 95Nb (γ-rays, 0.766 MeV; half-life, 35 h) was supplied in the form of niobium chloride in 6.0M HCl by NEN Life Science Products, Inc. USA. The radionuclidic purity of the isotope was 99.5%. Taking care to avoid oxidation of the specimen, the radioisotope was electroplated on the surface of the specimen with 14 mA cm^-2 for 0.5-2.0 min. The specimens were then sealed in quartz tubes under 10^{-4} Pa and diffused at a temperature in the range from 823 to 1163 K for 1.8 to 550.8 ks in furnaces controlled to ±0.5 K. Some specimens were diffused in a stream of the purified hydrogen gas. To measure the penetration profiles of the diffusing species into the specimen, three types of the serial sputter-microsectioning apparatus were used; the ion beam type with the sputtering rate of 7-10 nm/min and the radio-frequency type with the sputtering rate of 30-60 nm/min were used to measure short penetration profiles and the magnetron type with the sputtering rate of 150-300 nm/min was used to measure long penetration profiles. The details of the methods are described elsewhere. For each specimen, 15-35 successive sections were sputtered. A constant fraction of the sputtered-off material was collected on an aluminum foil. The intensity of the radioactivity of the isotope in each section was measured by a well-type Tl-activated NaI detector with a 1024 channels pulse height analyzer.

3. Results

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

\[ I(X, t) \propto C(X, t) = \frac{M}{\sqrt{\pi D t}} \exp\left(-X^2/4Dt\right) \]

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

Figures 1 and 2 show the plots of \( \ln I(X, t) \) vs. \( X^2 \) for the diffusion of 95Nb in α-iron at higher and lower temperatures, respectively. In accordance with eq. (3), all the plots in Figs. 1 and 2 are linear, indicating that the concentration profiles are governed by the volume diffusion. As seen in Fig. 1, very near the surface, a few points shown by open circles deviate apparently from a linear line for the volume diffusion because of oxidation of the tracer on the surface. The diffusion coefficients calculated from the slope of the plot are listed in Table 2, and their Arrhenius plots are shown in Fig. 3 along with the diffusion coefficients obtained by Geise and Herzig and by Herzig et al. The temperature dependence of the self-diffusion coefficient in α-iron is also drawn in Fig. 3. The self-diffusion coefficients obtained by Iijima et al. and Lübbehuesen and Mehrer are in good agreement with each other and hence, individual experimental points are not shown in Fig. 3 to avoid the cluttering of data points. It is seen that the diffusion coefficient of niobium determined by the present work is about two times as large as the self-
The diffusion coefficient of niobium is about twice the self-diffusion coefficient obtained by the present work shows a linear Arrhenius behavior with the pre-exponential factor, $D_0$, $(1.40^{+1.17}_{-1.05}) \times 10^{-1} \text{m}^2\text{s}^{-1}$ and the activation energy, $Q^\alpha$, $(299.7 \pm 12.7) \text{kJmol}^{-1}$. In $\alpha$-iron of the ferromagnetic state the diffusion coefficient of niobium is smaller than that extrapolated from the paramagnetic state, as is the case for self-diffusion.5,6,18)

### 4. Discussion

As seen in Figs. 1 and 2, the penetration profiles for diffusion of niobium in $\alpha$-iron show the Gaussian behavior in accordance with the lattice diffusion. However, it seems that the diffusion depth with the linear relation is somewhat short in comparison with those for chromium19) and cobalt20) in $\alpha$-iron. These Gaussian profiles are usually followed by tails due to the diffusion along short-circuit paths such as dislocations and grain boundaries.21) As mentioned earlier, niobium has a large atomic radius9) and small solubility in $\alpha$-iron10) in comparison with other transition metal solutes. Hence, niobium has an easy tendency to segregate at dislocations or grain boundaries in $\alpha$-iron. This characteristic of niobium is probably concerned with the short Gaussian profiles.

The diffusion coefficient of niobium is about twice the self-diffusion coefficient, as shown in Fig. 3. The enhanced diffusion can be explained by the larger atomic radius of niobium. The distortion of the iron lattice due to the oversized solute atom results in attractive interactions between solute atoms and vacancies. This Gibbs free enthalpy of binding between a vacancy and a solute atom leads to a decrease in the vacancy formation enthalpy and
thus to an increase in diffusion. Table 3 summarizes the Arrhenius parameters for the self-diffusion and the solute diffusion of molybdenum, chromium, cobalt, and niobium obtained by our research group using the radioactive tracer method with serial sputter-microsectioning techniques. The activation energies for diffusion of niobium and molybdenum in the paramagnetic \( \alpha \)-iron are larger than that for self-diffusion. Figure 4 shows a plot of the activation energy \( Q_p^* \) for self-diffusion and diffusion of transition elements in iron.

![Fig. 4 Plot of \( Q_p^* \) vs. \( (r_s - r_F)/r_F \).](image)

To evaluate the magnetic contribution to the activation energy for diffusion of niobium in the ferromagnetic iron, eq. (1) is rewritten as follows

\[
\ln \frac{D(T)}{D_0^R} = -\frac{Q^*}{R} - \left( \frac{\alpha Q^*}{R} \right) s^2.
\]

Substituting the values of \( D(T) \) and \( D_0^R \) obtained by the present work and the empirical value of \( s(T) \) for pure iron obtained by Potter and Crangle and Goodman into the eq. (5), \( T \ln[D(T)/D_0^R] \) was calculated as a function of \( s^2 \) and plotted in Fig. 6. A linear relationship between \( T \ln[D(T)/D_0^R] \) and \( s^2 \) in Fig. 6 shows that in iron of the ferromagnetic state the temperature dependence of diffusion coefficient of niobium obeys eq. (1). From the slope and intercept of the straight line in Fig. 6, the values of \( \alpha \) and \( Q^* \) were determined and listed in Table 3. These are compared with the values for self-diffusion and for diffusion of chromium and cobalt and molybdenum in \( \alpha \)-iron. Here.

### Table 3: Preexponential factor, activation energy and constant \( \alpha \) for self-diffusion and diffusion of niobium, molybdenum, cobalt and chromium in \( \alpha \)-iron.

<table>
<thead>
<tr>
<th>Diffusant</th>
<th>( D_0^R / m^2 s^{-1} )</th>
<th>( Q_p^*/kJ mol^{-1} )</th>
<th>( Q_{p0}^*/kJ mol^{-1} )</th>
<th>( \alpha )</th>
<th>( Q^* = Q^*(1 + \alpha)/kJ mol^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>2.76 (+1.04\times10^{-4})</td>
<td>250.6 (+3.8)</td>
<td>250.5 (+0.4)</td>
<td>0.156 (+0.003)</td>
<td>289.7 (+5.1)</td>
</tr>
<tr>
<td>Niobium</td>
<td>1.40 (+1.05\times10^{-4})</td>
<td>299.7 (+12.7)</td>
<td>299.0 (+8.8)</td>
<td>0.061 (+0.007)</td>
<td>318.0 (+15.6)</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>1.48 (+1.31\times10^{-4})</td>
<td>282.6 (+6.4)</td>
<td>283.1 (+0.6)</td>
<td>0.074 (+0.005)</td>
<td>303.5 (+7.5)</td>
</tr>
<tr>
<td>Cobalt</td>
<td>2.76 \times10^{-4}</td>
<td>-</td>
<td>-</td>
<td>0.23</td>
<td>309</td>
</tr>
<tr>
<td>Chromium</td>
<td>3.73 (+1.40\times10^{-4})</td>
<td>267.1 (+4.4)</td>
<td>267.5 (+0.5)</td>
<td>0.133 (+0.003)</td>
<td>303.0 (+6.3)</td>
</tr>
</tbody>
</table>

Table 3: Preexponential factor, activation energy and constant \( \alpha \) for self-diffusion and diffusion of niobium, molybdenum, cobalt and chromium in \( \alpha \)-iron.

![Fig. 5 Plot of \( D_0^R \) against \( Q^* \) for diffusion of transition elements in \( \alpha \)-iron.](image)
the value of $Q^p$ calculated in this way is denoted by $Q^p_{\text{cal}}$. It is noted that the value of $Q^p$ determined directly from the Arrhenius plot of $D(T)$ in the paramagnetic state is in good agreement with $Q^p_{\text{cal}}$, as shown in Table 3. Using the values of $\alpha (= 0.061)$, $D^p_0 (= 1.40 \times 10^{-1}$ m$^2$s$^{-1}$) and $Q^p (= 299.7$ kJmol$^{-1}$) obtained by the present work, $D(T)$ is calculated, and its Arrhenius plot is drawn as a solid line in Fig. 3. As shown in Table 3, the value of $\alpha$ for the diffusion of niobium in $\alpha$-iron is about 60% smaller than 0.156 for the self-diffusion, indicating that the effect of magnetic transformation in iron on the solute diffusion of niobium is smaller than that on the self-diffusion. Using the value of $Q^p (= 299.7$ kJmol$^{-1}$) for the diffusion of niobium in the paramagnetic iron, the activation energy $Q^f (= (1 + \alpha)Q^p)$ in the ferromagnetic iron can be estimated to be $318.0$ kJmol$^{-1}$. Thus, the increment of the activation energy $\alpha Q^p$ by the magnetic transformation is $18.3$ kJmol$^{-1}$ for the diffusion of niobium, while it is $39.1$ kJmol$^{-1}$ for the self-diffusion. Thus, in the paramagnetic iron the activation energy for the diffusion of the magnetic field around a solute cobalt atom is stronger than that of the impurity moment and it remains so even above the Curie temperature. However, in the case of chromium, molybdenum and niobium solute atoms, the magnetic field is weaker than that of the pure iron matrix and becomes zero at the Curie temperature. The experimentally determined values of the change in magnetization $\Delta M$ of $\alpha$-iron on diluting with 3d, 4d and 5d elements are compiled by Pepperhoff and Acet. They are $+1.0 \mu_B$/atom for cobalt, $-2.6 \mu_B$/atom for chromium, $-2.3 \mu_B$/atom for molybdenum and $-2.75 \mu_B$/atom for niobium. The value $\Delta M$ consists of contributions arising from the influence of the impurity atoms on the magnetic moment of the surrounding iron atoms and from the contribution of the local impurity moment. The latter is the difference between the iron atom moment and the local impurity moment. Thus, $\Delta M$ is the sum of contributions from all neighbors extending out to several shells. According to theoretical calculations of $\Delta M$ for transition-metal impurities in iron by Drittler et. al., the values of $\Delta M$ are $+0.79 \mu_B$ for cobalt, $-3.29 \mu_B$ for chromium, $-3.31 \mu_B$ for molybdenum and $-3.68 \mu_B$ for niobium, although the local moments of impurities in iron are $+1.65 \mu_B$ for cobalt, $-1.29 \mu_B$ for chromium, $-0.52 \mu_B$ for molybdenum and $-0.46 \mu_B$ for niobium. Drittler et al. have calculated the change of the total moment summed over the impurity and five shells of iron atoms. At present, it is difficult to connect the value of $\Delta M$ to the values of $\alpha_f$ and $\alpha_m$ in eq. (2). However, it can be concluded that the value of $\Delta M$ is related qualitatively to the order of magnitudes of $\alpha s^2$ for these solutes in Fig. 7.

5. Conclusion

Using the serial sputter-microsectioning techniques with radioactive tracer $^{95}$Nb, the diffusion coefficient of niobium in $\alpha$-iron has been determined in the temperature range from 823 to 1163 K. The diffusion coefficient of niobium is about twice the self-diffusion coefficient in $\alpha$-iron. The temperature
dependence of the diffusion coefficient of niobium is influenced by the magnetic transformation in a way similar to that for the self-diffusion. The increase in activation energy due to the magnetic transformation for solute diffusion of niobium is found to be 18.3 kJmol\(^{-1}\) which is smaller than the corresponding value of 39.1 kJmol\(^{-1}\) for the self-diffusion of iron.

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