Hyperfine Interactions and Crystallization Kinetics of Co-Substituted NANOPERM-Type Alloys

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Abstract. Evolution of structural changes after (as well as during) heat treatment and their consequence upon hyperfine interactions is discussed for (Fe¹⁻ₓCoₓ)₇₉Mo₈Cu₁B₁₂ and (Fe¹⁻ₓCoₓ)₇₆Mo₈Cu₁B₁₅ (0 ≤ x ≤ 0.75) alloys which eventually exhibit nanocrystalline arrangement. Along with Mössbauer spectrometry, results obtained from AFM, and MFM are reported. The kinetics of crystallization is characterized by in-situ diffraction of synchrotron radiation. Substitution of Fe by Co has a remarkable effect on the average hyperfine field and average isomer shift values in the as-quenched alloys. This indicates structural modifications which lead to increase of Curie temperature with higher Co contents. In nanocrystalline state, presence of bcc FeCo crystalline phase is identified. The progress of crystallization is shown to depend upon the annealing conditions as well as on the Co contents. Differences in the onset of crystallization on both sides of the ribbon-shaped samples are revealed. They correlate with the degree of quenched-in surface crystallization.

1. Introduction

NANOPERM nanocrystalline alloys attract a lot of attention mainly due to their excellent soft magnetic properties provided by the interplay between the reduced dimensionality of the nanograins and the large fraction of grain boundaries [1]. Even though still some fundamental properties are not well understood presently these materials find increasing industrial applications [2]. Partial substitution of Fe by Co in NANOPERM alloys has introduced a new class of these materials, the so-called HITPERM alloys [3].

Investigations of Co-substituted NANOPERM-type alloys can be effectively performed namely by the help of Mössbauer spectrometry. In nanocrystalline (Fe₁⁻ₓCoₓ)₉₀Zr₇B₆Cu₁ (0<x<0.6) alloys, Co was reported to be preferentially partitioned to the residual amorphous phase, and the bcc grains were accordingly enriched by Fe [4]. In the heat-treated amorphous Fe₄₂.₇Co₄₂.₇Zr₆₆.₄₆N₅B₈.₆₆Cu₁ (x = 0; 1) alloy an ordered nanocrystalline α'-FeCo phase was identified by the help of Mössbauer spectroscopy [5]. It has developed after 10 min annealing at 723 K. Neither of these works provides details on the fitting used to reconstruct the spectral contribution namely of the crystalline component.

While original HITPERM alloys contain Zr as one of its constitution elements, investigation of other types of materials where Zr is replaced by Hf [6], Nb [7, 8], and/or Mn [9] has recently started. Again, Mössbauer spectrometry was used as a principal method of characterization. In the (Fe₁₋ₓCoₓ)₉₀Hf₅B₆Cu₁ alloy [6], crystalline phase, interface, and residual amorphous matrix were found after nanocrystallization. It was concluded that Co addition increases the hyperfine field. In addition, the Fe concentration in bcc-FeCo crystals and the fraction of crystalline phase influenced by Co...
addition are opposite. The line profile used for reproduction of the crystalline phase is not mentioned. Room and high temperature (474 and 673 K) Mössbauer spectra of annealed Fe$_{78-x}$Co$_x$Nb$_6$B$_{16-y}$Cu$_y$ ($x = 18, 39, 60; y = 0, 1$) alloys were decomposed into their spectral components by the help of up to 4 discrete sextets and one continuous distribution of hyperfine fields [7]. The former represented crystalline phase whereas the latter was ascribed to the amorphous + interface contribution. One continuous distribution of hyperfine fields was eventually decomposed into two separate distributions during the evaluation of room temperature Mössbauer spectra of a nanocrystalline Fe$_{60-x}$Co$_{18}$Mn$_x$Nb$_6$B$_{16}$Cu$_1$ alloy [8]. In both cases, a correlation between magnetic parameters and the nanocrystallization process is discussed. Similar fitting model was applied to the study of kinetics of nanocrystallization and microstructure of the Fe$_{60-x}$Co$_{18}$Mn$_x$Nb$_6$B$_{16}$ alloys ($x = 0, 2, 4$) alloys [9]. Mössbauer spectra of amorphous and heat treated samples show that the effect of Mn addition is clear on the amorphous phase but crystalline sites are not affected.

In our earlier work [10], we have reported on the effect of Mo on the progress of crystallization in the Fe$_{91-x}$Mo$_x$Cu$_1$B$_{12}$ and Fe$_{76-x}$Mo$_x$Cu$_1$B$_{15}$ alloys were substituted with Co ranging from $x = 0$ to $x = 0.75$. They were prepared in a form of 6 mm wide and about 20 µm thick ribbons by planar-flow casting at the Institute of Physics, Slovak Academy of Sciences in Bratislava. Samples with different contents of nanocrystallites were prepared by 30 min annealing of the as-quenched alloys at temperatures covering the first crystallization peak as determined by differential scanning calorimetry.

The acquisition of surface topographic images was carried out by scanning probe microscope NTEGRA Aura in a map topography mode (AFM) as well as magnetic properties mode (MFM). Monochromatic synchrotron radiation of 7 keV ($\lambda = 0.178$ nm) provided in the KMC-2 beamline at BESSY Berlin was used for diffraction experiments. Selected as-quenched ribbons were placed in an evacuated furnace and continuously heated up to 800 °C with a temperature increase of 10 K/min. Diffraction patterns from a 2Θ region covering the main (110) bcc FeCo reflection were recorded in situ every 10 seconds using a 2D multiwire detector. The picture in figure 1 shows the furnace with a beryllium hemispherical dome and an evacuated conical tube attached to the 2D detector.

2. Experimental Details
Two basic compositions of (Fe$_{1-x}$Co$_x$)$_{78}$Mo$_9$Cu$_1$B$_{12}$ and (Fe$_{1-x}$Co$_x$)$_{76}$Mo$_8$Cu$_1$B$_{15}$ alloys were substituted with Co ranging from $x = 0$ to $x = 0.75$. They were prepared in a form of 6 mm wide and about 20 µm thick ribbons by planar-flow casting at the Institute of Physics, Slovak Academy of Sciences in Bratislava. Samples with different contents of nanocrystallites were prepared by 30 min annealing of the as-quenched alloys at temperatures covering the first crystallization peak as determined by differential scanning calorimetry.

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![Figure 1. Evacuated furnace with hemispherical Be-dome.](image)
Mössbauer effect experiments were carried out in transmission geometry at room temperature using a $^{57}$Co/Rh source mounted on a constant acceleration driving system. The spectra are plotted with velocity scales calibrated by a 12.5 μm thick α-Fe foil at room temperature. Evaluation of Mössbauer spectra was accomplished with the Confit [11] fitting program using up to 5 discrete sextets to reconstruct the crystalline phase and continuous distribution of hyperfine fields to describe the amorphous residual and interface phase [7, 12].

With respect to the different surfaces of the ribbons we will use the following convention. The side of the ribbon, which was in direct contact with the quenching wheel, will be referred to as the wheel-side. The opposite side of the ribbon, i.e. the one which was exposed to the surrounding atmosphere, will be denoted as the air-side.

3. Results and Discussion

3.1. As-quenched alloys
Substitution of Fe by Co has a remarkable effect on the shape of Mössbauer spectra of the as-quenched amorphous precursors as demonstrated in figure 2. Depending on the B-contents, the Co-free alloys ($x = 0$) exhibit different magnetic arrangement. While for 12 at% B the corresponding Mössbauer spectrum shows pure paramagnetic doublet, weak magnetic hyperfine interactions can be seen in the 15 at% B alloy. Substitution of Fe by Co leads in both alloys to enhanced formation of magnetic regions which is demonstrated by a gradual formation of broadened sextuplet spectra.

![Figure 2](image-url)

**Figure 2.** Room temperature Mössbauer spectra of as-quenched (Fe$_{1-x}$Co$_x$)$_{78}$Mo$_8$Cu$_1$B$_{12}$ (a) and (Fe$_{1-x}$Co$_x$)$_{75}$Mo$_8$Cu$_1$B$_{15}$ (b) alloys.
The Mössbauer spectra in figure 2 are characteristic for amorphous material and they were fitted using distributions of hyperfine magnetic fields $P(B)$ except for the $x = 0, 12$ at% B sample where distribution of quadrupole splitting was used. A progressive increase in magnetic hyperfine interactions is observed with rising Co-substitution, $x$ in both alloys. 3D mappings of $P(B)$ distributions derived from the spectra are illustrated in figure 3. A bi-modal character of $P(B)$ for low $x$ in the 12 at% B alloy suggests presence of regions with low hyperfine fields which progressively vanish as the Co-contents increases. For Co-substitution $x > 0.2$ both alloys depict rather high magnetic fields. A tendency towards magnetic order in both alloys is demonstrated also by appearance of spontaneous formation of magnetic domains. They can be visualised by the help of MFM.

![Figure 3](image3.png)

**Figure 3.** 3D mappings of $P(B)$ distributions derived from room temperature Mössbauer spectra of as-quenched $(\text{Fe}_{1-x}\text{Co}_x)_{79}\text{Mo}_8\text{Cu}_1\text{B}_{12}$ (a) and $(\text{Fe}_{1-x}\text{Co}_x)_{76}\text{Mo}_8\text{Cu}_1\text{B}_{15}$ (b) alloys.

An example of magnetic domain formation in the $(\text{Fe}_{0.5}\text{Co}_{0.5})_{79}\text{Mo}_8\text{Cu}_1\text{B}_{12}$ as-quenched alloy is illustrated in figure 4. Presence of magnetic domains on the wheel and air side can be clearly seen from the MFM images in figure 4b and 4d. They are formed in the amorphous part of the alloy. In addition to the domains, dark spots can be also noticed. They are associated with magnetic moments of nanocrystallites which are present on both surfaces of the ribbon as documented also by the respective AFM images in figure 4a and 4c. It is noteworthy that the surface crystallization is more pronounced on the air side of the ribbon. Nevertheless, the total amount of crystallites is so small that they cannot be recognized by transmission Mössbauer spectroscopy which scans the entire bulk of the samples.

![Figure 4](image4.png)

**Figure 4.** AFM (a, c) and MFM (b, d) images of the as-quenched $(\text{Fe}_{0.5}\text{Co}_{0.5})_{79}\text{Mo}_8\text{Cu}_1\text{B}_{12}$ alloy taken from the wheel side (a, b) and from the air side (c, d) of the ribbon. The size of scanned area is $3 \times 3 \mu m$ and $5 \times 5 \mu m$, respectively.
Quantitative description of Mössbauer spectra is presented in figure 5 where average isomer shift \( \langle IS \rangle \) and average hyperfine fields \( \langle B \rangle \) are depicted as a function of Co-substitution, \( x \). Changes in \( \langle IS \rangle \)- and \( \langle B \rangle \)-values indicate structural modifications which lead toward increase in Curie temperature with higher Co contents. Changes in \( \langle IS \rangle \) are caused primarily by deviations in chemical composition around the Fe resonant atoms while the increase in \( \langle B \rangle \) might be associated, along with the influence of composition, also by topology.

![Figure 5](image.png)

**Figure 5.** Average isomer shift, \( \langle IS \rangle \) (a) and hyperfine field, \( \langle B \rangle \) (b) plotted against the relative Co contents \( x \) in the as-quenched \( (\text{Fe}_{1-x} \text{Co}_x)_{76} \text{Mo}_8 \text{Cu}_1 \text{B}_{15} \) (open symbols) and \( (\text{Fe}_{1-x} \text{Co}_x)_{79} \text{Mo}_8 \text{Cu}_1 \text{B}_{12} \) (solid symbols) alloys.

### 3.2. Nanocrystalline alloys

The progress of crystallization in the studied alloys was followed by Mössbauer spectrometry and diffraction of synchrotron radiation. Mössbauer effect experiments were performed at room temperature upon samples that were first heat treated in a vacuum furnace at certain temperatures for 30 min and then cooled down to room temperature. In this way, different amount of crystalline phase was obtained and its influence on structural changes was investigated. In diffraction experiments, the as-quenched samples were exposed to temperature which was continuously increasing with the ramp of 10 K/min. Diffractograms were collected *in situ* during the temperature change every 10 s.

#### 3.2.1. Mössbauer spectrometry.

Typical examples of some Mössbauer spectra taken from the heat-treated \( (\text{Fe}_{1-x} \text{Co}_x)_{76} \text{Mo}_8 \text{Cu}_1 \text{B}_{15} \) alloys are shown in figure 6 for \( x = 0.33, 0.5, \) and 0.67. They exhibit sharp lines, which belong to bcc-FeCo nanocrystals, that are superimposed upon broadened features assigned to the amorphous rest and interface phase. Crystalline components were fitted by up to five narrow sextets, the relative contributions of which were derived from binomial distribution describing the Co nearest neighbours of Fe resonant atoms in a bcc arrangement. The progress of crystallization (i.e., relative fraction of the crystalline phase) depends upon the annealing conditions as well as upon the Co contents as illustrated in figure 7. With rising Co substitution, the decrease of Fe contents in the amorphous + interface regions is more rapid with respect to the temperature of annealing. A tendency of Fe atoms to leave the amorphous precursor and preferentially partitioned into bcc crystalline grains was reported in [4].

#### 3.2.2. Diffraction of synchrotron radiation.

Kinetics of crystallization process can be effectively followed by in situ diffraction of synchrotron radiation. Diffraction patterns have been obtained by integration of data from the 2D detector over angle \( \chi \). A typical example is illustrated in figure 8a and 8b as 3D mapping and contour plot, respectively, for the wheel side of the \( (\text{Fe}_{1-x} \text{Co}_x)_{76} \text{Mo}_8 \text{Cu}_1 \text{B}_{15} \) sample. The onset of the first and the second crystallization is marked by \( T_{x1} \) and \( T_{x2} \), respectively. Up to about 600 °C \( (T_{x2}) \), a presence of bcc-FeCo crystalline phase is detected.
The principal (110) reflection peak was decomposed into broad and narrow components which are assigned to the amorphous residual matrix and crystalline grains, respectively. Quantitative analysis of the diffraction patterns is presented in figure 9 where the relative crystalline fraction is plotted against the temperature for the wheel and the air side of this investigated alloy. Results from two independent experiments performed upon the air side of two different samples from the same alloy are provided to...
enable an estimation of error margins in the determination of relative crystalline fraction. The onset of crystallization ($T_{x1}$) was determined to be of 371(2) °C and 395(2) °C for the wheel and air side of the ribbon, respectively. The difference of about 20 degrees in the start of crystallization could be assigned also to distinct number of quenched-in surface crystallites as was discussed for the ($Fe_{0.5}Co_{0.5})_{76}Mo_8Cu_1B_{15}$ alloy in the previous section.

![Figure 8](image1.png)

**Figure 8.** 3D diffractograms of the (110) reflection acquired from the wheel side of the ($Fe_{0.5}Co_{0.5})_{76}Mo_8Cu_1B_{15}$ alloy during in situ annealing (a) and corresponding contour plot (b) in which the onset of the first ($T_{x1}$) and the second ($T_{x2}$) crystallization temperature is indicated by the arrows.

![Figure 9](image2.png)

**Figure 9.** The evolution of crystalline fraction in the ($Fe_{0.5}Co_{0.5})_{76}Mo_8Cu_1B_{15}$ alloy during *in situ* heat treatment as derived from the wheel and air side of the ribbon-shaped samples.

![Figure 10](image3.png)

**Figure 10.** Lattice parameter of the ($Fe_{1-x}Co_x)_{76}Mo_8Cu_1B_{15}$ ($x = 0$, 0.25 and 0.5) alloy derived from diffraction of synchrotron radiation during in situ annealing.

In figure 10, lattice parameters, $a$, of a bcc-FeCo phase, which were derived from the diffraction patterns, are plotted against temperature for the wheel side of the ($Fe_{1-x}Co_x)_{76}Mo_8Cu_1B_{15}$ alloy, $x = 0$, 0.25 and 0.5. Higher $a$-values as compared with the one of bcc-Fe phase ($a = 0.2866$ nm) are most probably caused by incorporation of small amounts of Mo into the bcc lattice which has caused an expansion of the latter. This effect is the most pronounced for the Co-free ($x = 0$) alloy. Already small Co substitution tends to expel Mo atoms from the bcc lattice, thus reducing the lattice parameter. The initial decrease in the lattice parameter with temperature is connected with the first stage of crystallization during which the bcc lattice continuously evolves and tends to reach the best possible crystallographic arrangement close to the one observed for pure bcc-Fe. Beyond 600 °C, when the bcc
crystals start to grow into rather big (several µm in size) grains, a sudden increase in the lattice parameter is observed which is associated with the thermally induced lattice expansion.

4. Conclusions

Mössbauer spectrometry proves to be a powerful tool for the investigation of nanocrystalline alloys. It provides close information on structural as well as magnetic arrangement in their amorphous precursors via distributions of respective hyperfine interactions. Adopting a suitable fitting model for the reconstruction of crystalline phase (viz. binomial distribution of relative contributions), further details on the nearest neighbours and their impact on hyperfine magnetic fields can be obtained. In this work, we have not discussed this topic to more details due to limited space. Nevertheless, in order to achieve solid conclusions about structural and magnetic features of nanocrystalline alloys, along with Mössbauer effect studies also the use of complementary techniques of investigation is inevitable. Here, we have demonstrated how AFM and MFM can help in unveiling surface crystallization and magnetic arrangement, respectively. We have also shown how the kinetics of crystallization can be followed by employing in situ recording of diffraction of synchrotron radiation during temperature increase. In our ongoing research we utilize nuclear resonant scattering of synchrotron radiation which combines the sensitivity of nuclear-based techniques with a possibility of very fast data acquisition. In this way it is possible to investigate in situ the evolution of hyperfine interactions which pushes forward the frontiers in the research of nanocrystalline alloys.

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