Diffusivity and Solubility of Cu in a Reactor Pressure Vessel Steel Studied by Atom Probe Tomography*¹

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The diffusivity and solubility limit of Cu in A533B steel, which is used in reactor pressure vessels, were studied by atom probe tomography (APT). Cu-A533B steel diffusion couples were annealed at temperatures of 550, 600, and 700°C, and the resulting Cu concentration profiles were measured. At the temperature of 700°C, the diffusivity of Cu in A533B steel was about 3 times higher than that in pure Fe, whereas at the temperature of 550°C, the diffusivity of Cu in A533B steel is almost closer to that in pure Fe. The solubility limit of Cu in A533B steel was similar to pure Fe. APT was also used to study the effect of the grain boundary (GB) diffusion. The results indicated that no Cu segregation occurred at GB near the Cu/A533B steel interface, which may imply that GB diffusion of Cu was not effective in A533B steel.
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1. Introduction

The prediction for radiation-induced embrittlement of the nuclear reactor pressure vessel (RPV) steels is critically important for the safe operation of nuclear power plants.^{1,2)} Nanoscale Cu-rich precipitate induced or enhanced by neutron irradiation is one of the main origins for embrittlement of RPV steels.³⁾ The evolution of the precipitation leads to hardening of RPV steels, which causes the ductile-brittle transition temperature to increase.⁴⁾ Therefore, a detailed understanding of Cu precipitation kinetics is necessary to predict the embrittlement of RPV steels. Thereby, accurate estimation of the diffusion coefficient and solubility limit of Cu in RPV steels is very important, although those have not been.

To fully understand Cu diffusion mechanisms in operating RPVs, the effects of neutron irradiation should be considered. However, there is as yet insufficient information available on normal thermal diffusion. Typically, the diffusion coefficient of Cu in pure Fe has been determined using Cu-Fe diffusion couples, based on activity measurement,^{5,6)} electron probe microanalysis⁷⁾ and laser-induced breakdown spectrometry.⁸⁾ However, since the spatial resolution of these techniques is only about 2–3 μm, only long-range diffusion can be studied. Thus, measurements have been carried out on specimens subjected to temperatures of ≥690°C, which are much higher than the typical operating temperatures of about 300°C for light water reactors. Temperatures in excess of the Curie temperature, which is about 760°C for Fe, can cause a paramagnetic-ferromagnetic transition to occur, and this affects the diffusivity of Cu.⁷⁾ Thus, the diffusion coefficient for ferromagnetic Fe at lower temperatures can only be

obtained by extrapolation of data acquired in a very limited temperature range from about 690 to 760°C, or by computer simulation,^{9,10)} and more reliable values are strongly required.

Atom probe tomography (APT) can obtain Cu concentration profiles in the range of several hundreds of nanometers because of its atomic-scale resolution. Recently, the diffusion coefficient and solubility limit of Cu in ferromagnetic Fe were measured in our work¹¹⁾ down to a temperature of 550°C, which is much lower than previous studies, thereby improving the reliability of values obtained by extrapolation to the reactor temperature.

In the present study, the method employed in our previous study on pure Fe was applied to study the diffusion coefficient and solubility limit of Cu in an A533B steel, a typical RPV steel. APT measurements were performed on Cu-A533B steel diffusion couples, in order to obtain information on the diffusion behavior and solubility limit of Cu in an A533B steel containing many kinds of impurities and solutes. In addition to the high depth resolution of the APT technique, APT can estimate the diffusivity using polycrystalline materials, including the A533B steel, by selecting matrix region sufficiently far from grain boundary (GB) using focused-ion beam (FIB) apparatus.¹²⁾ The FIB technique can be also used to observe the GB diffusion by selecting APT needle specimens containing the GB.

2. Experimental

The A533B steel used in this study was low-Cu (0.04 mass%) steel, which is well below than solubility limit at the annealed temperatures. Table 1 lists its chemical composition. The steel was first heat treated at 860–893°C for 7 h, and then quenched in cold water. The average grain size was estimated to be about 10–20 μm by electron backscatter diffraction measurement. Tempering was subsequently conducted at 650–660°C for 6 h. Finally, the steel was annealed at 610–623°C for 42 h, and then cooled at a rate of 35°C/h. The A533B steel was cut into sheets with dimensions of

*¹This paper is the revision of the retracted one; Mater. Trans. Vol. 55 No. 9 (2014) pp. 1460–1463. The equation (1) was corrected by taking the nominal Cu concentration of the studied A533B steel, c_{A533B} , into account. Accordingly the estimated values of diffusion coefficients and solubility limits were corrected, then the Figs. 2–4 were also corrected.

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Table 1 Chemical composition of A533B steel.

	C	Si	Mn	S	Cu	Ni	Cr	Mo	P
mass%	0.19	0.17	1.42	0.001	0.04	0.65	0.13	0.50	0.005

5 mm × 5 mm × 1 mm from the test piece of the Charpy impact test. The surface damage layer produced by the cutting process was removed by mechanical polishing, followed by electropolishing at 30 V for 20–30 s at a temperature of ≤20°C using a platinum electrode. The polishing solution was mixture of acetic acid (91%) and perchloric acid (9%). The sheets were then immediately transferred to an ultra-high vacuum chamber (10^{−5} Pa) and coated with Cu to a thickness of 3 μm using vapor deposition. Finally, the Cu-coated A533B steel sheets were sealed in quartz ampoules under a 10^{−4} Pa vacuum together with degassed, cleaned pure Zr foil to absorb any residual gas. Diffusion annealing was performed at 550, 600, and 700°C for 1008000, 250000, and 3000 s, respectively. The annealing temperature was controlled to an accuracy of ±1°C.

The needle-shaped specimens for APT measurements were fabricated from the sheets using an FIB apparatus vertically to the Cu/A533B steel interface. For bulk diffusion measurements, a piece with dimensions of about 5 μm × 5 μm × 10 μm was obtained from intragranular region sufficiently far from GBs, and sharpened to a needle specimen. For the observation of GB diffusion, a specimen containing a GB close to the Cu/A533B steel interface was also fabricated from the sheet annealed at 600°C.

In this study, laser-assisted APT was employed in order to reduce fracture probability of specimens particularly around the Cu/A533B steel interface, similar to our recent report.¹¹⁾ The measurements were performed using an ultraviolet (UV) laser-assisted local-electrode atom probe (LEAP4000XHR, AMETEK-CAMECA) at an evaporation rate of 0.4% per laser pulse, a laser power of 0.1 nJ, a pulse repetition rate of 200 kHz, a DC voltage of typically 3 to 8 kV and a specimen temperature of 50 K. The analysis software of APT (IVAS, AMETEK-CAMECA) was employed for data reconstruction.

3. Results and Discussion

Figure 1 shows typical set of atom maps for Cu, Fe, Ni, Mn, Si, C, Mo, and P obtained for the specimen annealed at 700°C. The Cu layer is present near the tip of the specimen (left-hand side in the figure), and Cu diffusion from the Cu/A533B steel interface into the A533B steel matrix was observed. In addition, diffusion of Ni and Mn into the Cu layer was observed, and their concentrations near the interface decreased. The slight enrichment of Mn near the interface was also observed.

The Cu concentration profiles were obtained for a rectangular parallelepiped region from a cross-section perpendicular to the Cu/A533B steel interface. The APT measurements were performed at least three times for each set of annealing conditions, and the mean values were used for the Cu concentration profile. The resulting Cu concen-

Fig. 1 Atom maps for Cu, Fe, Ni, Mn, Si, C, Mo, and P for specimen annealed at 700°C for 3000 s.

tration profiles including the error bars are shown in Fig. 2, with the profiles previously obtained for pure Fe¹¹⁾ shown for comparison. Assuming a concentration-independent diffusion coefficient, a semi-infinite medium, and a constant surface concentration, Fick's second law gives

$$c = (c_0 - c_{A533B}) \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] + c_{A533B}, \quad (1)$$

where $c(x, t)$ is the concentration profile, x is the distance from the interface, t is the diffusion time, c_0 is the solubility limit of Cu in A533B steel, c_{A533B} is the nominal Cu concentration of the studied A533B steel, 0.04 mass%, as listed in Table 1, erf is the error function and D is the diffusion coefficient. The measured profiles were fitted by eq. (1), with c_0 and D as fitting parameters, and the diffusivity and solubility limit of Cu were estimated. Data from regions within 15 nm of the Cu/A533B steel interface were not employed for the fitting due to artifacts¹³⁾ caused by the evaporation condition difference between Fe and Cu. The fitted curves indicated by solid lines in Fig. 2 are seen to agree well with the measured data.

Figure 3 shows the Arrhenius plot of the diffusion coefficients of Cu in A533B steel, together with those previously obtained for pure Fe.¹¹⁾ Note that the error bars in this study are within the closed circles. Estimated diffusion coefficients of Cu in A533B steel are $(1.4 \pm 0.2) \times 10^{-16}$, $(1.7 \pm 0.1) \times 10^{-15}$, and $(3.1 \pm 0.1) \times 10^{-13}$ cm²/s for 550, 600, and 700°C, respectively. At the temperature of 700°C, the diffusivity of Cu in A533B steel is about 3 times higher than that in pure Fe, whereas at the temperature of 550°C, the diffusivity of Cu in A533B steel is almost closer to that of pure Fe. Although only three data points are present, the linearity appears good. Thus the obtained data set was fitted using Arrhenius equation

Fig. 2 Concentration profiles of Cu near the Cu/A533B steel interface and corresponding fitting curves, together with profiles for pure Fe.

$$D = D_0 \exp\left(-\frac{Q}{k_B T}\right), \quad (2)$$

where D_0 is the pre-exponential factor, Q is the activation energy, k_B is the Boltzmann constant and, T is the annealing temperature. The obtained values were $D_0 = 89 \text{ m}^2/\text{s}$ and $Q = 3.45 \times 10^5 \text{ J/mol}$ (3.58 eV/atom) for A533B steel, whereas $D_0 = 0.48 \text{ m}^2/\text{s}$ and $Q = 3.11 \times 10^5 \text{ J/mol}$ (3.22 eV/atom) were previously obtained for pure Fe.¹¹⁾ If we can assume that simple linear extrapolation is valid, the diffusivity of Cu in A533B steel is lower than the diffusivity of Cu in pure Fe at the operating temperatures for light water reactors.

The solubility limit of Cu in A533B steel is shown in Fig. 4 together with that in pure Fe. The error bars are within the closed circles. The values of the solubility limits of Cu in A533B steel are 0.088 ± 0.003 , 0.156 ± 0.002 , and $0.460 \pm 0.004 \text{ mass\%}$ for 550, 600, and 700 °C, respectively, which are similar to those in pure Fe obtained in our previous work.¹¹⁾ The solubility limit is an important parameter to consider the driving force of precipitation. The values obtained in this study for the first time will be the benchmark for future theoretical work.

It is well known that GB diffusion is generally much faster than bulk diffusion.^{14,15)} Therefore, the GB near the Cu/

Fig. 3 Arrhenius plot for Cu diffusion coefficient in A533B steel and that in pure Fe.

Fig. 4 Solubility limit of Cu in A533B steel and that in pure Fe.

A533B steel interface was observed in order to study the effect of the GB diffusion in the RPV steel. Figure 5 shows the obtained atom maps for Cu, Fe, Ni, Mn, Si, C, Mo, and P of the specimen containing a GB at annealing temperature of 600 °C. The GB traverses the specimen near the center of the images. It can be seen that although clear segregation of Mo, C, and P was observed at the GB, neither Cu segregation at the GB nor Cu enrichment around the GB was clearly observed. This may imply that the GB diffusion of Cu was not effective in A533B steel. Further study, observing different GBs with better statistics, is necessary to confirm this claim. In case that GB is not the fast diffusion path, it is possible to interpret that the segregated solutes such as Mo and P, which are known to segregate at GBs in A533B steel,¹⁶⁾ suppress the diffusion of Cu along GBs. The studies on Cu behavior near the GBs in pure Fe (i.e. segregation free GBs) might give us important insight.

It should be mentioned that the diffusivity estimated in this study might include a certain error due to the diffusion of Ni and Mn into the Cu-layer and/or slight enrichment of Mn near the interface, as shown in Fig. 1. Nevertheless, the important finding of this study is that it clearly shows that in an A533B steel, the Cu diffusivity is differed compared to that in pure Fe. Determining the origin of this difference is a

Fig. 5 Atom maps for Cu, Fe, Ni, Mn, Si, C, Mo, and P for specimen containing a GB, following annealing at 600°C for 250000 s.

subject for future work. The difference of vacancy formation enthalpy by the alloying elements and more complex interactions among Cu, vacancy and other solute elements can be possible reasons. Finally, it should be also mentioned that the study of the irradiation enhancement effect on Cu diffusion is very important future work in order to understand the Cu behavior in A533B steel under irradiation.

4. Conclusions

The diffusivity and solubility limit of Cu in a RPV steel, A533B steel, were estimated using APT in the temperature

range from 550 to 700°C. At the temperature of 700°C, the diffusivity of Cu in A533B steel is about 3 times higher than that in pure Fe, whereas at the temperature of 550°C, the diffusivity of Cu in A533B steel is almost closer to that in pure Fe. The solubility limits of Cu in A533B were similar to pure Fe. No GB segregation of Cu was observed, which may imply that GB diffusion of Cu in A533B steel was not effective.

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