Structural and magnetic phase formation in nanophase brass–iron electron compounds

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Abstract. Starting with $Cu_{0.65}Zn_{0.35}$ with an e/a ratio of 1.35 we studied the phase formation in nanophase $(Cu_{0.65}Zn_{0.35})_{1-x}Fe_x$ alloys in the concentration range $0.1 \leq x \leq 0.7$ to see the effect of altering the electron concentration. The evolution of bcc phase from the fcc phase as a function of Fe concentration was investigated by Mössbauer spectroscopy and X-ray diffraction. The grain size, lattice parameters, and average hyperfine magnetic field distributions were estimated for the nanophase alloys. The fcc phase was observed to persist up to 40 atomic per cent Fe substitutions, a mixed (fcc + bcc) phase region up to 70 atomic per cent Fe and bcc phase beyond 70 atomic per cent Fe. The magnetic state of the alloys changed from nonmagnetic for $x \leq 0.3$ to magnetically ordered state at room temperature for $x \geq 0.33$, which lies in the fcc phase region. The fcc phase alloys of Fe with non-magnetic metals have very low magnetic transition temperatures. However, in this system the room temperature state is unusually magnetic.

Keywords. Electron compounds; nanophase alloys; Mössbauer spectroscopy; X-ray diffraction.

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1. Introduction

It has been proposed [1] that nanometer-sized structures provide a method of changing the electronic charge density and related properties of the solid. The interface regions in the nanostructured solid form a substantial volume fraction of the total volume and the charge density in these regions can be changed with respect to the bulk solid by application of an external field or the presence of internal electric fields. In an electron compound like Cu–Zn the crystal structure is a sensitive function of the electron-to-atom ratio (e/a) and different crystallographic structures are formed at different e/a ratios [2]. In this work we study the effect of addition of a ternary solute (Fe) to an α-brass composition ($Cu_{0.65}Zn_{0.35}$) close to the fcc–bcc phase boundary in the nanophase state.

2. Experimental techniques

First, nanocrystalline Fe powder was prepared by mechanical milling of 4N pure Fe chips (Aldrich-Sigma) in a SPEX 8000 mixer mill for 50 h using hardened steel vial

and a set of six steel balls (two of 1/2-inch diameter and four of 1/4-inch diameter). Nanocrystalline α-brass of composition $Cu_{0.65}Zn_{0.35}$ was prepared separately by mechanical alloying of electrolytic Cu (99.5%) powder from Loba Chemie and Zn (99.5%) powder from S.D. Fine Chem. Ltd in the mixer mill for 12 h. Subsequently, $(Cu_{0.65}Zn_{0.35})_{1-x}Fe_x$ ($0 \leq x \leq 0.70$) alloys were prepared by mechanical alloying of nanocrystalline Fe and α-brass for 36 h. It was observed that further milling beyond 36 h did not change the X-ray diffraction patterns and an optimum milling time of 36 h was adopted for these studies. The milling was carried out under argon atmosphere in a hardened steel vial with a ball-to-powder ratio of $5:1$.

X-ray diffraction studies were carried out on an INEL X-ray diffractometer equipped with CPS 120 wide-angle curved proportional counter using $CoK\alpha_1$ radiation. The X-ray diffraction (XRD) patterns were fitted using a Voigt profile by WINDIF software (also from INEL, France). The average grain size was calculated from the line-width of the fundamental (1 1 0) reflection for the bcc phase and (1 1 1) reflection for the fcc phase using Scherrer formula [3]. The instrumental broadening was corrected by recording the diffraction pattern of polycrystalline pure Fe powder and subtracting it from the observed line-widths.

Mössbauer spectra with good statistics (10^6 counts in each channel of the folded spectra) were recorded in transmission geometry and in constant acceleration mode, using a 15 m Ci ^{57}Co in Rh source from RITVERC Isotope Products, St. Petersburg, Russia. Hyperfine magnetic field (HMF) distributions and quadrupole splitting distributions were evaluated from the Mössbauer spectra using the method of Le Caër and Dubois [4]. A linear correlation between the isomer shift (I) and HMF (H) in the form $I = aH + b$ for magnetically split spectra, and between the isomer shift (I) and quadrupole splitting (Δ) in the form $\delta = a\Delta + b$ for quadrupole spectra, was assumed and the constant coefficients a and b were optimized to get the best fit.

3. Results and discussions

3.1 *X-ray diffraction*

The XRD pattern of nanocrystalline Fe powder and α-brass show broad peaks of bcc and fcc phases respectively. Figure 1 shows the X-ray diffraction patterns of the as-milled samples. For compositions in the range $0 \leq x \leq 0.40$ the predominant phase observed was fcc although a signature of very small amounts of bcc phase (less than 5%) could also be seen. In the Fe–Cu system also, the existence of small amounts of bcc Fe phase was observed which did not decrease any further with the increase of milling time [5]. Although they could not observe the bcc phase in X-ray patterns, the Mössbauer spectra showed hyperfine fields slightly less than that for Fe suggesting the presence of small amount of Cu dissolved in bcc Fe. A complete bcc phase was observed at $x \geq 0.70$. In the intermediate region $0.40 < x < 0.70$, mixed fcc + bcc phase lines were observed. Also there is a small but sharp increase in percentage composition of bcc phase and consequently a decrease in fcc phase at $0.30 \leq x \leq 0.33$ where we show later that a magnetic state is observed at room temperature for $x > 0.30$ alloys. Figure 2 shows the phase evolution as a function of Fe concentration.
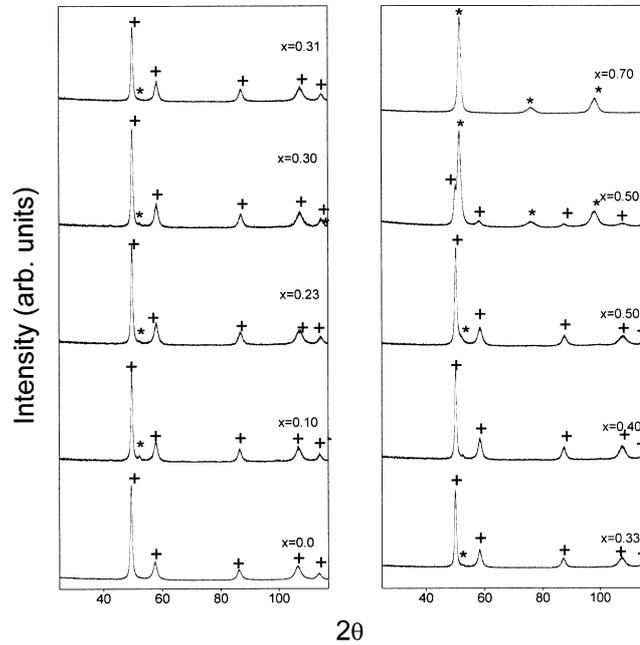
Figure 1. X-ray diffraction patterns of as-milled $(Cu_{0.65}Zn_{0.35})_{1-x}Fe_x$ alloys $(0 \leq x \leq 0.70)$. The bcc phase lines are marked as '*' and the fcc phase lines as '+'.
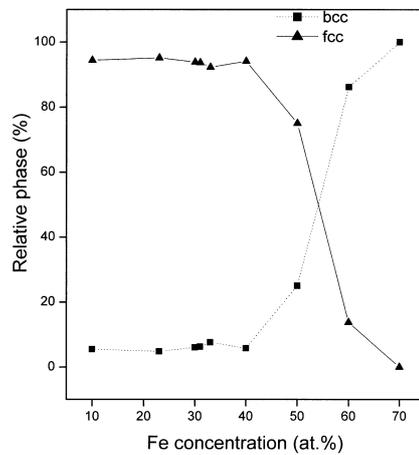

Figure 2. The evolution of the bcc and fcc phases with Fe concentration as determined from areas under the fundamental lines for the two phases.

Figures 3 and 4 show the behaviour of lattice parameter and average grain size respectively as a function of Fe concentration. There is a decrease in the lattice parameter of the fcc phase with increase in Fe concentration, whereas the lattice parameter of bcc phase remains approximately constant. Near $x = 0.3$ composition
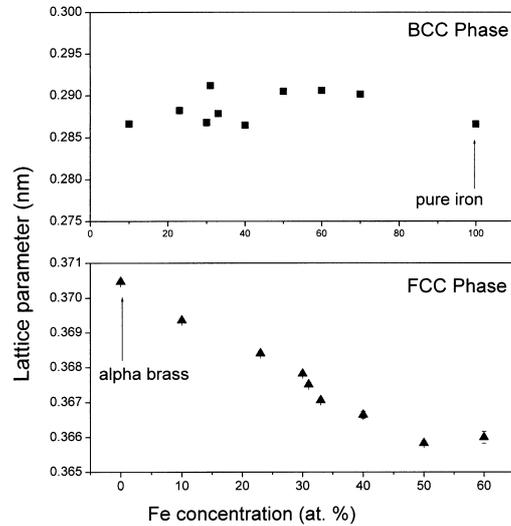
Figure 3. The behaviour of the lattice constants of the bcc and fcc phases with change in Fe concentration. An abrupt decrease in the lattice constant in the fcc phase is observable near 30 atomic per cent Fe concentration where the transformation from non-magnetic to magnetic phases takes place.
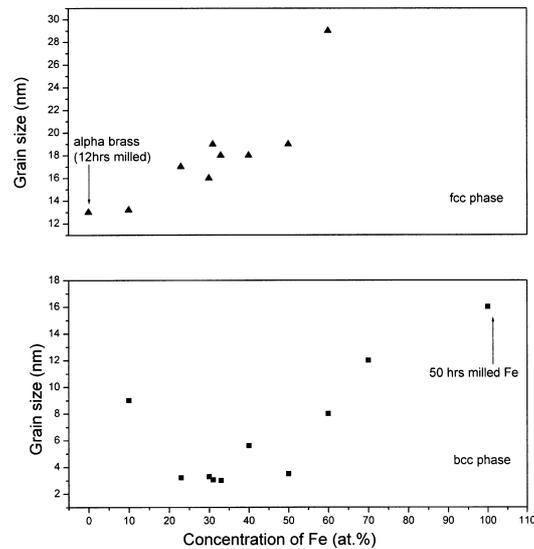

Figure 4. Change in grain size for the fcc and bcc phases as a function of Fe concentration. The grain size of the starting nanocrystalline Fe and brass samples are also shown.

there is a discontinuous decrease in lattice parameter which is related to the magnetic phase formation as seen in the Mössbauer spectra. The grain size of the fcc phase increases from 13 nm (for $x = 0$) to 29 nm (for $x = 0.60$) due to alloying with
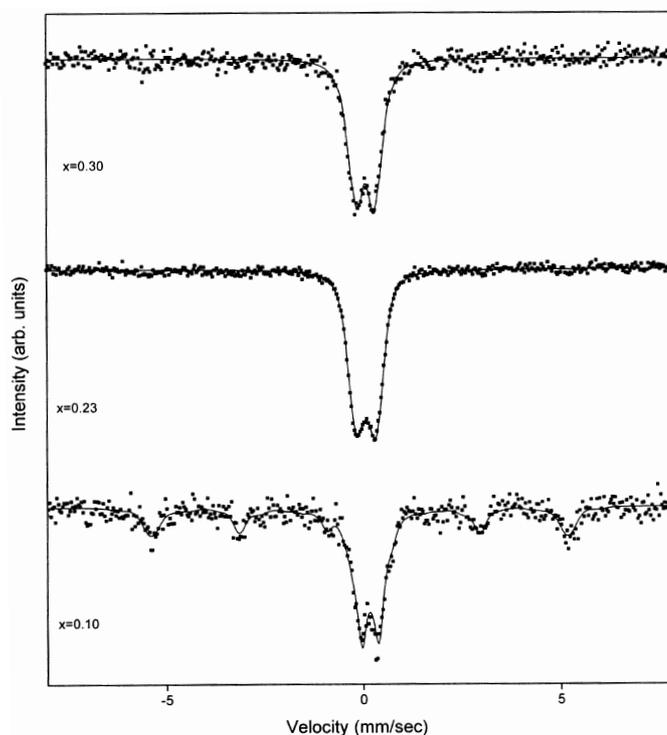
Figure 5. Room temperature Mössbauer spectra of the alloys in the non-magnetic fcc phase region. Solid lines are fits to data using the Le Caër and Dubois program assuming a hyperfine quadrupole distribution.

Fe, whereas the grain size of bcc phase decreases from 9 nm to about 3 nm in the region $0.23 \leq x \leq 0.50$ and increases again thereafter. Our observation of reaching a small grain size of 3 nm for the bcc phase when the alloying and formation of fcc phase starts, finds support in the thermodynamic model put forth by Yavari *et al* [6] who have estimated that a critical grain size of about 2 nm is needed for the bcc Fe to dissolve in the fcc phase.

3.2 *Mössbauer spectroscopy*

Figures 5 and 6 show the room temperature Mössbauer spectra as a function of Fe concentration. For $x \leq 0.3$, the spectra consist of quadrupole doublets, and these spectra were fitted to quadrupole distributions as described in §2. In accordance with the X-ray data, the $x = 0.1$ sample also shows a magnetic phase with a field less than that for Fe. As discussed earlier the grain size of the bcc phase at this composition is 9 nm and hence the solubility in the fcc phase is low. The $x = 0.31$ alloy shows a broadened line with no quadrupole splitting. This can be ascribed to a low hyperfine magnetic field splitting and suggests that there is an onset of a
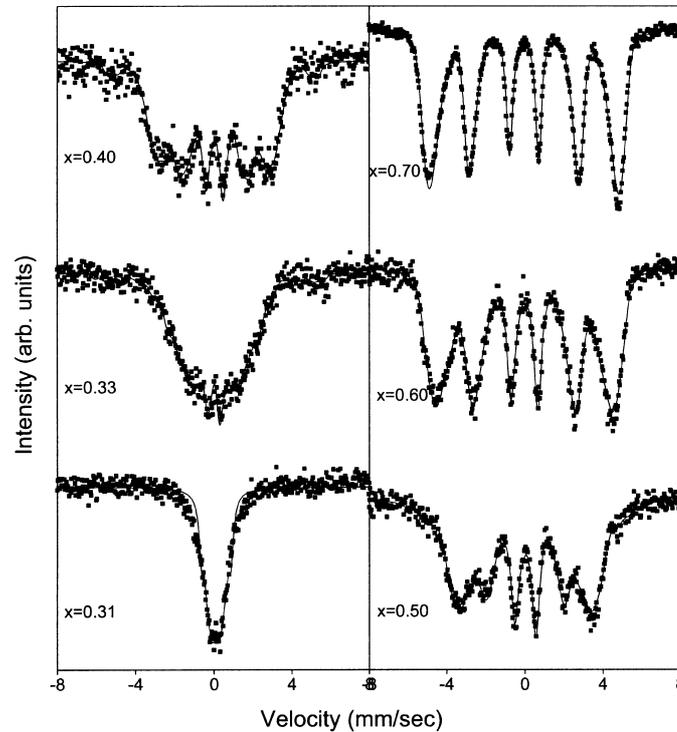
Figure 6. Room temperature Mössbauer spectra of alloys in the magnetic phase region. Solid lines are fits to data using the Le Caër and Dubois program assuming a hyperfine magnetic field distribution.

magnetically ordered state at this composition. Magnetic measurements would be undertaken to find the magnetic moment and magnetic transition temperature of this alloy. For $x \geq 0.33$ alloys there is a hyperfine magnetic field splitting with a broad distribution. The field distributions are shown in figure 7. One can clearly observe from these distributions that in the predominantly fcc phase region the field distribution is centered at low values of magnetic hyperfine fields (10 T to 20 T) whereas for the bcc phase alloy ($x = 0.7$) the field distribution is centered at a higher field value of 30 T. This suggests that the magnetic moment is the highest for the $x = 0.5$ alloy in the fcc phases. In the Cu–Fe system also, magnetization measurement shows the maximum magnetic moment of 1.04 Bohr magnetons at the equiatomic composition for the fcc alloy [5]. Magnetic measurements have been done to confirm this behaviour.

The occurrence of magnetic fcc phase at an electron-to-atom ratio of about 1.5 may have its origin in the Hume–Rothery rules which predict a transformation from fcc to bcc phase at an e/a ratio of 1.5 to accommodate additional electrons in the Brillouin zone of the bcc lattice. We believe that the phase change from non-magnetic to magnetic phase also serves to lower the electronic energies and this lowering of electronic energy leads to the phase transformation.
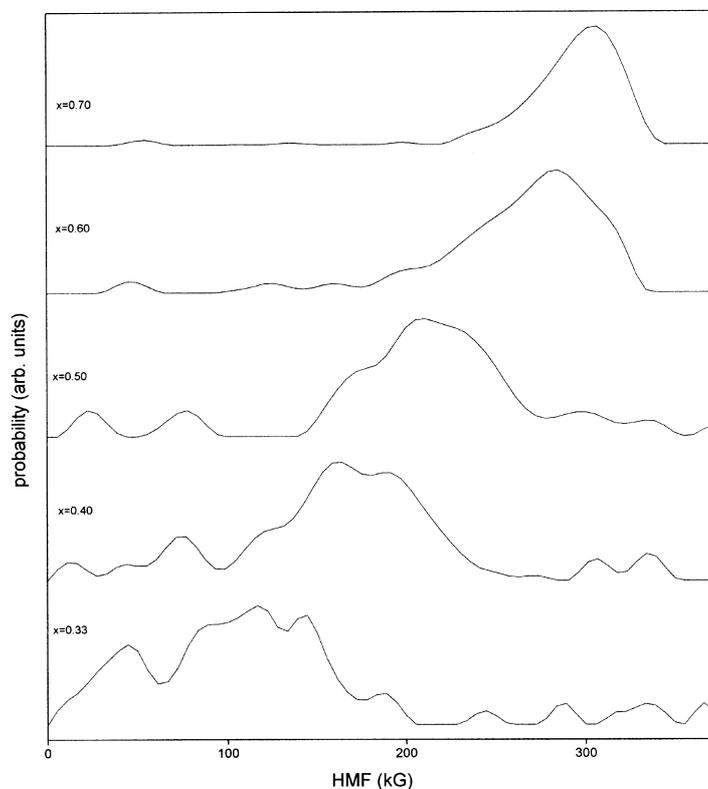
Figure 7. Hyperfine magnetic field distributions evaluated from the Mössbauer spectra of figure 6. We attribute the peaks in the low-field region (5–20 T) to the fcc phase and peaks in the 30 T region to the bcc Fe-rich phase.

4. Conclusions

The effect of Fe addition in the electron phase Cu–Zn alloy system was studied in detail by X-ray diffraction and Mössbauer spectroscopy and a distinct transformation from the non-magnetic to magnetic phase in the fcc crystalline structure region was observed at 31 atomic per cent Fe composition at an electron-to-atom ratio of 1.5. There was also a structural transformation to bcc structure at a higher Fe concentration of 70 atomic per cent.

Acknowledgements

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