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# A Mössbauer study of early precipitation in Cu–Fe alloy

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**Abstract.** Mössbauer spectroscopy was used to study the early stages of precipitation in Cu–0.6 at.% Fe alloy. A set of data for the concentration of iron in solution was obtained for annealing times from 1 to  $10^5$  s at 400°C. The results were interpreted in terms of quenched monovacancies and divacancies. A proposed analytical expression describes the annealing fairly well. The application of the Mössbauer spectroscopy in short-time-scale annealing experiments seems to promise new possibilities for investigation of the diffusion properties.

## 1. Introduction

A copper-rich Cu–Fe alloy has been studied by different techniques including Mössbauer spectroscopy, clustering and precipitation being two of the main items of investigation (see, e.g. Gonser *et al* (1966), Window (1972), Gould and Vincent (1974), Clark *et al* (1979), Klein *et al* (1990), Jain and Longworth (1978) and Gonser and Ron (1980) and references therein). It is well known that the Mössbauer effect is very attractive because of its sensitivity to the nearest-neighbour environment of the probe atom (in this case  $^{57}\text{Fe}$ ). In diluted Cu–Fe alloys, iron atoms occupy substitutional sites of the copper FCC lattice and at least three distinct iron environments are possible (Gonser and Ron 1980):

- (1) Fe atoms with 12 Cu atoms as nearest neighbours, iron in solution, denoted  $\text{Fe}_s$ ;
- (2) Fe atoms with 12 Fe atoms as nearest neighbours, inner atoms of  $\gamma$ -Fe precipitates, denoted  $\text{Fe}_\gamma$ .
- (3) Fe atoms from small clusters or surface atoms of relatively large precipitates with a mixed environment, denoted  $\text{Fe}_n$  where  $1 \leq n \leq 11$  is the number of Fe nearest neighbours.

In the known Mössbauer experiments on precipitation in Cu–Fe alloys, no results are available for annealing times shorter than 20 min. The solubility of iron in copper is so small that even fast quenching produced samples with observable clustering.

In the present paper an experiment including early precipitation stages in Cu–0.6 at.% Fe alloy is described. The results are interpreted in terms of quenched and equilibrium vacancy concentrations and their annealing at 400°C.

## 2. Experimental details

Alloy samples containing 0.6 at.% Fe were prepared by melting appropriate quantities of 99.99% copper and enriched to 90%  $^{57}\text{Fe}$  in a graphite crucible using an Ar + 20 vol.%  $\text{H}_2$  atmosphere. The alloy obtained was cold rolled into foils with a thickness of about 10  $\mu\text{m}$ .

The low concentration of iron was preferred as more convenient for experiments on the early stages of precipitation.

A furnace similar to that shown by Tomov *et al* (1983) was used for annealing and quenching the samples at 400 °C and 1000 °C, respectively. The end of the quartz tube immersed in water had a plug which could be removed easily a short time before quenching. For real isothermal annealing, the sample was mounted initially in the bottom part of the furnace, which was always kept at ambient temperature. After the heated zone reached the required temperature, the sample was pulled into the zone. The sample reached 400 °C after 3–4 s. At the end of the anneal the same was allowed to fall into the water. The furnace was filled with an Ar + 20 vol.% H<sub>2</sub> atmosphere. A small overpressure was maintained to compensate for the gas leakage. The temperature was kept stable within several tenths of a degree Celsius by means of a proportional controller (Asenov *et al* 1981).

A glass jar filled with mineral oil was used for short annealing times (less than 5 min). The temperature of the oil was stabilized at 400 °C with a temperature controller. The sample foil was immersed in the oil bath for the time required; it was then pulled out and quenched in water. Our estimates show that for thin, nearly pure copper foils a time much shorter than 1 s is needed to reach thermal equilibrium.

Mössbauer spectra were taken in transmission geometry with a conventional constant-acceleration spectrometer using a <sup>57</sup>Co–Cr source and an argon-filled proportional counter. An iron foil was used to calibrate the spectrometer and all isomer shifts are relative to  $\alpha$ -Fe. The high long-term and temperature stability of the velocity scale (Tomov *et al* 1973) allows confident determination of small differences between similar spectra.

### 3. Results and discussion

Figure 1 shows three typical room-temperature spectra of the investigated sample for annealing times of 0 (as quenched), 10<sup>3</sup> and 10<sup>5</sup> s. A simple three-line model was used to fit the experimental spectra: one Lorentzian line for Fe<sub>s</sub> plus two Voigt-profile lines representing all other states of iron. More complicated models were also used:

(a) two Lorentz lines for Fe<sub>s</sub> and Fe<sub>v</sub> plus a doublet with individual Voigt-profile lines of equal areas (Jain and Longworth 1978);

(b) two single lines as in (a) plus three doublets (Clark *et al* 1979).

The fits with all three models yielded similar results especially for short annealing times (up to 10<sup>3</sup> s). The simplest model was preferred because the main interest of the study was the Fe<sub>s</sub> component.

The position and the width of Fe<sub>s</sub> line were fixed at 0.22 mm s<sup>-1</sup> and 0.26 mm s<sup>-1</sup> respectively. The isomer shift of Fe<sub>s</sub> was obtained from the best fits of many different spectra and is very close to the value quoted in the literature. We believe that there is no physical reason to fit this line with free parameters; the effect of a variation in the environment in the next-nearest-neighbour shell is small compared with the statistical errors inherent in such poorly resolved spectra.

The differences between the calculated and experimental points are shown in figure 1 as a demonstration of the quality of the fit. An important detail about the fitting procedure was that parameters obtained from each spectrum were used as the input for fitting the next spectrum in the order of the annealing time.

Two fractions are shown in figure 2;  $A_s(t)$  and  $A_v(t)$  are the areas of the Fe<sub>s</sub> and Fe<sub>v</sub> lines, respectively, as functions of annealing time. The data for the third component

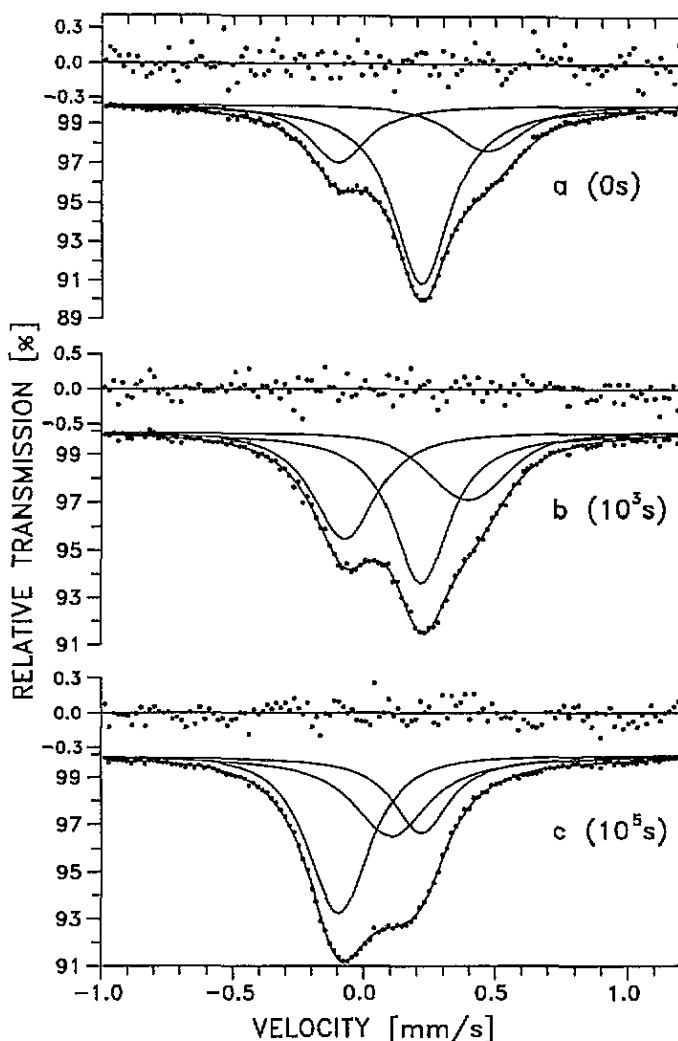


Figure 1. Mössbauer spectra of the Cu-0.6 at.% Fe sample for various annealing times (a) 0 s (as quenched from 1000 °C); (b)  $10^3$  s; (c)  $10^5$  s.

$Fe_n$  can be obtained easily because the curves are normalized to 100%. The result for  $A_\gamma$  is the difference between the areas of the left and the right Voigt-profile lines. No thickness correction was made and the areas of the lines are used as a measure of the phase concentrations. It can be seen that the form of the  $A_s(t)$  curve suggests a more complicated dependence than the simple exponent proposed by Clark *et al* (1979). It is well known that the initial state of the quenched alloys does not correspond to the equilibrium vacancy concentration but to a concentration characteristic of higher temperatures (Shewmon 1963, p 82). When starting the anneal we have to take into account the effect of the quenched vacancies too.

The procedure for obtaining an equation for the concentration  $A_s(t)$  of iron in solution is the following. For 'small' systems which are nearly homogeneous (Shewmon 1963, p 24) we can write

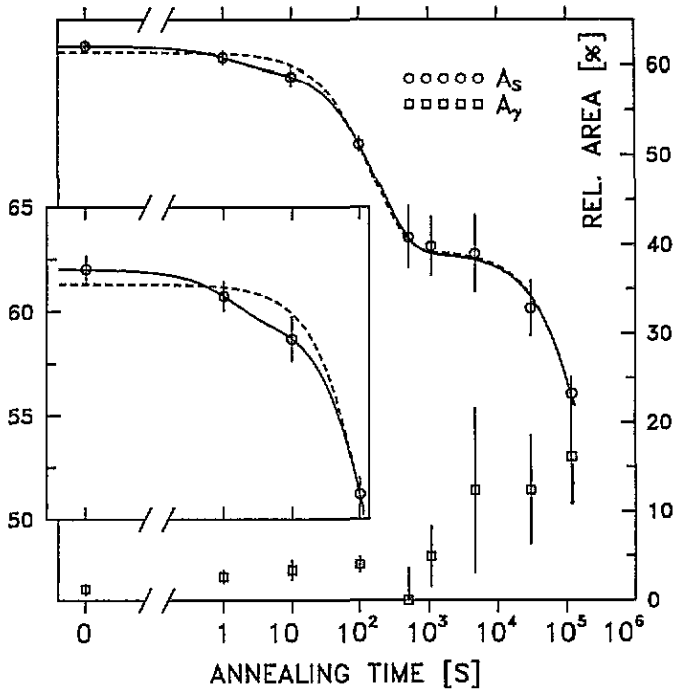


Figure 2. Dependence of the concentration of iron in solution and  $\gamma$ -iron on the annealing time. In the inset, the vertically expanded part of the  $A_s(t)$  curve is shown. The best fits with two different expressions (see the text) are displayed too.

$$dA_s(t)/dt = -bDA_s(t) \tag{1}$$

where  $b$  is a positive constant and  $D$  is a time-independent diffusion coefficient. The solution of (1) is

$$A_s(t) = A_{s0} \exp(-bDt). \tag{2}$$

In the case when there are quenched monovacancies with concentration  $C_{1v}^q$ ,

$$D = f_{1v}D_{1v}[C_{1v}^e + C_{1v}^q(t)] \tag{3}$$

where  $D_{1v}$  is the microscopic monovacancy diffusion coefficient and  $C_{1v}^e$  is the equilibrium concentration of monovacancies at the annealing temperature.  $f_{1v}$  is the geometrical correlation factor for which a value of 0.781 may be used<sup>†</sup>. If we assume that the concentration of quenched monovacancies decreases exponentially with a characteristic time  $\tau_1$  according to

$$C_{1v}^q(t) = C_{1v}^{q0} \exp(-t/\tau_1) \tag{4}$$

then the solution of (1) is

$$A_s(t) = A_{s0} \exp(-B^q\tau_1) \exp[-B^e t + B^q\tau_1 \exp(-t/\tau_1)] \tag{5}$$

<sup>†</sup> In the present work all the numerical data for vacancy properties are from the work of Mehrer and Seeger (1969).

where  $B^e = bf_{1v}D_{1v}C_{1v}^e$  and  $B^q = bf_{1v}D_{1v}C_{1v}^{q0}$ .

The fit of the experimental data using (5) is shown in figure 2 as a dashed curve; the parameters obtained are  $B^e = 4.5 \times 10^{-6} \text{ s}^{-1}$ ,  $B^q = 2.3 \times 10^{-3} \text{ s}^{-1}$  and  $\tau_1 = 190 \text{ s}$ . In the inset a vertically expanded part of  $A_s(t)$  demonstrates the pronounced deviation of the fit from experimental data for times less than 100 s. It is well known (Shewmon 1963, p 82) that high quenching temperatures produce a significant concentration of divacancies with a larger mobility compared with monovacancies. Thus, if we add another exponential term to (3) for the divacancy contribution,

$$D = f_{1v}D_{1v}[C_{1v}^e + C_{1v}^q(t)] + 4f_{2v}D_{2v}C_{2v}^q(t) \quad (6)$$

where  $f_{2v} = 0.475$ ,  $D_{2v}$  is the microscopic coefficient of divacancy diffusion and  $C_{2v}^q(t) = C_{2v}^{q0} \exp(-t/\tau_2)$ . On the assumption that

$$\tau_1/\tau_2 = D_{2v}/D_{1v} \quad D_{2v} = D_{1v}(\tau_1/\tau_2) \quad (7)$$

and on insertion of the last equation into (6), the diffusion coefficient becomes

$$D = f_{1v}D_{1v}[C_{1v}^e + C_{1v}^{q0} \exp(-t/\tau_1)] + 4f_{2v}(\tau_1/\tau_2)D_{1v}C_{2v}^{q0} \exp(-t/\tau_2)$$

and the solution of (1) is

$$A_s(t) = A_{s0} \exp[-\tau_1(B_1^q + B_2^q)] \exp\{-B^e t + \tau_1[B_1^q \exp(-t/\tau_1) + B_2^q \exp(-t/\tau_2)]\}. \quad (8)$$

Here  $A_{s0}$  denotes the concentration of  $\text{Fe}_s$  in the as-quenched sample,  $B^e = bf_{1v}D_{1v}C_{1v}^e$ ,  $B_1^q = bf_{1v}D_{1v}C_{1v}^{q0}$ ,  $B_2^q = 4bf_{2v}D_{1v}C_{2v}^{q0}$ ,  $\tau_1$  and  $\tau_2$  are the characteristic times for annealing of the quenched monovacancies and divacancies at  $400^\circ\text{C}$ .

The fit of the experimental data with equation (8) is fairly good (see the full curve in the inset in figure 2). The parameters obtained are  $B^e = 4.5 \times 10^{-6} \text{ s}^{-1}$ ,  $B_1^q = 1.9 \times 10^{-3} \text{ s}^{-1}$ ,  $B_2^q = 1.6 \times 10^{-4} \text{ s}^{-1}$ ,  $\tau_1 = 220 \text{ s}$  and  $\tau_2 = 1.3 \text{ s}$ .

At least three essential assumptions were made in the above consideration.

- (i) The diffusion of iron in copper is very close to self-diffusion in copper.
- (ii) The geometries of the sinks for monovacancy and divacancy migration are identical.
- (ii) There is no interaction between these two types of vacancy in the annealing process.

Evidence for assumption (i) can be found in the paper by Steinmetz *et al* (1986) where no impurity-vacancy binding was detected, while the last two can be regarded as more or less considerable simplifications.

Two calculations with the parameters obtained were made to demonstrate the adequacy of the proposed approach.

(i) From the ratio  $B^e/B_1^q$  the relative concentration of the quenched monovacancies can be obtained directly:  $C_{1v}^e/C_{1v}^{q0} \simeq 2.4 \times 10^{-3}$ . With the help of the well known expression for the equilibrium concentration of the monovacancies as a function of absolute temperature and using data for the monovacancy formation energy and entropy this leads to an estimate for  $C_{1v}^{q0} \simeq 10^{-5}$ . This value is not in contradiction to the values accepted in the literature.

Using the known energy and entropy of the vacancy formation in copper the equivalent temperature  $T_e$  was calculated.  $T_e$  is defined as the temperature at which the equilibrium concentration of monovacancies is equal to  $C_{1v}^{q0}$ . The result (1000 K) is acceptable and can serve as a measure of the quench cooling rate (Clark *et al* 1979).

(ii) From the equations for  $D_{1v}$  and  $D_{2v}$  (Mehrer and Seeger 1969) the ratio of the characteristic times (7) may be written as

$$\tau_1/\tau_2 = (1/6)[\{\nu_{2v}^0 \exp(S_{2v}^M/k)\}/\{\nu_{1v}^0 \exp(S_{1v}^M/k)\}] \exp(E_{1v}^M - E_{2v}^M) \quad (9)$$

where  $\nu^0 \exp(S/k)$  is the frequency factor for vacancy migration,  $E^M$  is the energy of vacancy migration and the subscripts  $1v$  and  $2v$  stand for monovacancy and divacancy, respectively. Inserting in (9) the values for frequency factors and energies for vacancy migration in pure copper, one obtains  $\tau_1/\tau_2 \simeq 190$  while the experimental ratio is about 170. The closeness of the two numbers may be coincidental taking into account the experimental errors and the uncertainty of the self-diffusion parameters used.

#### 4. Conclusion

The application of Mössbauer spectroscopy in short-time-scale annealing experiments seems to be promising for the study of vacancy properties. Quenching and annealing experiments in this area are usually done by measuring the resistivity of the investigated sample. However, the resistivity methods are very sensitive not only to vacancy concentration but also to impurities and to various defects (Ramsteiner *et al* 1965). For example, an impurity concentration of the order of the vacancy concentration or even smaller can change the result drastically. In this respect, Mössbauer spectroscopy is less sensitive and in some cases the longer measuring times can be compensated by the simplicity of the quenching and annealing techniques.

The numerical results obtained in this work can be regarded as preliminary and are quoted only to prove the consistency of our model with the experimental data. More detailed measurements at different annealing temperatures are required and the experiments are in progress.

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