MÖSSBAUER SPECTROSCOPY STUDY OF AGING AND FAST NEUTRON IRRADIATION EFFECTS IN A COPPER-RICH Cu-Fe ALLOY

T. Gould, Jr, D. Vincent

To cite this version:

HAL Id: jpa-00215807
https://hal.science/jpa-00215807
Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
MÖSSBAUER SPECTROSCOPY STUDY OF AGING
AND FAST NEUTRON IRRADIATION EFFECTS
IN A COPPER-RICH Cu-Fe ALLOY (*)

T. H. GOULD, Jr (**) and D. H. VINCENT

Department of Nuclear Engineering
The University of Michigan, Ann Arbor, Michigan, U. S. A.

Résumé. — Les effets du recuit thermique et de l’irradiation par des neutrons rapides sur les
processus de précipitation dans un alliage Cu-Fe (0.6 % at) ont été étudiés par spectroscopie Mössbauer
ainsi que par mesures de résistivité. Les caractéristiques des spectres d’échantillons ayant subi un
recuit en solution et d’échantillons vieillis servent de base à l’interprétation des effets complexes
ayant lieu lors des irradiations. Des vieillissements induits par irradiation ainsi que des effets de
dissolution ont été observés en fonction du traitement thermique antérieur à l’irradiation. Les
neutrons rapides provoquent la formation de très petits agrégats de fer (< 12 atomes) dans des
echantillons de trempe directe. Dans les échantillons vieillis, les pics de déplacement induits par les
neutrons rapides provoquent la dispersion des atomes de fer se trouvant dans des agrégats ou des
précipités. L’effet de dissolution dépend du degré de vieillissement ou de la taille initiale des agrégats
de fer.

Abstract. — Mössbauer spectroscopy, supplemented by resistivity measurements, was used to
follow the effects of thermal aging and fast neutron irradiation on precipitation processes in a Cu-
0.6 at % Fe alloy. The characterization of spectra of solution annealed and aged alloy samples
provides background for interpretation of the complex effects occurring in irradiated alloys. Both
irradiation-induced aging and dissolution effects were observed as a function of pre-irradiation heat
treatment. In as-quenched alloys, fast neutrons cause the formation of very small Fe clusters
(< 12 atoms). In aged alloys, fast neutron induced displacement spikes disperse Fe atoms existing
in clusters and precipitates. The dissolution effect is dependent upon the stage of aging or initial Fe
cluster size.

1. Introduction. — Copper-rich CuFe is an age-
hardenable alloy system. The solubility of iron in
copper decreases from about 3 at % near the melting
point to practically zero at room temperature [1]. Aging
solution treated alloys with Fe concentrations below
about 1.2 % produces a metastable γ-Fe precipitate
which is initially coherent with the Cu matrix [2].
Plastic deformation transforms large (R > 100 Å) fcc
γ-precipitates into stable bcc α-Fe [3].
The irradiation of age-hardenable alloys by fast
neutrons produces two primary effects: precipitation
of solute atoms caused by radiation enhanced diffusion,
dissolution of existing precipitate particles by
displacement spikes or cascades. Boltax [4] observed
both of these effects in copper-rich CuFe alloys by
measuring resistivity to determine the concentration of
Fe remaining in solid solution. The major disadvantage
of the resistivity technique is its inability to discern the
presence of very small Fe clusters in the copper matrix
of aged and irradiated alloys.

(*) Supported by NSF Grant GK-17073.
(**) Presently with E. I. du Pont de Nemours and Co., Savannah
River Laboratory, Aiken, S. C.

The Mössbauer technique is ideally suited to follow
the aging and dissolution effects of radiation in copper-
rich CuFe. Several researchers [5-8] have studied the
Mössbauer spectroscopy of iron in this alloy system.
Four distinct iron environments or phases have been
identified in the room temperature spectra:

1) Fe atoms with only Cu nearest neighbors displaying
a single line centered at ~ 0.48 mm/s (reference:
SNP), designated γ₀-Fe ;
2) « Surface » iron or iron clusters with a combina-
tion of Cu and Fe nearest neighbors displaying a
quadrupole-split doublet at the base of γ₀-Fe, desig-
nated γ₁-Fe ;
3) fcc iron in γ-Fe precipitates displaying a singlet
centered at ~ 0.17 mm/s, designated γ₁-Fe ;
4) Equilibrium bcc iron precipitates displaying the
well known six line magnetically split spectrum of
α-iron.

The first two phases above dominate the spectra of
copper-rich alloys (0.2 ≤ c ≤ 1.2 %) which have been
solution annealed or aged at low temperatures
(< 400 °C). Window [7] has recently interpreted the
γ₁-Fe doublet as representing iron atoms which form
small spherical clusters or G. P. zones during the early stages of aging. In as-quenched alloys the $y_2$-doublet is well defined (see Fig. 1), displaying a quadrupole split-
ing of $\sim 0.58$ mm/s and isomer shift of $\sim 0.45$ mm/s. It is produced by iron pairs and small clusters formed during the quench [8]. With less efficient quenching or aging at low temperatures, the doublet broadens, shifts slightly to lower energy, decreases in splitting and increases in area as a result of iron cluster growth. At higher aging temperatures ($\geq 400^\circ$C), these clusters become $\gamma_1$-Fe precipitates, the predominant phase in well aged alloys.

In the work summarized by this paper, we have used Mössbauer spectroscopy to study changes in the state of iron clustering and precipitation in a Cu-0.6 at. % Fe alloy as a function of heat treatment and fast neutron exposure.

2. Experimental procedure. — Alloy samples of 0.6 at. % Fe in copper were prepared by vacuum induction melting appropriate quantities of 99.999 % copper and enriched iron (\(~ 70 \, \%^{57}\)Fe). The resulting ingot was cold rolled into strips of $\sim 15$ μm thickness from which rectangular foils measuring $13 \times 18$ mm$^2$ were precisely cut. These samples served for both Mössbauer and resistivity studies. All samples received a three hour solution treatment at 1 000°C in a reducing atmosphere prior to aging and/or irradiation. The aging and quenching methods used were similar to those described by Gonser et al. [5]. Irradiations were performed in the Ford Nuclear Reactor at peak flux positions between fuel plates. The foils, tin-plated prior to irradiation, were in intimate contact with the coolant/moderator at $\sim 55$ °C. Fast neutron exposures (n/cm$^2$, $E > 0.1$ MeV) were determined by iron wire activation.

Mössbauer spectra were taken at room temperature with a conventional spectrometer using a 50 mCi $^{57}$Co/Cu source, which gave a corrected line width of 0.21 mm/s against a thin iron absorber. Sodium nitroprusside (SNP) and $\alpha$-iron standard absorbers were used to calibrate the spectrometer; all isomer shifts are referred to SNP. Resistivity measurements were performed by a potential-comparison method (with gold foil standards) at room temperature with an estimated accuracy of $\sim 1 \%$.

3. Aging results. — Prior to irradiation a majority of solution treated samples were aged for various times at temperatures in the range 285°C-600°C to produce a variety of Fe cluster and precipitate sizes. The effects of progressive aging on the Mössbauer spectra of Cu-0.6 % Fe are shown in figure 1. Spectral parameters of a few representative samples are given in table I. Well aged samples (600°C) were satisfactorily analyzed using standard Lorentzian functions. Spectra of as-quenched and mildly aged samples ($T \leq 400^\circ$C) were analyzed in a manner similar to Window [7] as described below.

To account for line broadening caused by variations in iron near neighbor configurations during the early stages of clustering, we analyzed a majority of the Mössbauer spectra as a sum of Gaussian-Lorentzian convolution (G-L) functions of the general form

$$
G(v) = A_i \int_{-\infty}^{\infty} \frac{dv'}{(v - v')^2 + \left(\frac{l}{2}\right)^2} \times \frac{1}{\sqrt{\pi} \theta_i} \exp \left[ -\left(\frac{v - v'}{\theta_i}\right)^2 \right].
$$

The fitting parameters are $v_0$, $A_i$, and $\theta_i$; the centroid, area and Gaussian broadening of the $i$th component. The Lorentzian width $l$ was fixed in the fitting at 0.21 mm/s, corresponding to the thickness corrected line width of $\alpha$-iron. The near coincidence of $\gamma_1$-Fe with the doublet's low energy member, $\gamma_2(R)$, makes interpretation of spectra from samples aged at low temperatures problematic. In cases where the doublet's high energy member $\gamma_2(L)$ is partially resolved, the spectra were fit to (a) three individual G-L functions ($\gamma_1 + \gamma_2(L)$, $\gamma_2(R)$ and $\gamma_0$) as well as to (b) a G-L doublet ($\gamma_2$-Fe) constrained with equal areas under the peaks and a single G-L component ($\gamma_0$-Fe). The two types of fits produced essentially identical parameters for the low energy peak, $\gamma(L)$, which represents only iron in clusters or precipitates. There was little difference in quality of the two fits; both gave normalized chi-square values of about unity. Spectra where only
MÖSSBAUER SPECTROSCOPY STUDY OF AGING AND FAST NEUTRON IRRADIATION EFFECTS

Table I

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Position (mm/s)</th>
<th>Line Width (º) (mm/s)</th>
<th>Relative Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>γ(L) (º)</td>
<td>y0 (º)</td>
<td>γ2(R) (º)</td>
</tr>
<tr>
<td>As-Quenched (*)</td>
<td>0.170(4)</td>
<td>0.484(4)</td>
<td>0.738(6)</td>
</tr>
<tr>
<td>Aged-285°-1000 m (*)</td>
<td>0.176(6)</td>
<td>0.479(4)</td>
<td>0.676(6)</td>
</tr>
<tr>
<td>-1000 m</td>
<td>0.176(4)</td>
<td>0.481(6)</td>
<td>0.687(6)</td>
</tr>
<tr>
<td>335°-1000 m</td>
<td>0.202(5)</td>
<td>0.484(1)</td>
<td>0.58 (3)</td>
</tr>
<tr>
<td>600°-1000 m (*)</td>
<td>0.178(4)</td>
<td>0.479(5)</td>
<td>0.755(7)</td>
</tr>
<tr>
<td>400°-1000 m</td>
<td>0.180(5)</td>
<td>0.461(5)</td>
<td>0.085(3)</td>
</tr>
</tbody>
</table>

(*) Spectra fit to area constrained G-L doublet (γ2-Fe) plus G-L singlet (γ0-Fe).
(º) y(L) = γ(L) + γ1.
(º) Line widths are given in terms of Gaussian broadening parameter, θ, of eq. (1) except for the alloy aged at 600 °C; its line widths are reported as Lorentzian FWHM.
(+) Fit to sum of three Lorentzians.
(+?) Constrained at position of γ0 in as-quenched samples.

Two peaks were resolvable (400 °C samples) were analyzed using only two G-L distributions.

As pointed out by Window [7], the Mössbauer spectra of aged CuFe can be interpreted in terms of the spherical growth of iron clusters. On the assumption of spherical growth, it is possible to determine the ratio of surface to total atoms in a cluster. During the incipient stages of cluster formation, Fe surface atoms (γ2-Fe) greatly outnumber internal Fe atoms (γ1-Fe). Not until about 6 to 7 shells of Fe atoms are built up does one expect the γ1-Fe component to begin to dominate the behavior of γ(L). Taking the ratio of areas, γ2/(γ1 + γ2), to represent the fraction of surface atoms in a cluster, the three component fitting results predict that aging at 335 °C and below produces Fe cluster sizes ranging from a few atoms to at most three near neighbor shells in radius (< 3 Å) [9]. The two component model predicts clusters of 12 atoms or less at these aging temperatures. Poor resolution prevents such an estimate of cluster size in alloy samples aged at 400 °C, although a significant amount of γ1-Fe appears to be present. Aging at 600 °C (≥ 100 min) is known to produce γ1-precipitates with radii of the order of 100 Å or greater [3].

The small iron clusters formed during aging or from the dissolution of precipitates during irradiation make a significant contribution to the alloy's resistivity. Their effect is seen in figure 2, where measured resistivity values (ordinate) are plotted against the concentration of Fe in solid solution as determined from the area fraction of the γ0-Fe peak. The solid line of slope 8.2 μΩ-cm/at % Fe in the figure represents the residual resistivity of dispersed Fe atoms in copper. The effective resistivity δρ/C(2) of Fe clusters, where δρ is the difference between measured and residual resistivity and C(2) the concentration of iron associated with clusters (γ1 + γ2), decreases from its maximum value for the as-quenched 0.6 % alloy to essentially zero for well aged samples. As the clusters grow their effective-ness for scattering conduction electrons decreases; however, the small clusters formed in alloys aged below 400 °C still contribute significantly to the total resistivity. This contribution was misinterpreted by Boltax [2, 4] as representing Fe atoms in solid solution. Since changes in resistivity were used to determine changes in the concentration of Fe in solid solution, Boltax's conclusions on the effects of aging [2] and irradiation [4] in CuFe alloys are partially in error. As discussed below, the Mössbauer results provide a clearer interpretation of the effects of irradiation in CuFe.

4. Irradiation results.—Mössbauer spectral parameters of representative Cu-0.6 % Fe alloy samples irradiated to a fast neutron fluence of ~ 2.7(10)^19 n/cm² are summarized in table II (see Table I for comparison
T. H. GOULD, JR. AND D. H. VINCENT

Spectral Parameters for Irradiated Cu-0.6 % Fe

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Position (mm/s)</th>
<th>Line Width (°) (mm/s)</th>
<th>Relative Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \gamma(L) (^o) ) ( \gamma_0 ) ( \gamma_2(R) )</td>
<td>( \gamma(L) ) ( \gamma_0 ) ( \gamma_2(R) )</td>
<td>( \gamma(L) ) ( \gamma_0 ) ( \gamma_2(R) )</td>
</tr>
<tr>
<td>As-Quenched (*)</td>
<td>0.174(4) 0.483(3) 0.717(4)</td>
<td>0.067(2) 0.046(3) 0.105(3)</td>
<td>0.27(4) 0.45(2) 0.27(2)</td>
</tr>
<tr>
<td>Aged-335°C-1000 m (*)</td>
<td>0.174(4) 0.483(4) 0.729(6)</td>
<td>0.067(2) 0.055(3) 0.099(4)</td>
<td>0.27(4) 0.495(2) 0.23(6)</td>
</tr>
<tr>
<td>285°C-1000 m (*)</td>
<td>0.178(5) 0.479(4) 0.675(5)</td>
<td>0.077(2) 0.036(3) 0.152(4)</td>
<td>0.33(4) 0.34(3) 0.33(4)</td>
</tr>
<tr>
<td>1000 m</td>
<td>0.174(1) 0.483(5) 0.699(6)</td>
<td>0.077(2) 0.051(3) 0.116(4)</td>
<td>0.33(2) 0.399(5) 0.289(6)</td>
</tr>
<tr>
<td>335°C-1000 m</td>
<td>0.180(4) 0.484(5) 0.63(1)</td>
<td>0.096(2) 0.047(6) 0.16(1)</td>
<td>0.41(4) 0.273(2) 0.32(2)</td>
</tr>
<tr>
<td>600°C-1000 m (*)</td>
<td>0.172(4) 0.48(4) 0.758(8)</td>
<td>0.251(2) 0.255(4) 0.24(1)</td>
<td>0.66(8) 0.293(9) 0.046(6)</td>
</tr>
<tr>
<td>400°C-1000 m</td>
<td>0.168(5) 0.482(6)</td>
<td>0.076(4) 0.156(4)</td>
<td>0.40(7) 0.59(3)</td>
</tr>
</tbody>
</table>

Footnotes are given in Table I.

with pre-irradiation parameters). Alloy samples given identical pre-irradiation heat treatments were irradiated to fluences of \( \sim 0.4 \) and \( 9.0 \times 10^{19} \) n/cm\(^2\).

For as-quenched samples, fast neutrons produce similar changes in spectral parameters as observed for low temperature aging. A definite increase in the area of \( \gamma_2\)-Fe occurs, accompanied by only a slight decrease in splitting and small negative shift of its centroid. These are indications that only small Fe clusters (< 12 atoms) are formed, and that iron pairs and small clusters existing in the as-quenched alloy prior to irradiation have grown only slightly. Boltax erroneously associated a decrease in resistivity (our \( \Delta \rho \) measurements agree) in quenched-irradiated CuFe with the formation and growth of \( \gamma_1\)-precipitates. The satisfactory fits of the spectra to the constrained two component \( \gamma_0 + \gamma_2 \) model confirm that \( \gamma_1\)-Fe is not formed in significant quantities during irradiation. An additional, fluence dependent effect was observed in the as-quenched samples. Namely, the ratio of Fe atoms clustering to the number of primary neutron collisions (\( N_{\gamma\sigma\rho} \)) decreases significantly with increasing fluence. This phenomenon is the combined result of a gradual depletion of Fe atoms from solution and the competitive process of irradiation-induced dissolution.

The effect of irradiation on CuFe alloys aged at low temperature is illustrated in figure 3 (also compare Tables I and II). Two competing irradiation induced processes occur simultaneously to produce the observed effect: enhanced diffusion leading to an increase in iron clustering, and the dissolution of existing clusters within large displacement cascades or spikes [10]. For samples aged at 335°C for 1 000 min the dissolution effect is predominant, causing the spectra to revert to forms characteristic of less advanced stages of aging.
The decrease in area fraction of $\gamma(L)$, which is sensitive only to iron occurring in clusters (i.e., either as $\gamma_2(L)$ or $\gamma_1$-Fe), indicates that dissolution has definitely occurred. The apparent increase in $\gamma_2(R)$'s area fraction along with its shift to higher energy can be interpreted as an increase in the amount of iron associated with smaller clusters. This increase is likely caused, in part, by an incomplete break-up of larger clusters by displacement spikes.

The results of the irradiations at $2.7(10)^{19}$ n/cm$^2$ are summarized in figure 4 in terms of the change in area fraction of $\gamma(L)$ (solid symbols), converted to atom \% Fe. The abscissa shows aging time; the lines connect points which belong to the same aging temperature. The changes, $\Delta \gamma(L)$, are quantitative for alloy samples with either very small Fe clusters (as-quenched, aged-285$^\circ$) or very large precipitates (aged-600$^\circ$); they show only qualitative trends for intermediate cluster sizes. Points above a horizontal line at $\Delta \gamma(L) = 0$ indicate a prevalence of irradiation aging over dissolution, while those below show a net dissolution effect. The extent of irradiation-induced dissolution is illustrated in figure 4 by the open symbols connected by dashed lines. These points represent $\Delta \gamma(L)$ values which were corrected for aging effects occurring concurrently during irradiation. The corrections were made with the aid of irradiation-aging results of as-quenched samples [9].

Summarizing, irradiation aging is seen to predominate in CuFe alloy samples with either very small Fe clusters (as-quenched) or with large $\gamma_1$-precipitates (aged-600$^\circ$). Between these extremes, displacement spikes cause a net dissolution or partial break-up of the Fe clusters. The extent of dissolution is very dependent upon cluster size, initially increasing with thermal aging until a critical cluster size is reached and then decreasing upon further aging (400 $^\circ$C results).

References