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Evolution of hyperfine parameters in Co-doped FINEMET

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The influence of Co addition on the microstructure and hyperfine parameters of $(Fe_{1-x}Co_x)_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloys was studied by the ^{57}Fe Mössbauer spectrometry. In amorphous ribbons fabricated by melt-spinning technique, the mean hyperfine field and isomer shift changed systematically with cobalt content. In annealed, nanocrystalline samples, the DO_3-type structure of Fe(Co)-Si grains evolves into a *bcc* (Fe,Co)Si substitutional solid solution when increasing x. Simultaneously, the amorphous matrix is depleted in iron and cobalt. The observed increase in the mean hyperfine field is attributed to the enrichment of nanocrystallites in magnetic elements as well as the segregation of iron.

Key words: *nanocrystalline alloys; Co-doped FINEMET; Mössbauer spectroscopy; hyperfine interactions*

1. Introduction

Two-phase Fe-Cu-Nb-Si-B alloys, known as FINEMET [1], exhibit excellent soft magnetic properties attributed to the presence of Fe-Si nanocrystallites, magnetically coupled via the amorphous matrix [2]. The addition of other metals (e.g., Cr, Al, Co) modifies the magnetic properties of these materials [3–7]. The aim of this work is to analyse the influence of Co admixtures on FINEMET microstructure and hyperfine parameters, investigated with the transmission Mössbauer spectrometry based on ^{57}Fe. Systematic alterations of the composition are particularly important in considering the complex evolution of magnetic characteristics.

2. Experimental

Samples of thin amorphous ribbons with compositions $(Fe_{1-x}Co_x)_{73.5}Cu_1Nb_3Si_{13.5}B_9$ ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 0.9) were prepared by the melt-spinning technique. Nanocrys-

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talline specimens were obtained after heat treatment in a vacuum furnace at 570 °C for 1 hour. Room temperature ^{57}Fe Mössbauer measurements were performed using a transmission spectrometer with a ^{57}Co(Rh) source of gamma radiation. The drive system was working in a constant acceleration mode and the velocity scale was divided into 256 channels.

3. Results and discussion

Mössbauer spectra of the as-quenched alloys were fitted using a histogram-like hyperfine field (HF) distribution, linearly correlated with the isomer shift (IS) distribution. Several local peaks or bulges can be distinguished in the hyperfine field distribution (at about 10 T, 20 T, and 24 T), reflecting the preferential environments of iron atoms. As a general tendency, increasing mean values of HF with Co increasing concentration are observed in the range $x \leq 0.5$, although for higher Co contents the average HF slowly decreases. Simultaneously, a monotonic growth of the mean isomer shift is noticed (Table 1), indicating a decreasing charge density on iron nuclei.

Table 1. Mean value of hyperfine field and isomer shift (with respect to α-Fe foil) for the as-quenched, amorphous $(Fe_{1-x}Co_x)_{73.5}Cu_1Nb_3Si_{13.5}B_9$ samples as function of cobalt content

x(Co)	0	0.1	0.2	0.3	0.4	0.5	0.7	0.9
<B> [T]	21.29	21.85	21.85	22.26	22.33	22.79	22.56	22.42
<IS> [mm/s]	0.103	0.114	0.117	0.123	0.139	0.146	0.153	0.156

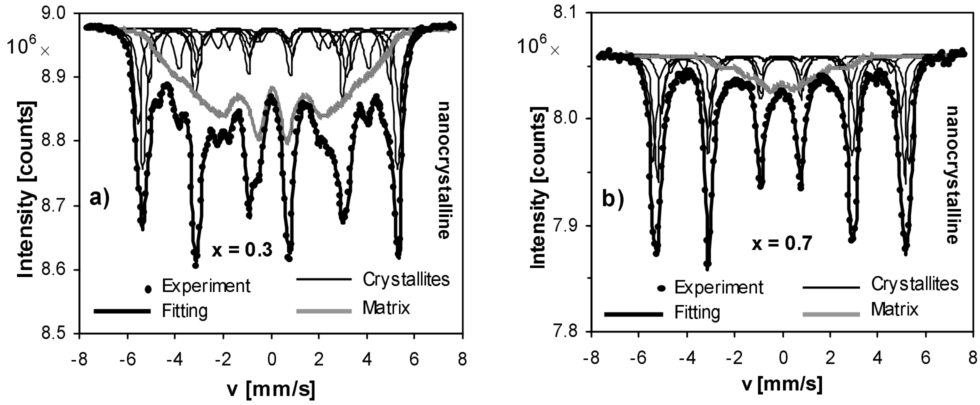

Fig. 1. Mössbauer spectra for annealed, nanocrystalline $(Fe_{1-x}Co_x)_{73.5}Cu_1Nb_3Si_{13.5}B_9$ samples with a) $x = 0.3$ and b) $x = 0.7$

The spectra with complex shapes, collected for nanocrystalline samples (Fig. 1), were fitted with a set of several (up to six) sharp Zeeman sextets attributed to the nanocrystalline phase, and with a broad HF distribution originating from the amorphous matrix. The relative intensities of the sextets and their hyperfine parameters give information about the structure of the grains. The compositional evolution of the above-mentioned values (Fig. 2) points to a significant contribution of Co atoms to the crystalline phase. Additionally, a new component with the highest hyperfine field (above 33 T) appears in the spectra for $x \geq 0.2$, attributed to iron atoms that have a few Co atoms as near neighbours. For $x \leq 0.3$, we observed a significant intensity of the A4 sextet (with the lowest HF value being about 19.3 T), characteristic of the DO_3 structure (Fig. 2a). It is known that in pure FINEMET the crystallites comprise a DO_3 -type Fe-Si alloy. Assuming that cobalt atoms substitute iron in the crystalline lattice, we can evaluate the silicon percentage inside grains, which is equal to about 16–20%. For higher Co contents, the A4 sextet decreases and eventually disappears. Collaterally, sextets with hyperfine fields above 30 T grow up to 90% of the discrete component. Such proportions between the intensities of individual sextets can give evidence of a *bcc* (Fe,Co)Si substitutional solid solution with about 5% of silicon.

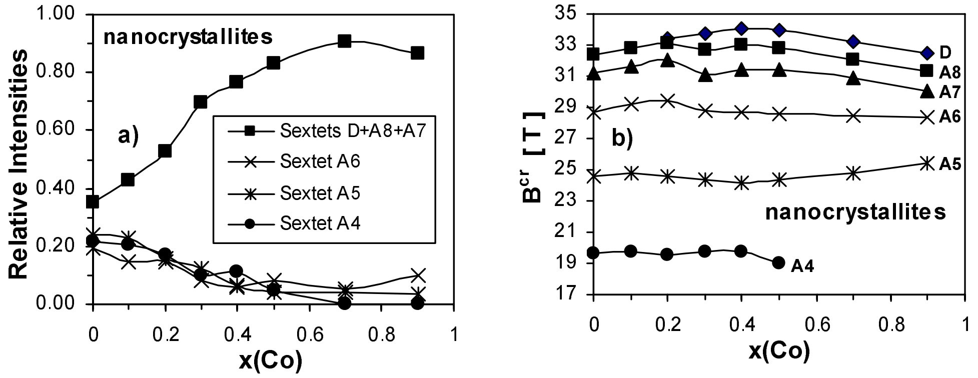

Fig. 2. Relative intensities of the sextets (a) and their hyperfine fields (b) for nanocrystallites in annealed $(Fe_{1-x}Co_x)_{73.5}Cu_1Nb_3Si_{13.5}B_9$ samples as a function of cobalt content x

The relative content of iron atoms belonging to the crystalline phase, p, has been derived from the relation between the intensities of the discrete and continuous components. It decreases from 72% for $x = 0$ to 51% for $x = 0.3$, and then increases up to 86%. In the range $x > 0.7$, p has a nearly constant value. Taking into account the similar heat treatment of all samples, these results point to some differences in the crystallization procedure in the ranges $0 < x < 0.3$ and $0.4 < x < 1$. The real volumetric fraction of the crystalline phase has been evaluated, considering that the concentrations of iron atoms in nanocrystallites and in the amorphous matrix are different due to the different contents of metalloids. For simplicity, we assume similar proportions between iron and cobalt concentrations in the nanocrystalline and amorphous phase. Evaluations (based on the method described, e.g., in [8]) show that the volumetric fraction of nanocrystallites does not differ significantly for minimal and maximal Co contents, being however clearly lower for intermediate values of x (Fig. 3a). The percentage of iron inside the amorphous matrix diminishes considerably with increasing x. Therefore, the distribution of iron atoms becomes more inhomogeneous.

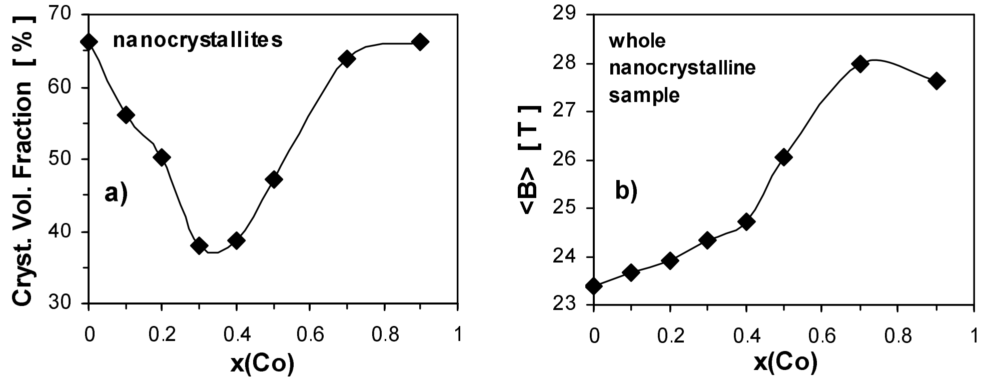

Fig. 3. The volumetric fraction of the nanocrystalline phase (a) and mean hyperfine field (b) in annealed $(Fe_{1-x}Co_x)_{73.5}Cu_1Nb_3Si_{13.5}B_9$ samples as a function of cobalt content x

The mean hyperfine field in general increases with Co concentration, except for the highest Co contents (Fig. 3b). The effect is caused by an increasing hyperfine field in crystallites, owing to larger (Fe + Co) concentration. This is accompanied by a depletion of iron in the amorphous matrix, resulting in a distinct drop of its mean hyperfine field, observed for $x > 0.4$. Simultaneous segregation of iron atoms inside grains causes the observed mean values of the magnetic hyperfine field not to reflect areas without iron or with very small iron concentration. Thus, the mean hyperfine field calculated for a whole sample is overestimated. This is probably the main reason that the compositional evolution of the mean hyperfine field is not well correlated with changes in magnetization (derived from magnetic measurements).

4. Conclusions

A non-monotonic dependence of the mean hyperfine field of as-quenched alloys on cobalt concentration was detected. In the case of annealed ribbons, the structural evolution of the crystalline phase was found accompanied with the substitution of iron by cobalt. Moreover, a growing chemical inhomogeneity was observed, manifesting itself by a depletion of iron in the amorphous matrix and, consequently, the alteration of the hyperfine parameters.

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