Effect of Rhenium Addition on Tungsten Diffusivity in Iron-Chromium Alloys

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The alloying effect of Re on the diffusivity of W in Fe-15 mol%Cr based alloys was investigated experimentally using the Fe-15Cr/Fe-15Cr-5W and Fe-15Cr-1Re/Fe-15Cr-5W diffusion systems. In these systems, a single ferrite phase existed stably at 1473 K, and Fe and W atoms interdiffused at 1473 K without any attendant changes in the Cr concentration of 15 mol% in them. The measured diffusion length of W atoms was shorter in the Re-containing diffusion system than the Re-free one. Following the binary Boltzmann-Matano method, an apparent interdiffusion coefficient at 1473 K was estimated to be $7.1 \times 10^{-15} \text{m}^2/\text{s}$ in the Re-free diffusion system and $1.5 \times 10^{-15} \text{m}^2/\text{s}$ in the Re-containing diffusion system. Thus, the presence of Re in the alloy worked to suppress the atomic diffusion of W in a ferrite phase.

1. Introduction

The refractory elements such as Mo, W and Re play an important role in strengthening high temperature creep of high Cr heat resistant ferritic steels.1–3) In these steels, it is known that the (Fe, Cr)$_2$(W, Mo) type Laves phase precipitates together with M$_{23}$C$_6$ carbide and the MX carbonitride.4,5) Recently, it has been shown that the long-term creep strength at 923 K becomes much smaller than the extrapolated strength from the short-term creep test.6) This is related mainly to the microstructure changes in the steel during creep. Recently, it has been reported that the addition of a small amount of Re is effective in improving the long-term creep strength of the W-containing steels.7–9) This implies that the presence of Re in the steel lowers the W diffusivity in some ways, because the microstructure evolution during creep is subjected more or less to the coalescence of the Laves phase, (Fe, Cr)$_2$(W, Mo), and M$_{23}$C$_6$ carbide.

The diffusivity of refractory elements in heat resistant steels is crucial for the basic understanding of the microstructural stability during creep.10) The purpose of this study is to investigate the alloying effect of Re on the W diffusivity in the ferritic steel. For this aim, Fe-15 mol%Cr was chosen as a base alloy for the bcc matrix phase in high Cr ferritic steels. This alloy is suitable for the present diffusion experiment, as a bcc phase is stable up to the melting temperature in it.

2. Experimental Procedures

Fe-15Cr binary alloy, Fe-15Cr-1Re and Fe-15Cr-5W ternary alloys were used in this study. Here, the alloy compositions are given in mol% units. According to the Fe-Cr and Fe-Cr-W phase diagrams, these three alloys should consist of a bcc phase at 1473 K. The button ingots of these alloys were prepared by arc melting in a high purity argon gas atmosphere. Plate specimens with about 1 cm in thickness were cut from the ingots. The homogenization and the grain growth of each specimen were accomplished by 50% cold rolling, followed by the annealing at 1473 K for 24 h. The grain size of each specimen was estimated by an optical microscope (OM) and a scanning electron microscope (SEM) equipped with an instrument for taking an electron back-scattered diffraction pattern (EBSD). The grain size of each alloy was as large as about 1 mm after the annealing. The diffusion temperature, 1473 K, employed in this study was about 0.8T$_m$ (T$_m$: melting temperatures of the experimental alloys). In general, it is believed that when the temperature is higher than 0.75T$_m$, there is little effect of interfacial diffusion on lattice diffusion in the alloy.11)

A diffusion couple shown in Fig. 1 was prepared in the following way. First each side of the plate specimen was ground, and then one surface of each specimen was polished mechanically with emery papers and 0.25 μm diamond
slurry. Subsequently, the diffusion couple of Fe-15Cr/Fe-15Cr-5W and Fe-15Cr-1Re/Fe-15Cr-5W was assembled as shown Fig. 1. There were the two diffusion systems in this assembly. Alumina fibers were sandwiched between the plate specimens as a marker of the initial interface. This couple was held tightly with a molybdenum holder. Then, it was encapsulated in a quartz tube with argon gas and annealed at 1473 K for 100 h. After the annealing, the cross section of the diffusion couple was examined by the scanning electron microscopy (SEM) and the energy dispersive X-ray spectroscopy (EDX) to measure concentration profiles across the diffusion interface. The origin of the concentration profile was set at the position of the alumina fiber.

3. Results and Discussion

3.1 Concentration profiles and diffusion path

It was confirmed from the optical microscopic observation that the as-annealed specimens contained only the ferrite (bcc) single phase without any precipitates in them. Figure 2 shows typical SEM images taken from the diffusion couple annealed at 1473 K for 100 h. After the annealing, the cross section of the diffusion couple was examined by the scanning electron microscopy (SEM) and the energy dispersive X-ray spectroscopy (EDX) to measure concentration profiles across the diffusion interface. The origin of the concentration profile was set at the position of the alumina fiber.

Fig. 2 Typical SEM microstructures showing the initial interface (alumina fiber) in (a) Fe-15Cr/Fe-15Cr-5W and (b) Fe-15Cr-Re/Fe-15Cr-5W diffusion system, both annealed at 1473 K for 100 h.

Fig. 3 Concentration profiles of W and (Fe + Cr) obtained from (a) Fe-15Cr/Fe-15Cr-5W diffusion system and (b) Fe-15Cr-Re/Fe-15Cr-5W diffusion system, both annealed at 1473 K for 100 h.

Fe-15Cr-5W. These concentration profiles exhibited the S curves without any discontinuity, indicating that the diffusion occurred in the single ferrite phase without precipitating any phases in the alloy. From Fig. 3, it was found that W atoms diffused into the region of about 800 µm apart from the interface in the Re-containing system. Such a diffusion region of W atoms was further extended over above 1000 µm in the Re-free system. This result indicates that W atoms diffuse more easily in the Re-free alloy than in the Re-containing alloy.

The diffusion path of each diffusion system was obtained by plotting the data shown in Fig. 3 in the Gibbs triangle. The result is shown in Fig. 4. The concentrations of Cr did not change during annealing in both the diffusion systems. A very small difference in the diffusion paths between the two systems was attributable to the existence of 1 mol% Re in the Fe-15Cr-Re/Fe-15Cr-5W, but the absence in the Fe-15Cr/Fe-15Cr-5W. This result implies that the presence of Cr scarcely affects the W diffusion in the Fe-15Cr based diffusion couples. In other words, W atoms diffuse in the
3.2 Interdiffusion coefficients

In order to compare the W diffusivity quantitatively in each diffusion system, interdiffusion coefficients were estimated by assuming that the diffusion occurs in the (Fe, Cr)-W pseudo-binary system. The apparent interdiffusion coefficient was calculated using the binary Boltzmann-Matano method.\(^\text{12}\)

The calculated interdiffusion coefficients at 1473 K in the two diffusion systems are shown in Table 1. The interdiffusion coefficient was about 5 times larger in the Re-free alloy than in the Re-containing alloy. This result indicates that the existence of Re suppresses the diffusion of W atoms in Fe-Cr alloys. The reason why the presence of Re retards the W diffusion in Fe-15Cr alloys is not clear at the moment, but there are two possibilities. One is the existence of attractive force between W and Re due to the trend of the formation of an intermetallic compound between them. The other is the vacancy trapping effect of Re in the alloy.

4. Conclusion

The alloying effect of Re on the W diffusivity was examined experimentally using both the Fe-15Cr/Fe-15Cr-5W and the Fe-15Cr-1Re/Fe-15Cr-5W diffusion systems. The apparent interdiffusion coefficient for the Re-containing alloy was found to be about one fifth of that for the Re-free alloy. It was concluded that the existence of Re retarded significantly the W diffusion in Fe-15 mol\% Cr based alloy.

Acknowledgments

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REFERENCES


Table 1  Apparent interdiffusion coefficients obtained from Fe-15Cr/Fe-15Cr-5W and Fe-15Cr-1Re/Fe-15Cr-5W diffusion systems.

<table>
<thead>
<tr>
<th>diffusion system</th>
<th>diffusion coefficient (m²·s⁻¹)</th>
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<tbody>
<tr>
<td>Fe-15Cr/Fe-15Cr-5W</td>
<td>7.1 × 10⁻¹⁴</td>
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<tr>
<td>Fe-15Cr-1Re/Fe-15Cr-5W</td>
<td>1.5 × 10⁻¹⁵</td>
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</table>

![Fig. 4 Diffusion paths in Fe-15Cr/Fe-15Cr-5W and Fe-15Cr-1Re/Fe-15Cr-5W diffusion systems.](image-url)