DIFFERENCE IN Fe ATOM ENVIRONMENTS BETWEEN CuFe (2% Fe) AND CuAuFe (1 AND 3% Fe) ALLOYS


To cite this version:
J. Budnick, M. Choi, G. Hayes, D. Pease, Z. Tan, et al.. DIFFERENCE IN Fe ATOM ENVIRONMENTS BETWEEN CuFe (2% Fe) AND CuAuFe (1 AND 3% Fe) ALLOYS. Journal de Physique Colloques, 1986, 47 (C8), pp.C8-1037-C8-1040. <10.1051/jphyscol:19868200>. <jpa-00226108>

HAL Id: jpa-00226108
https://hal.archives-ouvertes.fr/jpa-00226108
Submitted on 1 Jan 1986
DIFFERENCE IN Fe ATOM ENVIRONMENTS BETWEEN CuFe (2% Fe) AND CuAuFe (1 AND 3% Fe) ALLOYS

J. I. BUDNICK, M. H. CHOI, G. H. HAYES(1), D. M. PEASE, Z. TAN, E. KLEIN* and B. ILLERHAUS*

Department of Physics and Institute of Materials Science, University of Connecticut, Storrs, CT 06268, U.S.A.

*Institut für Atom und Festerkorper Physik, Freie Universität Berlin, D-1000 Berlin 33, F.R.G.

Abstract.--- According to recent $^{57}$Fe-Mössbauer measurements made at 4.2K, Fe atoms in Cu$_{68}$Au$_{32}$Fe$_2$ and Cu$_{67}$Au$_{33}$Fe$_3$ are dominantly (>80%) ferromagnetic, whereas Fe atoms in Cu$_{98}$Fe$_2$ manifest antiferromagnetic interactions (<10% ferromagnetic). The Fe K-edge XANES and EXAFS measurements have been made on these alloys. Fluorescence, as well as transmission, data have been obtained. The XANES and EXAFS spectra for the CuAuFe alloys are quite similar to the spectra for $\alpha$-Fe, which seems to reflect the clustering of ferromagnetic bcc Fe. On the other hand, the XANES and EXAFS for Cu$_{98}$Fe$_2$ closely resemble those of fcc Ni, strongly indicating the environment of antiferromagnetic fcc $\gamma$-Fe. Moreover, the Fourier transform for Cu$_{98}$Fe$_2$ shows more smeared out higher shell peaks compared with those for CuAuFe$_2$. This may be the result of varying sizes of Fe clusters.

Introduction

The equilibrium solubility of Fe in Cu which is 3 at. % at 1060°C drops sharply with decreasing temperature and is only 0.5 at. % at 600°C (1). A supersaturated copper-rich Cu-Fe solid solution obtained by quenching from a high temperature thus has provided a most interesting system for studying the environment of dilute concentration Fe atoms. Bitter and Kaufmann (2) originally suggested that, in such a copper-rich Cu-Fe solid solution, Fe atoms initially precipitate as particles of face-centered cubic (fcc) $\gamma$-Fe coherent with the Cu matrix, and that the $\gamma$-Fe phase transforms to the incoherent body-centered cubic (bcc) $\delta$-Fe phase during cold rolling or long aging. This mechanism of coherent $\gamma$-Fe precipitation was confirmed in the case of Cu$_{98}$Fe$_2$ by Newkirk (3) with the X-ray diffraction and other techniques. The $\gamma$-Fe precipitates, unless cold-rolled, transform to $\delta$-Fe at and below room temperature only over an extended period of time. Hence, Abrahams et al. (4) carried out neutron diffraction measurements on the precipitates in Cu-Fe alloys with 2.8 and 3.3 at. % Fe to investigate the magnetic structure of $\gamma$-Fe, and determined that the $\gamma$-Fe particles are antiferromagnetic. However, according to a Mössbauer study of Cu$_{98}$Fe, by Window (5), the precipitates consist of varying sizes of Fe clusters with different numbers of Fe near neighbors, and only large clusters behave as $\gamma$-Fe.

On the other hand, in 1980, Gonser et al. (6) reported that ferromagnetic fcc $\gamma$-Fe precipitates were found in a Cu$_{68}$Au$_{32}$Fe$_2$ alloy. They interpreted the finding in terms of the change in the lattice constant by postulating that, when the lattice parameter of the Cu host increases with an addition of Au, the increase in the

(1) Present Address : Optical Group Research, Perkin-Elmer Corporation, Danbury, CT 06810, U.S.A.

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphyscol:19868200
atomic distance changes the sign of the exchange interaction thus causing a transition from antiferromagnetic to ferromagnetic \( \gamma \)-Fe. This finding was later corrected by Schneweiss et al. \((7)\) based on the discovery that the precipitates were actually Fe\textsubscript{8}C formed by a graphite crucible used in sample preparation.

Moreover, according to recent \(^{57}\)Fe-Mossbauer measurements made at 4.2K by Klein et al., there is a definite difference in Fe atom environments between CuFe (2\% Fe) and CuAuFe (1 and 3\% Fe) alloys: Fe atoms in Cu\textsubscript{68}Au\textsubscript{32}Fe\textsubscript{3} and Cu\textsubscript{66}Au\textsubscript{34}Fe\textsubscript{3} are dominantly (>80\%) ferromagnetic, whereas Fe atoms in Cu\textsubscript{98}Fe\textsubscript{2} manifest antiferromagnetic interactions (<10\% ferromagnetic). The detailed results will be published elsewhere.

To clarify whether this difference is due to a lattice parameter shift or a structural change, in the present investigation, X-ray absorption and fluorescence measurements have been made on these three alloys.

**Experimental**

The samples Cu\textsubscript{98}Fe\textsubscript{2}, Cu\textsubscript{68}Au\textsubscript{32}Fe\textsubscript{3}, and Cu\textsubscript{66}Au\textsubscript{34}Fe\textsubscript{3} were melted, rolled, and annealed to dissolve all the Fe atoms. This annealing continued for 24 hours at 1000°C for Cu\textsubscript{98}Fe\textsubscript{2} and at 900°C for Cu\textsubscript{68}Au\textsubscript{32}Fe\textsubscript{3} and Cu\textsubscript{66}Au\textsubscript{34}Fe\textsubscript{3}. Then, to induce the precipitation, Cu\textsubscript{98}Fe\textsubscript{2} and Cu\textsubscript{66}Au\textsubscript{34}Fe\textsubscript{3} samples were further annealed for 120 minutes at 620°C and the Cu\textsubscript{68}Au\textsubscript{32}Fe\textsubscript{3} sample was annealed for 2 days at 540°C. Melting and annealing processes were done in a quartz tube under H\textsubscript{2}-atmosphere. The samples were quenched after annealing by dropping quartz tubes into cold water.

The Fe K-edge XANES and EXAFS measurements have been made on these samples using the beamline X-11A at the National Synchrotron Light Source at Brookhaven National Laboratory. Fluorescence, as well as transmission, data have been obtained for the sample alloys, and transmission data have been obtained for the standard Fe and Ni foils at the corresponding K edges. These data have been taken with silicon (111) monochromator crystals in a two-crystal mode.

**Results and Discussion**

In Fig. 1, the Fe K-edge XANES spectra for the three samples are shown in comparison with the XANES for pure Fe. The XANES for Cu\textsubscript{98}Fe\textsubscript{2} or Cu\textsubscript{68}Au\textsubscript{32}Fe\textsubscript{3}, though slightly broadened and distorted, still looks similar to that for pure Fe. The broadening is more pronounced for the 1\% Fe sample. Whereas the XANES for Cu\textsubscript{98}Fe\textsubscript{2} closely resembles the Ni K-edge XANES spectrum for fcc Ni. These spectra have been obtained from the fluorescence data by proper background subtractions and a normalization. The corresponding transmission data exhibited poor quality spectra with spurious scatter peaks which rendered the background subtraction extremely difficult, except in the case of Cu\textsubscript{98}Fe\textsubscript{2}, and thus are not shown here. When the lattice parameter changes within the same structure in an alloy system, the change is known to result in energy shifts of features in the corresponding XANES \((8)\).

However, such a drastic difference in electronic structure, as shown in the comparison of the Fe K-edge XANES spectra for Cu-Fe and Cu-Au-Fe alloys, is not expected to result from a mere change in the lattice parameter.

Therefore it is concluded that the XANES spectra for the Cu-Au-Fe alloys reflect the clustering of ferromagnetic bcc Fe, whereas the XANES for the Cu-Fe alloy originates from the environment of antiferromagnetic fcc \( \gamma \)-Fe. This interpretation is also supported by the corresponding similarities manifested in the EXAFS spectra. In Fig. 2, the normalized Fe K-edge EXAFS data for Cu\textsubscript{98}Fe\textsubscript{2} obtained by fluorescence and transmission measurements are shown in comparison with the normalized Ni K-edge EXAFS for pure Ni. All the features in the EXAFS agree well between the fluorescence and transmission data except that there is a slight difference in amplitude \((9)\). The similarity observed in the figure strongly suggests that the environment of Fe atoms in Cu\textsubscript{98}Fe\textsubscript{2} is that of fcc.

Moreover, as shown in Fig. 3, when the Fe K-edge XANES spectrum for Cu\textsubscript{98}Fe\textsubscript{2} is compared with the Ni K-edge XANES for pure Ni, a shift of features toward lower energy which corresponds to a larger lattice parameter is observed. This is consistent with the fact that the reported lattice spacing of \( \gamma \)-Fe is 3.590\AA\ \((3)\) or 3.588\AA\ \((4)\), while that of fcc Ni is 3.5238\AA\.
Fig. 1. Fe K-edge XANES spectra:
(a) Cu₆₇Au₃₀Fe₃ (Fluorescence),
(b) Cu₆₉Au₃₀Fe₃ (F),
(c) Cu₉₈Fe₂ (F),
(d) pure Fe (Transmission).

Fig. 2. (a) Fe K EXAFS for Cu₉₈Fe₂ (F).
(b) Fe K EXAFS for Cu₉₈Fe₂ (T).
(c) Ni K-edge EXAFS for pure Ni (T).

Fig. 3. Solid line: Fe K-edge XANES for Cu₇₅Fe₁₅ (Fluorescence).
Dotted line: Ni K-edge XANES for pure Ni (Transmission).

Fig. 4. (a) Fe K-edge EXAFS for Cu₆₇Au₃₀Fe₃ (Fluorescence).
(b) Fe K-edge EXAFS for pure Fe (T).
A striking similarity between the Fe K-edge EXAFS for Cu$_{67}$Au$_{30}$Fe$_3$ measured in fluorescence and that for pure Fe is also shown in Fig. 4. Hence, the XANES and EXAFS results indicate that most Fe atoms in the Cu-Fe alloy are in antiferromagnetic β-Fe environments, while those in the Cu-Au-Fe alloys are in ferromagnetic bcc α-Fe environments, which is in good agreement with the result of recent 57Fe Mössbauer measurements by Klein et al.

Finally, definite supporting evidence for this is found in the Fourier transforms of the Fe K-edge EXAFS for these alloys shown in Fig. 5. The Fourier transform of the normalized Fe K EXAFS for Cu$_{67}$Au$_{30}$Fe$_3$ compares very well with that for pure Fe obtained by Fourier transforming the transmission data with a similar k range, though the amplitudes cannot be directly compared (9). Whereas, as shown in Fig. 6, the Fourier transform of the normalized Fe K EXAFS for Cu$_{98}$Fe$_2$ compares relatively well with that of the Ni K EXAFS for pure Ni with a similar transformation range. The Fourier transform for Cu$_{98}$Fe$_2$ shows more smeared out higher shell peaks which correspond less well in the comparison. This may be the result of varying sizes of γ-Fe clusters reported by Window (5).

Fig. 5. Fourier transform (k$^2$ weighted) of the normalized Fe K-edge EXAFS: Solid line-Cu$_{67}$Au$_{30}$Fe$_3$ (Fluorescence); Dotted line-pure Fe (Transmission).

Fig. 6. Solid line: Fourier transform (k$^2$ weighted) of the normalized Fe K-edge EXAFS for Cu$_{98}$Fe$_2$ (Transmission); Dotted line: Fourier transform (k$^2$ weighted) of the normalized Ni K-edge EXAFS for pure Ni (Transmission).

Acknowledgments

This research was supported by USDOE under contract numbers, DE-AS05-80ER10742 and DE-AC02-76CH00016. Support was also received by the University of Connecticut Research Foundation. This work was carried out at the National Synchrotron Light Source.

References

(3) J. B. Newkirk, AIME Trans., 202 (1957) 1214.
(5) B. Window, Phil. Mag., 26 (1972) 681.
(9) S. M. Heald, private communication.