



# The diffusivity and solubility of copper in ferromagnetic iron at lower temperatures studied by atom probe tomography

T. Toyama,\* F. Takahama, A. Kuramoto, H. Takamizawa, Y. Nozawa, N. Ebisawa, M. Shimodaira, Y. Shimizu, K. Inoue and Y. Nagai

*International Research Center for Nuclear Materials Science, Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan*

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The diffusion coefficient and the solubility limit of copper in ferromagnetic iron were directly measured using atom probe tomography at lower temperatures than in previous studies. Cu–Fe diffusion couples were annealed at temperatures from 550 to 750 °C. The diffusion coefficient was determined to be  $D = 0.48 \exp(-Q/k_B T) \text{ m s}^{-1}$  ( $Q = 3.22 \text{ eV}$ ), which, below 650 °C, is about 1.3 times higher than the extrapolation from a previous study considering the magnetic effect. The measured Cu solubility limit is in good agreement with literature.

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Copper precipitation plays an important role in the hardening of steels, such as high-strength low-carbon steels [1–3], maraging stainless steels [4–6] and transformation-induced plasticity steels [7]. Cu precipitation is also one of the main reasons for the hardening increase observed in nuclear reactor pressure vessel (RPV) steels [8,9]. Therefore, the precipitation of Cu has been the focus of many experimental [10–12] and theoretical [13–15] studies in binary Fe–Cu alloys and steels under various conditions. Accurate determination of the diffusion coefficient and the solubility limit of Cu in Fe are essential to the understanding of precipitation kinetics.

Diffusion coefficients have been precisely determined for Cu–Fe diffusion couples by activity measurement [16,17], electron probe microanalysis (EPMA) [18], and laser-induced breakdown spectrometry [19]. The diffusion temperature in these techniques is typically greater than ~700 °C, because these techniques require long-range diffusion at distances of at least several microns due to the spatial resolution limit. The paramagnetic–ferromagnetic transition at the Curie temperature (~760 °C),  $T_C$ , affects the diffusivity [18]. Thus, the diffusion coefficient for ferromagnetic Fe can only be

obtained directly for a very limited temperature range from ~700 to ~760 °C. On the other hand, Cu precipitation in steels is technologically relevant at temperatures of ~550 °C and below. In particular, Cu precipitation in RPV steels occurs at ~300 °C, which is the operating temperature of light water reactors. The diffusion coefficients at these lower temperatures are generally determined by extrapolation from the limited temperature range compatible with typical measurement techniques, leading to potentially significant errors.

A similar problem exists in the determination of the solubility limit of Cu in ferromagnetic Fe; experimental results have been obtained for a very limited temperature range thus far. The solubility limit in the lower temperature range from 500 to 700 °C was recently reported by Perez et al. [20]. However, Perez et al. used somewhat indirect experiments, in which the Cu concentration in solution was obtained from the voltage attributable to the Seebeck effect. Because the solubility limit is a key parameter for understanding the driving force of Cu precipitation, direct measurements at low temperature are necessary for accuracy enhancement.

In this study, we report the diffusion coefficient and solubility limit of Cu in ferromagnetic Fe in the temperature range from 550 to 750 °C. Atom probe tomography (APT) was employed to directly measure the Cu distribution in Cu–Fe diffusion couples. Because

\* Corresponding author. Tel.: +81 29 267 3181; fax: +81 29 267 4947; e-mail: [ttoyama@imr.tohoku.ac.jp](mailto:ttoyama@imr.tohoku.ac.jp)

APT can map solute distribution at atomic-level depth resolution, very short-range diffusion of Cu (across tens of nanometers) was achieved. Thus, lower temperature diffusion processes could be observed, thereby enhancing the accuracy of previously extrapolated values.

Table 1 lists the chemical composition of the pure Fe and pure Cu used in this work. The pure Fe was supplied by Toho Zinc Co., Ltd., at the 5N (99.999%) grade with a mean residual resistivity ratio,  $RRR_H$ , of  $>2000$ . The pure Cu was supplied by Johnson Matthey at the 5N grade. Fe was cold-rolled and cut into sheets with dimensions of  $10 \times 10 \times 1$  mm. Fe sheets were annealed for stress relief at 800 °C for 2 h in a  $10^{-4}$  Pa vacuum, together with degassed and cleaned pure Zr foil to absorb residual gas. After stress-relief annealing, the average grain size was 400–500  $\mu\text{m}$ . The surface was cleaned with a solution of 5% HF, 12%  $\text{H}_2\text{O}_2$  and 83%  $\text{H}_2\text{O}$ . The Fe sheets were then immediately transferred to an ultrahigh vacuum chamber ( $10^{-5}$  Pa) and coated with  $\sim 5$   $\mu\text{m}$  of Cu using vapor deposition. Finally, Cu-coated Fe sheet samples were sealed in quartz ampoules under a  $10^{-4}$  Pa vacuum with pure Zr foil. Diffusion annealing was performed at 550, 600, 650, 700 and 750 °C for 1,008,000, 250,000, 15,000, 1000 and 600 s, respectively. The annealing temperature was controlled within an accuracy of  $\pm 1$  °C.

The specimens for APT measurement were fabricated from the sheets using a focused-ion beam apparatus [21]. A piece with dimensions of about  $5 \times 5 \times 10$   $\mu\text{m}$  was obtained from the intragranular region sufficiently far from grain boundaries and then sharpened to a needle shape. Finally, very-low-energy Ga ions ( $<5$  kV) were used to remove regions that were potentially damaged during the milling process. The Cu–Fe interface was set near the top of the needle to enable observation of Cu diffusion just below the interface.

In this study, a laser-assisted atom probe was employed to reduce the probability of fracture of specimens, especially around the Cu–Fe interface. APT measurements were performed using an ultraviolet (UV) laser-assisted local-electrode atom probe (LEAP-4000XHR from AMETEK-CAMECA) at an evaporation rate of 0.3% per laser pulse, applying a laser power of 0.1 nJ, a laser pulse repetition rate of 200 kHz, a DC voltage usually in the range from 3 to 8 kV and a specimen temperature of 50 K. The charge state ratio,  $\text{Fe}^{2+}/\text{Fe}^+$ , was  $>1000$ .

The Cu concentration obtained via green laser-pulsing measurements is reported to be 10–20% lower than that obtained using voltage-pulsing measurements for low-C ferritic steel [22]. To evaluate this effect in this study, binary Fe–Cu alloys ( $0.95 \pm 0.03$  wt.% Cu) with supersaturated full-solid solutions of Cu in the Fe matrix were evaluated using both UV laser- and voltage pulsing. Voltage-pulsing measurements were performed at a pulse fraction of 20%, an evaporation rate of 0.3% per voltage pulse, a pulse repetition rate of

200 kHz, a DC voltage usually in the range from 2 to 7 kV and a specimen temperature of 50 K. More than 10 million events were accumulated for each measurement from both UV laser- and voltage pulsing. The obtained Cu concentrations were  $0.89 \pm 0.02$  and  $0.90 \pm 0.02$  wt.% from UV laser- and voltage-pulsing measurements, respectively. The measurements were in good agreement with each other; thus, we found that no correlation for Cu content is necessary in this study.

Figure 1 presents a typical set of atom maps obtained using APT for Cu, Fe, C, O and N. Copper diffusion from the Cu–Fe interface towards the Fe matrix was observed. Impurities, such as C, O and N, were seldom observed in the Fe matrix; measured amounts of impurities were  $\sim 8$  ppm C,  $\sim 20$  ppm O and  $\sim 15$  ppm N. These values were consistent with the chemical composition of the pure Fe, as listed in Table 1. No segregation of impurities was observed near the Cu–Fe interface.

The Cu concentration profiles were obtained for a rectangular parallelepiped region with dimensions of  $10 \times 10$  nm from a cross-section perpendicular to the Cu–Fe interface. APT measurements were performed at least three times for each set of annealing conditions, and the mean value was taken as the concentration profile, as shown in Figure 2 by open circles. Assuming a concentration-independent diffusion coefficient, a semi-infinite medium and a constant surface concentration, Fick's second law gives

$$c(x, t) = c_0 * \text{erfc} \left\{ \frac{x}{2\sqrt{Dt}} \right\}, \quad (1)$$

where  $c(x, t)$  is the concentration profile,  $x$  is the distance from the interface,  $t$  is the diffusion time,  $c_0$  is the constant saturation concentration of Cu in Fe according to the diffusion temperature (i.e. the solubility limit of Cu),  $\text{erfc}$  is a complementary error function and  $D$  is the diffusion coefficient. The measured profiles were fitted to Eq. (1), using  $c_0$  and  $D$  as the fit parameters. The fitted curves, indicated by solid lines in Figure 2, agreed well with the measured data.

Figure 3 shows Arrhenius plots for  $D$  obtained in this study by closed squares, together with reported experimental values [17,18]. Note that the error bars in this study are within the squares. The  $D$  values obtained at 700 and 750 °C were consistent with the reported values, thereby confirming the validity of the present

Table 1. The chemical compositions of the pure Fe and pure Cu.

	C	P	S	O	N	H	Cu
	ppm						
Fe	<10	<5	<5	<30	<20	<5	<5
Cu	–	–	–	<10	–	–	–

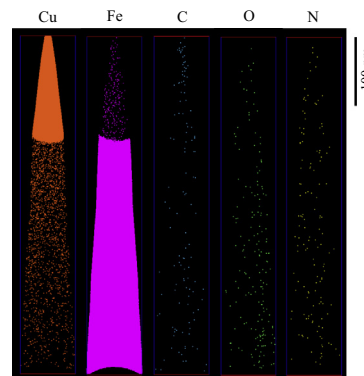


Figure 1. Typical 3-D atom maps for Cu, Fe, C, O and N. A specimen that was annealed at 750 °C for 600 s is shown as an example. 50% of the detected ions for Cu, 30% for Fe and 100% for C, O and N are plotted.

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