

TEMPERATURE STUDY OF A Cu - 0.2 AT.% Fe ALLOY[†]

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Résumé.- Par spectrométrie Mössbauer on a suivi entre 298 K et 919 K la mise en amas, la précipitation et l'oxydation des atomes de fer en fonction du temps et de la température dans un alliage métastable à 0,2 at.% de fer. Une solubilité du fer dans le cuivre de 2000 ppm à 891 ± 10 K a été déterminée. L'oxydation interne du fer se produit au-dessus de 843 K pour un vide d'environ 10^{-5} torr et conduit à des paramètres hyperfins qui ne sont caractéristiques d'aucun des oxydes suivants : FeO, Fe₂O₃, Fe₃O₄, ou CuFeO₂.

Abstract.- Mössbauer effect spectroscopy has been used to follow the temperature and time dependence of the clustering, precipitation and oxidation of Fe atoms in a metastable Cu-0.2 at.% Fe alloy. Spectra were obtained from 298 K to 919 K in regular intervals. The solubility of Fe in Cu was found to be 2000 at.ppm at 891 ± 10 K. Internal oxidation of the Fe occurred above 843 K in a vacuum of about 10^{-5} torr. The oxidation product has Mössbauer parameters which are not characteristic of FeO, Fe₂O₃, Fe₃O₄ or CuFeO₂.

The Cu-rich Cu-Fe alloy system has been studied extensively using ⁵⁷Fe Mössbauer effect spectroscopy (MES). The clustering and precipitation of the Fe atoms have been examined using quenching, cold-rolling, ion implantation, and isochronal annealing techniques whereby the MES measurements were done at room temperature and below /1-11/. These measurements have established the MES parameters of a variety of Fe sites in Cu-Fe alloys such as Fe in solution (monomers), Fe dimers (1 Fe nearest neighbor) and fcc(γ)-Fe (12 Fe nearest neighbors). However, there have been no systematic MES studies to follow the clustering and precipitation kinetics at temperature.

The solid solubility of Fe in Cu has been determined by magnetization /12/, X-ray /13/, MES /14/, and electron microprobe /15/ measurements for Fe concentrations down to about 0.2 at.%.

In this investigation, MES has been used to follow the time and temperature dependence of Fe clustering, γ-Fe precipitate growth and dissolution for temperatures up to 650°C. A major goal was the precise determination of the solubility of 0.2 at.% Fe in Cu.

The alloy was prepared from high purity Cu (99.999) and Fe enriched to 90 % ⁵⁷Fe. The components were weighed to give a concentration of 2000 ± 4 at. ppm, melted in a graphite crucible, and homogenized at 1050°C for 24 hours under a flowing atmosphere of high purity H₂. From the alloy melt, a foil of 13 micron thickness was prepared by

cold-rolling, annealed under flowing H₂ at 750°C (well above the solvus line) and water quenched. The foil was cut into three samples with areas of about 1.5 cm x 1.5 cm each. A piece of the alloy melt was analyzed by atomic absorption and found to have an Fe concentration of 1983 ± 30 at. ppm.

The MES measurements were carried out in the constant acceleration mode using a ⁵⁷Co:Pd 25 mCi source. The Cu-Fe foil sample was sandwiched between BN discs and mounted in the vacuum furnace. The vacuum was maintained at about 10^{-5} torr for all measurements and the temperature was controlled to within 0.5°C. Two or three spectra, each requiring about 20 hours, were accumulated at each temperature. Each spectrum was fitted with a superposition of Lorentzian lines restricted to have the same width.

Figure 1 shows a series of spectra from room temperature to 601°C. All of the spectra were fitted with three lines (referred to as line 1, 2, and 3 from left to right) up to 570°C above which two lines were added to account for the new resonance above 1 mm/s.

Figure 2 shows the relative resonance areas (A₁, A₂, A₃) of the three lines as a function of temperature and time. Identification of the 3 components was made by comparing line positions, line separations, and intensities with available data /1-11/ on the various Fe sites in Cu. For example, line 2 (center line at 25°C) is identified as coming from the monomer site over most of the temperature range, whereas line 1 is due to dimers at 25°C (line 3 being the other half of the quadrupole pair)

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and due to γ -Fe at 448°C.

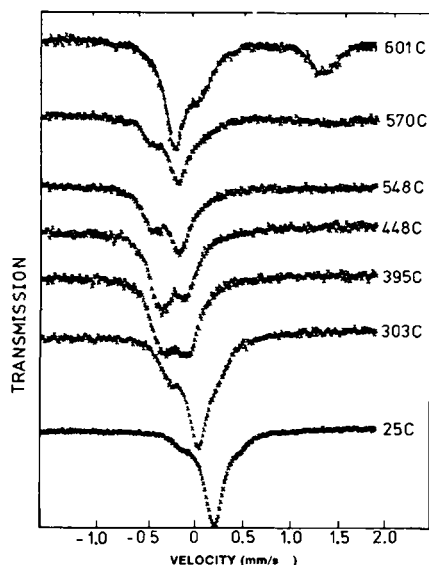


Fig. 1 : Mössbauer spectra for Cu-0.2 at.% Fe alloy sample No. 3. Each spectrum was obtained at the temperature indicated. Zero velocity corresponds to the center of the α -Fe spectrum.

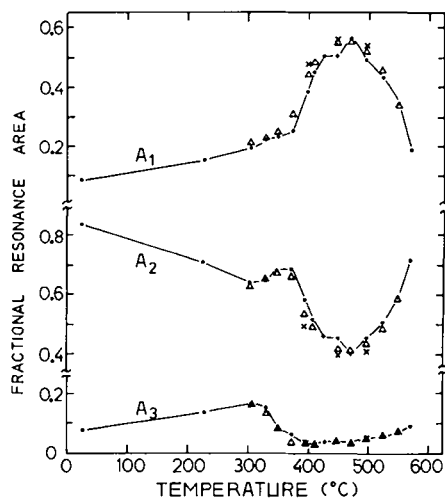


Fig. 2 : Fractional resonance areas from the three line fits to the spectra of sample No. 3. The symbols \bullet , Δ , and \times correspond to the first, second, and third spectrum, respectively, made at a given temperature at intervals of approximately 20 hours. The solid lines are drawn to guide the eye.

The time dependence can be seen in figure 2 where A_1 is observed to grow at the expense of A_2 at constant temperature (e.g., see 395°C and 448°C). This growth is occurring on a time scale comparable with the MES measuring time of about 20 hours per spectrum. From the data of figure 2 (and similar detailed data for the other 2 samples) we can describe four rather distinct processes which take place :

- (1) From 25°C to about 375°C, the Fe atoms

cluster to form dimers, trimers, quadramers, etc. but on a time scale too fast to be observed in our sequential MES spectra. The equilibrium diffusion coefficient of Fe in Cu /15/ is too small to account for this clustering. However, with the aid of a quenched-in vacancy, an Fe atom can diffuse a mean distance of about 20 Å (the average separation of Fe atoms in a 0.2 at.% alloy) in only 0.1 millisecond at 300°C whereas the equilibrium diffusion time (where vacancy formation energy is required) at the same temperature is over 300 hours. The increase in A_2 seen in figure 2 between 300°C and 375°C is not an increase in the number of monomers but is due to unresolved superposition of resonance from clusters several Fe atoms in size /2-11/.

- (2) From about 375°C to 500°C, diffusion controlled precipitation of γ -Fe takes place. From the time dependence of A_1 and A_2 indicated in figure 2 at 395°C, 448°C, and 500°C and the equilibrium diffusion coefficient of Fe in Cu /15/ we are able to explain the data using a simple diffusion-controlled spherical growth model /16/. These model calculations yield equilibrium γ -Fe precipitate diameters of about 6, 20, and 60 Å, respectively for the above 3 temperatures.

- (3) Above 500°C the precipitates begin to dissolve (decrease in A_1) and the number of monomers begins to increase (A_2). At the same time the fractional area A_3 also increases which indicates an increasing number of small clusters. Note from figure 1 that the spectrum at 570°C looks very similar to the one obtained at 303°C. It was our purpose to observe carefully the temperature at which $A_2 = 0.976$, i.e., a random distribution of 0.2 at.% Fe in Cu where 97.6 % of the Fe atoms are monomers. However, this was prevented by new resonance which began to appear at 570°C. Extrapolation of A_2 to 0.976 for all three samples yields $618 \pm 10^\circ\text{C}$ for the solubility of 2000 at.ppm Fe in Cu. This is in agreement with an extrapolation of the most recent work on the solubility of Fe in Cu /15/ which gives $633 \pm 16^\circ\text{C}$ as the solubility point of 0.2 at.% Fe in Cu.

- (4) At 570°C and above, new resonance appeared above 1 mm/s in all three samples. It was demonstrated to be an oxide by annealing one of the samples under a partial pressure of flowing H_2 gas at 900°C, after which the high velocity resonance was found to be absent. Through systematic temperature measurements we find the oxide resonance to consist of two equal intensity quadrupole pairs (the shoulder seen in the 601°C spectrum of figure 2 on the

right side of the strongest peak is the low velocity component of the quadrupole resonance) with the following room temperature parameters (for all three samples) : quadrupole splittings, $\Delta E_Q(1) = 2.66 \pm 0.03$ mm/s and $\Delta E_Q(2) = 2.42 \pm 0.03$ mm/s; velocity shifts relative to α -Fe, $S(1) = 1.19 \pm 0.02$ mm/s and $S(2) = 1.07 \pm 0.02$ mm/s. These values are characteristic of Fe in the 2+ oxidation state and clearly do not match parameters for FeO, CuFeO₂, nor superparamagnetic Fe₂O₃ or Fe₃O₄. All of these compounds except Fe₂O₃ were observed in a previous MES internal oxidation study of Fe in Cu /17/ carried out at higher pressures and temperatures than used here. Is it possible that we are observing the initial stages of internal oxidation where Fe-O pairs are being formed ? This simple interpretation is complicated by the two quadrupole pairs which indicate two different Fe sites associated with the oxide.

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