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A Mössbauer spectroscopy study of electrodeposited $(Co_xNi_{1-x})_{1-y}Fe_y$ alloys with $0 \leqslant x \leqslant 1$ and $y \leqslant 0.01$

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Abstract. Specimens of $(Co_xNi_{1-x})_{1-y}Fe_y$ with $0 \leqslant x \leqslant 1$ and $y \leqslant 0.01$ obtained by electrochemical deposition were tested by x-ray diffraction and Mössbauer spectroscopy. The structural transformation from the face-centred cubic to the hexagonal close-packed structure has been observed in the range $0.685 < x < 0.795$. The dependence of the hyperfine interaction parameters on the changes in atom number in the nearest-neighbour (NN) shell of the ^{57}Fe nuclear probe has been determined. Changes in the preferred direction of domain magnetization with the increase in the number of Co atoms in the NN shell have also been observed.

1. Introduction

The magnetic properties of the transition metals Fe, Co and Ni and their alloys have been studied for many years. Fe, Co and Ni constitute solid solutions over the entire concentration range (0–100%).

Our earlier studies concerned hyperfine interactions in electrodeposited Fe–Ni and Fe–Co alloys [1, 2]. They suggest that there is no long-range order in electrodeposited alloys. Electrolysis is a good method for obtaining the disordered alloys; however, thermal methods often require complicated treatment, e.g. annealing, cooling or freezing.

In this work we deal with electrodeposited Co–Ni alloys doped with ^{57}Fe (iron content not exceeding 1 at.%). The purpose of the research described below was to determine the crystalline structure and to evaluate how the changes in the average number of Co atoms in the nearest-neighbour (NN) shell of ^{57}Fe influence the hyperfine interaction parameters, i.e. the hyperfine magnetic field (HMF), isomer shift (IS) and quadrupole splitting (QS).

2. Experimental details

Specimens of $(Co_xNi_{1-x})_{1-y}Fe_y$ alloys were prepared by electrodeposition onto graphite. The electrolyte consisted of $CoCl_2.6H_2O$ (0.25 N), $NiCl_2.6H_2O$ (0.25 N) and H_2O. In order to obtain specimens with various compositions, suitable amounts of $CoCl_2.6H_2O$ and $NiCl_2.6H_2O$ solutions were mixed. During electrolysis, 12 ml of the 0.002 N $^{57}FeCl_2$ solution were added to the bath in order to obtain Co–Ni alloys with a ^{57}Fe admixture.

The specimens were deposited at room temperature and at a constant cathode potential $U = -2.5$ V. The concentration of hydrogen ions in the electrolyte was kept constant at

pH 1.6. The current density was between 11.5 and 20.6 mA cm^{-2}; the time of deposition was between 2 and 2.5 h.

The thickness of the deposited films was determined on the basis of the mass, the area of the specimens and the average density of the alloy. The average thickness of the obtained layers was between 4.0 and 15.3 μm.

X-ray diffraction studies were performed using an x-ray diffractometer and the Bragg–Brentano method.

Mössbauer measurements were carried out at room temperature using a standard constant-acceleration spectrometer. The source was ^{57}Co(Cr) of 20 mCi activity.

The alloy composition was determined using the x-ray energy analysis system TESLA NL 2001A and the numerical program EXQAN1. The accuracy of the determination of the composition was about 2–3% of the element content in the alloy. The correlation between the alloy composition and the relative Co and Ni concentrations in the electrolyte is shown in figure 1. The curves presented may serve as calibration curves which allow us to obtain specimens with the required composition.

3. Results and discussion

Nickel and cobalt constitute a solid solution over the whole concentration range. In this experiment, alloys with Co concentrations between 0.0 and 68.5 at.% were face-centred cubic (FCC) and between 83.8 and 100 at.% were hexagonal close packed (HCP). Alloys with 68.5–79.5 at.% Co consist of a mixture of cubic and hexagonal structures. These results are in agreement with [3].

The lattice constants were calculated for the Co concentration range 0–80 at.% on the basis of the x-ray diffractograms (figure 2). It should be noted that the lattice parameter of Co–Ni: ^{57}Fe alloys does not change, within the limits of experimental error, with Co concentration.
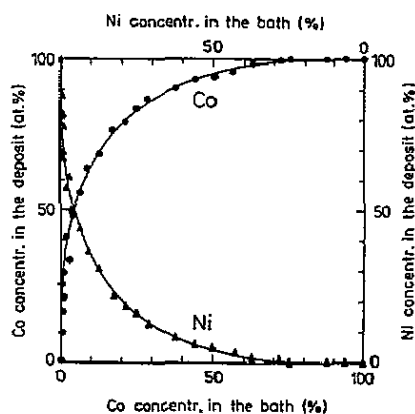
Figure 1. Relation between the composition of the alloy and the initial composition of the electrolyte.
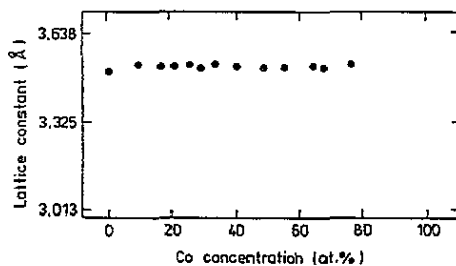
Figure 2. Lattice parameter of $(Co_xNi_{1-x})_{1-y}Fe_y$ alloys as a function of the Co concentration for $x < 0.8$. The uncertainty is contained within the circle.

As a result of the Mössbauer measurements, magnetically split patterns with six lines were obtained. Figure 3(a) shows the typical Mössbauer spectra for various Co concentrations. Asymmetry in the intensities of lines 2 and 5 is observed for some spectra.

The experimental spectra are the superposition of the sextets corresponding to the various configurations of atoms around ^{57}Fe. For each sextet the intensities of lines 2 and 5 are equal. Because the IS depends on the hyperfine magnetic field, then as a result of the superposition of the sextets with various ISs the observed asymmetry is obtained in the final spectrum.
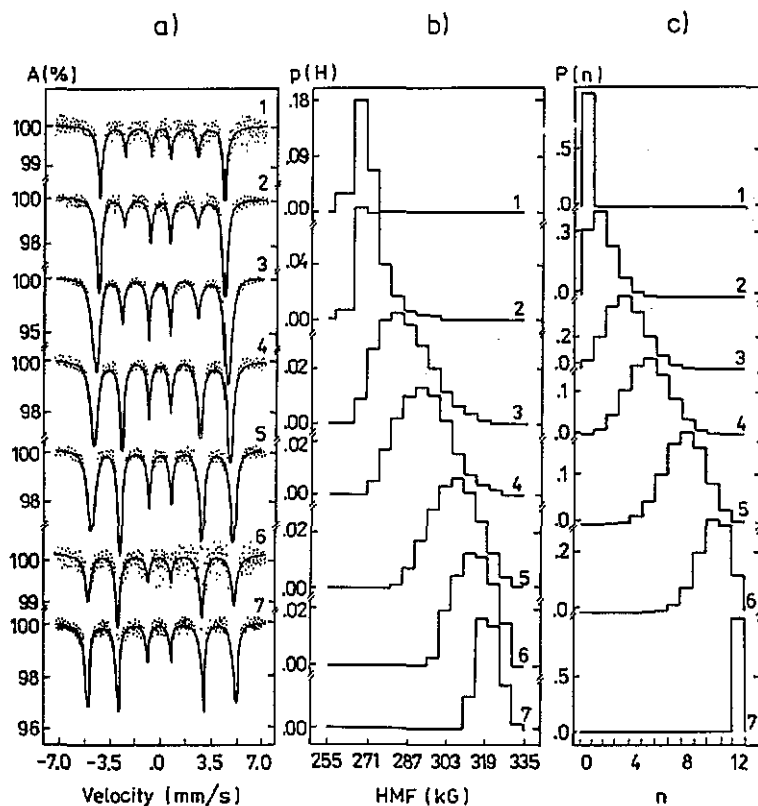

Figure 3. (a) Room-temperature Mössbauer spectra, (b) HMF distributions and (c) binomial distributions for the alloys with $x = 0$ (curves 1), $x = 0.098$ (curves 2), $x = 0.259$ (curves 3), $x = 0.406$ (curves 4), $x = 0.649$ (curves 5), $x = 0.838$ (curves 6) and $x = 1$ (curves 7). A (%) is the absorption; $p(H)$ is the unnormalized distribution and $P(n)$ is the normalized distribution, both in arbitrary units.

The continuous hyperfine field distributions $p(H)$ obtained by the Hesse–Rübartsch [4] method are presented in figure 3(b), for corresponding alloys. The hyperfine interaction parameters HMF, IS and QS were obtained from fitting the experimental spectra.

It was assumed that the Co and Ni atoms are distributed randomly at the lattice sites around the nuclear ^{57}Fe probes. On the basis of this assumption the atom arrangement is well described by the binomial distribution

$$P(n) = [12!/n!(12-n)!]x^n(1-x)^{12-n} \qquad (1)$$

where $P(n)$ is the probability for determining a ^{57}Fe nucleus which has n Co atoms in the NN shell and x is the Co concentration. The number 12 is the number of NNs of ^{57}Fe probe for both FCC and HCP structures.

The probability distributions $p(n)$ of occupation of the lattice sites by n Co atoms are shown in figure 3(*c*) for given Co concentrations. For these distributions the average numbers $\bar{n}$ of Co atoms in the NN shell of ^{57}Fe were calculated for the corresponding Co concentrations. Further results of the Mössbauer measurements for the alloys discussed are presented as a function of $\bar{n}$.

Figure 4 shows the average HMF as a function of $\bar{n}$. The HMF($\bar{n}$)-dependence is linear; no discontinuities have been observed during the phase transformation from FCC to HCP. This may be connected with the fact that there are 12 Co or Ni atoms as NNs of ^{57}Fe in both FCC and HCP structures.

Because the average distances d between the NNs in pure Ni and pure Co are almost the same ($d_{Ni} = 2.49$ Å and $d_{Co} = 2.50$ Å) and, as was found earlier, the lattice parameters of Co–Ni: ^{57}Fe alloys do not change with Co concentration, the changes in the hyperfine field originate from the changes in the number of Co atoms in the NN shell. The straight-line slope factor from figure 4 is a measure of these changes and its value is $d\bar{H}/d\bar{n} = 4.202 \pm 0.019$ kG/atom. This means that, when one Ni atom is replaced by one Co atom in the NN shell of ^{57}Fe with 12 Ni neighbours, the hyperfine field increases by about 4.202 kG. A similar linear dependence of the hyperfine field on the Co concentration was observed in [5] from the NMR measurements.

Additional confirmation of our results may come from the fact that, in Co–Ni alloys, both the spin and the orbital magnetic moments have approximately linear concentration dependences [6].

The IS depends on the electron structure of the ^{57}Fe nucleus and its environment. Figure 5 shows the IS as a function of the average number of Co atoms in the NN shell of a nuclear probe. This dependence is approximated by a linear function in the Co concentration range 0–80 at.%. The slope factor is $d(IS)/d\bar{n} = 0.001\,85 \pm 0.000\,04$ mm s^{-1}/atom. In the HCP region the IS is approximately constant and its value is about 0.165 mm s^{-1}.
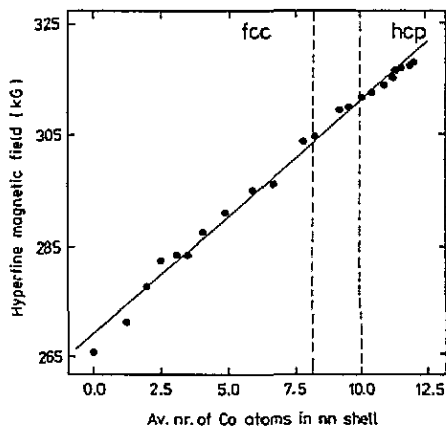

Figure 4. The average HMF as a function of the $\bar{n}$: ———, least-squares fit. The uncertainty in the HMF is contained within the circle.
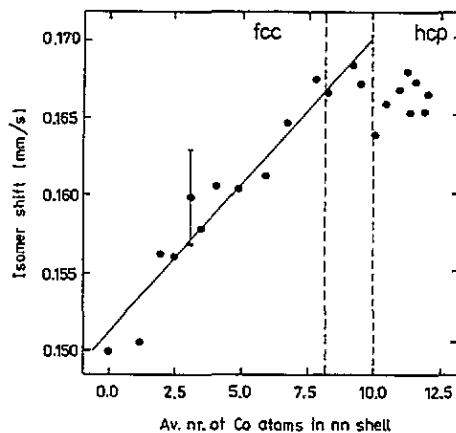
Figure 5. The average IS of ^{57}Fe as a function of the $\bar{n}$. The uncertainty in the IS is indicated by the vertical bar and it is nearly the same for all data.

For $x < 0.8$ a linear dependence between HMF and IS is also observed (figure 6). The slope factor is equal to 2313.2 ± 38.5 kG mm s^{-1}.

The QS is defined by the equation [7]

$$QS = \Delta_{12} - \Delta_{56} = -\tfrac{1}{2}e^2 q Q(3\cos^2\theta - 1) \tag{2}$$

where Δ_{ij} is the separation between the ith and jth lines, Q is the nuclear quadrupole moment and θ is the angle between the V_{zz} direction and the direction of HMF. The experimentally obtained QS is zero for FCC alloys within the limits of error. For HCP alloys, QS does not depend upon concentration and QS > 0.

The standard deviation or the dispersion was calculated for both distributions: σ_{exp} for p(H) and σ_{th} for $P(n)$. Figure 7(a) presents the dispersion $\sigma_{th} = (\langle n^2 \rangle - \langle n \rangle^2)^{1/2}$ obtained from the binomial distribution $P(n)$ and multiplied by $d\bar{H}/d\bar{n} = 4.202$ kG/atom in order to compare it with the experimental dispersion $\sigma_{exp} = (\langle H^2 \rangle - \langle H \rangle^2)^{1/2}$ (figure 7(b)). The measured dispersions for pure Ni and pure Co are not zero; this is connected with the fact that electrodeposited alloys contain some defects and grain boundaries exist in the polycrystalline specimens.
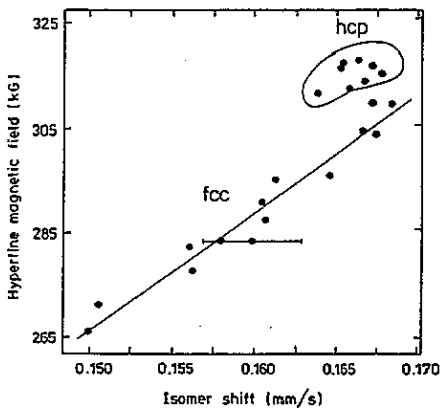

Figure 6. The average HMF as a function of the average IS at room temperature. The uncertainty in the HMF is contained within the circle and the uncertainty in the IS (indicated by horizontal bar) is nearly the same for all data.
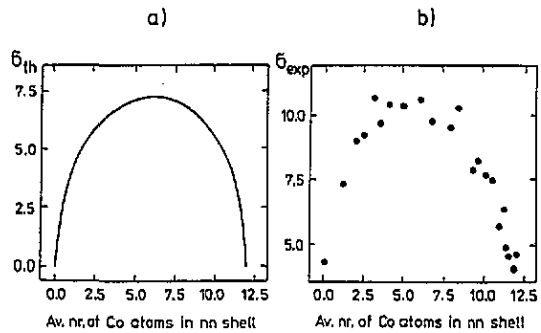
Figure 7. (a) The theoretical dispersion σ_{th} and (b) the experimental dispersion σ_{exp} as functions of $\bar{n}$.

The correlation between σ_{exp} and σ_{th} was approximated also by a linear function (figure 8). We can write that $\sigma_{exp} = \sigma_0 + \alpha\sigma_{th}$, where $\sigma_0 = 3.196 \pm 0.464$ and $\alpha = 0.95 \pm 0.02$.

This correlation is an additional argument for the correctness of the assumption that the HMF depends only on the changes in the average number of Co atoms in the NN shell of the Mössbauer nucleus ^{57}Fe.

The average angle θ between the hyperfine field direction and the direction of the absorbed γ-rays may be calculated on the basis of the intensity ratio of the sextet lines [7]:

$$D_{16}/D_{25} = 3(1 + \cos^2\theta)/(4\sin^2\theta) \tag{3}$$

$$D_{25}/D_{34} = (4\sin^2\theta)/(1 + \cos^2\theta) \tag{4}$$

where D_{16}, D_{25} and D_{34} are the intensities of lines 1 and 6, lines 2 and 5, and lines 3 and 4, respectively, in the sextet. The average angle $\varphi = 90° - \theta$ between the domain magnetization direction and the plane of the specimen was calculated for a given angle θ. The magnetization vector has no fixed direction but it changes its orientation. Figure 9 shows the change in the angle φ as a function of the average number of Co atoms in the NN shell. In Ni-rich alloys there is a preferential out-of-plane anisotropy whereas, for Co-rich alloys, an in-plane magnetization seems to be favoured.
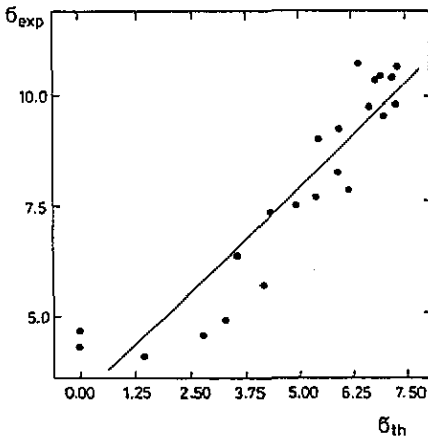
Figure 8. The correlation between $\sigma_{exp} = (\langle H^2 \rangle - \langle H \rangle^2)^{1/2}$ and $\sigma_{th} = (\langle n^2 \rangle - \langle n \rangle^2)^{1/2}$.
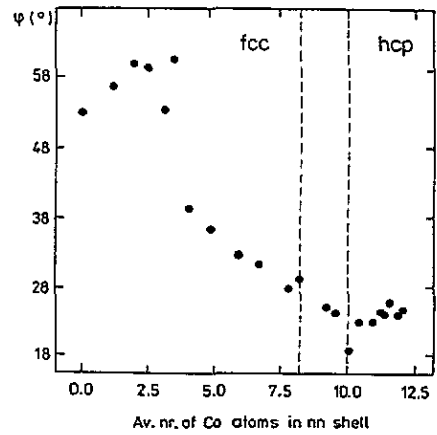
Figure 9. The change in the angle φ between the domain magnetization vector and the plane of the specimen with increase in $\bar{n}$. The uncertainty is contained within the circle.

4. Conclusions

The main conclusions regarding the results of Mössbauer measurements are as follows.

(i) The HMF in electrodeposited Co–Ni: ^{57}Fe alloys depends only on the number of Co or Ni atoms in the NN shell of ^{57}Fe. The one Co atom that substitutes for the Ni atom in the NN shell causes an increase in the HMF of about 4.202 kG.

(ii) Linear IS($\bar{n}$)- and HMF(IS)- dependences were observed for $x < 0.8$. In the hexagonal structure, linearity was not observed. In this region the IS is approximately constant and its value is about 0.165 mm s^{-1}.

(iii) The QS is approximately constant in the regions of FCC and HCP structures.

(iv) The average angle φ between the domain magnetization direction and the plane of the specimen decreases from about 58° to 23° when the average number of Co atoms in the NN shell of ^{57}Fe increases to ten atoms. In the region of the hexagonal structure the angle φ is almost constant.

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