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Microstructure and Some Magnetic Properties of Nanocrystalline Fe_{73.5-x}Co_{x}Cu_{1}Nb_{3}Si_{13.5}B_{9} Alloys

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PACS.76.80.+y – Mössbauer effect; other γ-ray spectroscopy
PACS.75.50.Kj – Amorphous and nanocrystalline magnetic materials; quasicrystals

Abstract. — The microstructure and magnetic properties, i.e. the initial susceptibility, coercivity and saturation magnetic polarization of nanocrystalline Fe_{73.5-x}Co_{x}Cu_{1}Nb_{3}Si_{13.5}B_{9} (x = 0 or 7) alloys with different volume fractions of crystalline and amorphous phases, are investigated. The crystalline phase in both conventionally annealed alloys (823 K for 1 h) has DO_{3} ordered structure. However, after the accumulative annealing of the samples (823 K for 5 s and then 10 and 60 min) only short range order in the crystalline phase is observed. The replacing of 7% Fe atoms by Co atoms in the Fe_{72.5}Cu_{1}Nb_{3}Si_{13.5}B_{9} alloy leads to the slight enhancement of the magnetic saturation polarization for both as-quenched and nanocrystalline samples. Moreover, the initial susceptibility distinctly increases and disaccommodation as well as coercivity decrease with annealing time for both investigated alloys. This behaviour is attributed to the annealing out of free volumes in the amorphous matrix and the increase of the volume fraction of the crystalline phase. Furthermore, the results reported in this paper indicate that processes occurring in the amorphous matrix are the main source of the magnetic after-effect in these alloys.

1. Introduction

Nanocrystalline Fe-Cu-Nb-Si-B alloys obtained by controlled crystallization of amorphous ribbons consist of a crystalline α-FeSi phase and an amorphous matrix [1–6]. The combined addition of Cu and Nb into Fe-Si-B amorphous alloys allows to obtain a nanostructured material with a mean grain size of the order of 10 nm [1,2,5,6] after annealing the amorphous ribbons at about 823 K for 1 h. The ultrafine grain structure of these alloys leads to the excellent soft magnetic properties which arise from the great reduction in the mean magnetocrystalline anisotropy and very low saturation magnetostriction [6]. The soft magnetic properties (e.g. coercivity, initial susceptibility) of the nanocrystalline alloys are highly influenced by their phase composition which results from annealing conditions [2]. The volume fraction of the amorphous and crystalline phases in these materials can be determined from X-ray diffraction [2] or Mössbauer spectroscopy studies [7]. However, local changes in the structure of these materials may be also detected by investigations of the magnetic after-effect [8] which

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is usually observed as a disaccommodation i.e. temporal decrease of the initial susceptibility after the sample demagnetization. The investigations of the disaccommodation also allow the contribution of the amorphous and crystalline phases to this effect to be found.

The Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloy is a typical example of the nanocrystalline alloys and has a promising application because of its high initial permeability and saturation flux density [1,6,9].

The aim of this paper is to investigate the microstructure, initial magnetic susceptibility, disaccommodation, saturation magnetic polarization and coercivity for the nanocrystalline Fe$_{73.5-x}$Co$_x$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ ($x = 0$ or 7) alloys containing a different quantity of crystalline phases.

2. Experimental Procedure

The amorphous Fe$_{73.5-x}$Co$_x$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ ($x = 0$ or 7) ribbons were obtained by a melt-quenching technique. The width and thickness of the ribbons were 10 mm and 20 μm, respectively.

The microstructures of the samples were examined by Mössbauer spectroscopy and X-ray diffractometry. The Mössbauer spectra were fitted with a superposition of seven components: five sextets for the crystalline phase and two sextets for the amorphous matrix (corresponding to low- and high-field components). From the numerical analysis of these Mössbauer spectra the magnetization distribution, average hyperfine field, content of iron in the crystalline and amorphous phases, their volume fraction and order degree in the crystalline phase were determined. The average hyperfine field was evaluated from the hyperfine field distribution obtained according to the Hesse-Rübertsch method [10].

In order to determine the iron content ($f_{am}$) in the amorphous phase, we assume that during the crystallization of the samples no significant structural changes occur in the amorphous matrix (as compared to the as-quenched state). However, a decrease of iron or iron and cobalt content takes place. The assumption that average hyperfine field is proportional to the iron (or iron and cobalt) content in the amorphous phase [11,12] seems to be a good approximation. Thus, $f_{am}$ for the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloy was calculated from equations:

$$ f_{am} = \frac{73.5\text{at} \% \langle H_{am} \rangle}{\langle H_{am,asq} \rangle} \cdot (1) $$

It is known that the volume fraction of a phase is proportional to the relative area of the Mössbauer spectrum. Taking into account a change of the iron content in the amorphous matrix and equation (1), the volume fraction ($V_{am}$) of the amorphous phase may be estimated from:

$$ V_{am} = \frac{R\langle H_{am,asq} \rangle}{\langle H_{am} \rangle} \cdot (2) $$

where $R$ is the relative area of subspectra corresponding to the amorphous matrix obtained from the Mössbauer spectra analysis, $\langle H_{am,asq} \rangle$ and $\langle H_{am} \rangle$ are the average hyperfine fields obtained for the amorphous as-quenched sample and amorphous matrix, respectively. Using the results obtained for the amorphous matrix it is possible to calculate the volume fraction of the crystalline phase and its composition. The volume fractions of the amorphous and crystalline phases and their compositions in the Fe$_{66.5}$Co$_7$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloy were estimated in a similar way. In these calculations we assumed the same probability of recoil free absorption for the amorphous matrix and crystalline phase.
Taking into account values of hyperfine fields and isomer shift, five sextets corresponding to the crystalline α-FeSi or α-(Fe,Co)Si phases were ascribed to the iron atoms having 8, 7, 6, 5 and 4 iron or iron and cobalt atoms as nearest neighbours. The probabilities \( P_i \) for iron atoms to have \( i \) iron atoms as nearest neighbours were determined from:

\[
P_i = \frac{R_i}{\sum_{i=4}^{8} R_i}
\]

where \( R_i \) are the relative areas of the corresponding sextets. Knowing values of these probabilities one may calculate the average number of Si atoms in the first coordination zone of iron atoms using the formula:

\[
n = 8 - \sum_{i=4}^{8} P_i i.
\]

The short range order parameter \( (\alpha_1) \) was calculated using the formula for binary Fe-Si alloys [13] from the equation:

\[
\alpha_1 = \frac{n - n_0}{n_0}
\]

where \( n_0 \) is the average number of Si atoms in the neighbourhood of Fe atoms arranged randomly on a bcc lattice obtained from a binomial distribution, and \( n \) is calculated from equation (4). The long range order parameter \( (\gamma) \) for the DO₃ structure is defined as:

\[
\gamma = \frac{N}{N_0}
\]

where \( N_0 \) is the total number of Si sites in the DO₃ superstructure, \( N \) is the number of Si atoms occupying Si sites. This parameter \( (\gamma) \) was calculated [13] from the following expression:

\[
P(n, \gamma) = \frac{0.75 - c(1 - \gamma)}{1 - c} \left\{ \frac{1}{3} C_8^n \left[ \frac{c(1-\gamma)}{0.75} \right]^n \times \left[ 1 - \frac{c(1-\gamma)}{0.75} \right]^{8-n} \right. \\
+ \frac{2}{3} \sum_{j=0}^{n} C_4^j \left[ \frac{c\gamma}{0.25} \right]^j \times \left[ 1 - \frac{c\gamma}{0.25} \right]^{4-j} \times C_4^{n-j} \left[ \frac{c(1-\gamma)}{0.75} \right]^{n-j} \times \left[ 1 - \frac{c(1-\gamma)}{0.75} \right]^{4-n+j} \\
+ \frac{0.25 - c\gamma}{1 - c} C_8^n \left[ \frac{c(1-\gamma)}{0.75} \right]^n \times \left[ 1 - \frac{c(1-\gamma)}{0.75} \right]^{8-n} \}
\]

where \( P(n, \gamma) \) are the probabilities for iron atoms to have \( n \) Si atoms as nearest-neighbours, and \( c \) is silicon concentration in the crystalline α-FeSi and α-(FeCo)Si phases.

Using a completely automated set-up, the magnetic susceptibility for toroidal samples of 30 mm inner diameter was measured within the temperature range from 250 up to 650 K. For the same samples the disaccomodation of the initial susceptibility was investigated. Before each measurement the samples were demagnetized by the sinusoidal magnetic field of frequency 120 Hz with exponentially decreasing amplitude from 500 A/m to zero during 1.1 s. The investigations were carried out in an ac magnetizing field of frequency \( f = 2 \) kHz and amplitude \( H = 0.16 \) A/m. The experimental results are presented as isochronal curves which are constructed such that:

\[
\Delta(1/\chi) = 1/\chi_2 - 1/\chi_1
\]

where \( 1/\chi_1 \) and \( 1/\chi_2 \) are reciprocal magnetic susceptibilities at times \( t_1 = 2 \) s and \( t_2 = 120 \) s after demagnetization, respectively. The coercive field was measured by a Förster coercimeter.
Fig. 1. — Temperature dependence of the initial magnetic susceptibility $\chi$ (measured 2 s after demagnetization) for the Fe$^{73.5}$Cu$_{1}$Nb$_{3}$Si$_{13.5}$B$_{9}$ alloy after accumulative annealing at 823 K for: (a) 5 s, (b) 10 min, (c) 60 min.

Fig. 2. — The initial magnetic susceptibility $\chi$ (measured 2 s after demagnetization) versus temperature for the Fe$^{66.5}$Co$_{7}$Cu$_{1}$Nb$_{3}$Si$_{13.5}$B$_{9}$ alloy after accumulative annealing at 823 K for: (a) 5 s, (b) 10 min, (c) 60 min.

for 10 cm long strips. All investigations were performed for the samples annealed at 823 K for 5 s, 10 min and 60 min (accumulative annealing) and for the ribbons treated at 823 K for 1 h (conventional annealing).

The saturation magnetic polarization was measured by a force magnetometer taking samples in the form of ten discs of 3.5 mm diameter cut out from ribbons and arranged along the rolling direction. These measurements were performed in the temperature range from 300 to 770 K for the samples in the as-quenched state and after the last step of the accumulative annealing (at 823 K for 1 h).

Additionally, for the as-quenched samples the saturation magnetostriction was measured by the transverse susceptibility method [14].

3. Results

The initial magnetic susceptibility $\chi$ (measured 2 s after the demagnetization) versus temperature for the Fe$^{73.5}$Cu$_{1}$Nb$_{3}$Si$_{13.5}$B$_{9}$ alloy after the accumulative annealing of the amorphous ribbons at 823 K for 5 s and then 10 min and 60 min is presented in Figure 1. As can be seen from this figure, the initial susceptibility reaches a maximum at temperatures between 450 to 570 K and then rapidly decreases with temperature. Moreover, the maximum value of the initial susceptibility distinctly increases with the annealing time.

Figure 2 shows the corresponding results of the initial susceptibility measurements for the sample of the Fe$^{66.5}$Co$_{7}$Cu$_{1}$Nb$_{3}$Si$_{13.5}$B$_{9}$ alloy after the same heat treatments as the previous one. The initial susceptibility of this sample runs through a maximum at temperatures between 350 and 550 K but $\chi(T)$ curves are quite different from those obtained for the Fe$^{73.5}$Cu$_{1}$Nb$_{3}$Si$_{13.5}$B$_{9}$ sample.
The isochronal disaccommodation curves $\Delta(1/\chi) = f(T)$ obtained from the initial susceptibility $\chi$ measurements at 2 and 120 s after the demagnetization (Eq. (7)) for the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ ribbon after the accumulative heat treatment are shown in Figure 3. The sample annealed at 823 K for 5 s shows a very broad relaxation maximum at about 500 K. Above 570 K the intensity of the disaccommodation rapidly increases. After the subsequent annealing of this sample at 823 K for 10 and 60 min. no relaxation processes are observed between 250 and 500 K except for an almost temperature independent background. Above 550 K the disaccommodation intensity distinctly increases.

Figure 4 shows the isochronal disaccommodation curves (constructed according to Eq. (7)) of the Fe$_{66.5}$Co$_7$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloy after the same treatments as for the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloy. It is seen that the curves $\Delta(1/\chi) = f(T)$ show similar shapes as those obtained for the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloy. However, the very broad maximum in $\Delta(1/\chi) = f(T)$ curve for the former alloy annealed at 823 K for 5 s is shifted towards the higher temperature.

The temperature dependence of the initial susceptibility and the isochronal $\Delta(1/\chi) = f(T)$ curves for the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ and Fe$_{66.5}$Co$_7$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloys annealed for 823 K for 1 h (conventional annealing) are shown in Figures 5 and 6. It is seen that the initial susceptibility for the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloy depends to some degree on temperature up to 500 K. At higher temperatures $\chi$ distinctly decreases. However, the initial susceptibility of the Fe$_{66.5}$Co$_7$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloy decreases slowly in the whole temperature range (from 250 to 650 K). Moreover, the disaccommodation amplitude for both samples increases rapidly above 500 K.

The magnetization curves $\mu_0 M_s = f(T)$ for the Fe$_{73.5-x}$Co$_x$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ ($x = 0$ or 7) alloys in the as-quenched state and after the last step of the accumulative annealing (823 K for 1 h), as an example, are shown in Figure 7. The magnetic saturation polarization $\mu_0 M_s$ decreases monotonically with temperature for both investigated samples. Moreover,
Fig. 5 — The initial magnetic susceptibility $\chi$ (measured 2 s after demagnetization) versus temperature (a) and the isochronal $\Delta(1/\chi) = f(T)$ curve (b) for the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloy after the conventional annealing at 823 K for 1 h.

Fig. 6 — The initial magnetic susceptibility $\chi$ (measured 2 s after demagnetization) versus temperature (a) and the isochronal $\Delta(1/\chi) = f(T)$ curve (b) for the Fe$_{66.5}$Co$_7$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloy after the conventional annealing at 823 K for 1 h.

The saturation polarization slightly increases after replacing 7% Fe atoms by Co atoms in the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloy.

In Figure 8 the Mössbauer spectra for the as-quenched and annealed at 823 K for 1 h (the last step of the accumulative annealing) samples are presented as an example. The results obtained from Mössbauer spectra analysis are shown in Table I. In this table the coercivity for the as-quenched and annealed samples, and saturation magnetostriction for the as-quenched ribbons are also shown.

4. Discussion

Mössbauer spectroscopy and X-ray diffractometry investigations show that the Fe$_{73.5-~z}$Co$_{2}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ ($z = 0$ or 7) alloys are fully amorphous in the as-quenched state. After the replacement of 7% Fe atoms by Co atoms in the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloy, the enhancement of the average hyperfine field at $^{57}$Fe nuclei (Tab. I) is observed. This is in agreement with the results obtained from measurements of magnetization curves (Fig. 7); the addition of Co atoms slightly increases the magnetic saturation polarization by comparison with $\mu_0 M_s$ for the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloy. Similar results were obtained by Guo et al. [15] from Mössbauer studies of amorphous Fe-Co-Si-B alloys. The increase of the saturation magnetization is also observed for crystalline Fe-Co alloys up to about 30% of Co [16].

From the changes of the ratios of the line intensities in the Zeeman sextets ($3$: $<A_{2,5}>$: 1) (Tab. I), it may be concluded that the tendency for the magnetization vector to align in parallel to the ribbon surface increases after annealing the investigated samples at 823 K for 5 s as compared to the as-quenched state. This is connected with the stress-relief of the ribbons during the treatment. However, the intensity of the second line in the Zeeman sextets decreases
after the subsequent heat treatments of these samples at 823 K for 10 and 60 min (Tab. I). This indicates that the accumulative annealing influences the magnetization distribution in the investigated samples [17].

The iron or iron and cobalt contents in both the crystalline and amorphous phases depends on the annealing time (Tab. I). It is known [18,19] that the α-FeSi grains grow from the nuclei which are formed in the iron-rich regions due to the diffusion of Cu, Nb and B atoms from these regions into the surrounding amorphous phase. When the annealing time is short, the diffusion of these atoms may be incomplete. With increasing time of the heat treatment more and more of the Cu, Nb and B atoms diffuse into the amorphous matrix and the iron content in the crystalline phase increases (Tab. I). Moreover, the amorphous phase is enriched with Nb, Cu and B. It is worth noticing that average hyperfine fields of the amorphous matrix are equal to 16.6 and 16.7 T for the Fe_{73.5}Cu_{1}Nb_{3}Si_{13.5}B_{9} and Fe_{66.5}Co_{7}Cu_{1}Nb_{3}Si_{13.5}B_{9} alloys (after accumulative annealing at 823 K for 1 h), respectively. However, the average hyperfine field for the nanocrystalline Fe_{66.5}Co_{7}Cu_{1}Nb_{3}Si_{13.5}B_{9} alloy is higher than for the Fe_{73.5}Cu_{1}Nb_{3}Si_{13.5}B_{9}
Table I. — The effective hyperfine field at $^{57}$Fe nuclei ($B_{\text{eff}}$), intensity of the second line in Zeeman sextets ($A_2$), volume fraction of the amorphous and crystalline phases ($V_{\text{am}}, V_{\text{cr}}$), iron content in the amorphous and crystalline phases ($f_{\text{am}}, f_{\text{cr}}$), iron and cobalt content in the amorphous and crystalline phases ($g_{\text{am}}, g_{\text{cr}}$), short and long range order parameters ($\alpha_1, \gamma$), coercivity ($H_c$) and saturation magnetostriction constant ($\lambda_s$) obtained for the as-quenched and annealed Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$Bg and Fe$_{66.5}$Co$_7$Cu$_1$Nb$_3$Si$_{13.5}$Bg alloys.

<table>
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<th>Treatment</th>
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<th>$A_2$</th>
<th>$V_{\text{am}}$</th>
<th>$V_{\text{cr}}$</th>
<th>$f_{\text{am}}$</th>
<th>$f_{\text{cr}}$</th>
<th>$\alpha_1$</th>
<th>$\gamma$</th>
<th>$\lambda_s \times 10^5$</th>
<th>$H_c$ [A/m]</th>
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<td>-</td>
<td>1.94</td>
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<td>0.17</td>
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<td>2.1</td>
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<tr>
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<td>83</td>
<td>0.75</td>
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From Mössbauer spectra analysis it was found (Tabs. II and III) that the probabilities (equal to relative areas of corresponding sextets) for iron atoms to have 8, 7, 6, 5 or 4 Fe atoms as the nearest neighbours (nn) in the crystalline $\alpha$-FeSi phase (in the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$Bg alloy) are different from those obtained from binomial distribution. It is seen that the probabilities of occurrence of 5 and 4 Fe atoms as nn are larger that those in the random model (binomial distribution) (Tab. II). Furthermore, the probability for iron atoms to have 8 Fe atoms as the nearest neighbours is much lower than it should be for the DO$_3$ structure ([13], Eq. (6)). Thus, we may conclude that in the crystalline $\alpha$-FeSi phase (after accumulative annealing of the sample at 823 K for 5 s, 10 and 60 min) only the short range order occurs (Tabs. I and II). Moreover, one can notice that the $\alpha$-FeSi phase becomes more ordered with the increase of annealing time (Tab. I). Similar effect is observed for the nanocrystalline Fe$_{66.5}$Co$_7$Cu$_1$Nb$_3$Si$_{13.5}$Bg alloy obtained by the accumulative annealing the amorphous ribbons (Tabs. I and III). However, the results obtained from Mössbauer spectra analysis for the conventionally annealed samples of the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$Bg and Fe$_{66.5}$Co$_7$Cu$_1$Nb$_3$Si$_{13.5}$Bg alloys (823 K for 1 h) are similar to those obtained for DO$_3$ structure (Eq. (6) and Tabs. II and III). This indicates that in the crystalline phase of conventionally annealed alloys, the long range order of DO$_3$-type is present (Tab. I).
Table II. — Probabilities ($P_8$, $P_7$, $P_6$, $P_5$, $P_4$) for iron atoms to have 8, 7, 6, 5 or 4 Fe atoms as the nearest neighbors in the crystalline $\alpha$-FeSi phase for the nanocrystalline $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ alloy obtained from Mössbauer spectrum analysis (exp.), from binomial distribution (bin.) and for $\text{DO}_3$ structure ($\text{DO}_3$) (from Eq. (6) for $\gamma = 0.85$, Tab. I).

<table>
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<tr>
<th>Probability</th>
<th>accumulative annealing</th>
<th>conventional annealing</th>
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<tbody>
<tr>
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<td>823 K / 5 s</td>
<td>823 K / 10 min</td>
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<tr>
<td></td>
<td>exp.</td>
<td>bin.</td>
</tr>
<tr>
<td>$P_8$</td>
<td>0.14</td>
<td>0.10</td>
</tr>
<tr>
<td>$P_7$</td>
<td>0.24</td>
<td>0.27</td>
</tr>
<tr>
<td>$P_6$</td>
<td>0.02</td>
<td>0.31</td>
</tr>
<tr>
<td>$P_5$</td>
<td>0.29</td>
<td>0.21</td>
</tr>
<tr>
<td>$P_4$</td>
<td>0.31</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table III. — Probabilities ($P_8$, $P_7$, $P_6$, $P_5$, $P_4$) for iron atoms to have 8, 7, 6, 5 or 4 (Fe + Co) atoms as the nearest neighbors in the crystalline $\alpha$-(Fe,Co)Si phase for the nanocrystalline $\text{Fe}_{66.5}\text{Co}_7\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ alloy obtained from Mössbauer spectrum analysis (exp.), from binomial distribution (bin.) and for $\text{DO}_3$ structure ($\text{DO}_3$) (from Eq. (6) for $\gamma = 0.75$, Tab. I).

<table>
<thead>
<tr>
<th>Probability</th>
<th>accumulative annealing</th>
<th>conventional annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>823 K / 5 s</td>
<td>823 K / 10 min</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>bin.</td>
</tr>
<tr>
<td>$P_8$</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td>$P_7$</td>
<td>0.24</td>
<td>0.32</td>
</tr>
<tr>
<td>$P_6$</td>
<td>0.03</td>
<td>0.30</td>
</tr>
<tr>
<td>$P_5$</td>
<td>0.24</td>
<td>0.16</td>
</tr>
<tr>
<td>$P_4$</td>
<td>0.28</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The microstructure of the nanocrystalline alloys influences their magnetic properties. The initial susceptibility for both investigated alloys increases with annealing time (Figs. 1 and 2) due to the annealing out of some structural defects in the amorphous matrix and the increase of the volume fraction of the fine grains (Tab. I) [6]. The $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ alloy after the last step of the accumulative annealing (823 K for 1 h) exhibits the higher magnetic susceptibility than the $\text{Fe}_{66.5}\text{Co}_7\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ one (Figs. 1 and 2). This behaviour indicates that the different microstructure is formed in these alloys during the annealing. Moreover, Mössbauer spectroscopy investigations show that the tendency for the magnetization vector to align in parallel to the ribbon surface of the $\text{Fe}_{66.5}\text{Co}_7\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ alloy is lower than for the $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ alloy (Tab. I).

It is worth noting that the nanocrystalline $\text{Fe}_{66.5}\text{Co}_7\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ alloy obtained by the conventional annealing (823 K for 1 h) exhibits better soft magnetic properties (higher initial susceptibility and lower coercivity at room temperature) than the $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ one (Figs. 5 and 6).

The magnetic after-effect spectra for the $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ and $\text{Fe}_{66.5}\text{Co}_7\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ samples annealed at 823 K for 5 s (Figs. 3 and 4) are similar to those obtained for Fe-based
amorphous alloys [20, 21]. A very broad relaxation maximum and the rapid increase of the
disaccommodation intensity near the Curie temperature of the amorphous matrix is observed.

Generally, for an analysis of the disaccommodation curves for the amorphous materials
the box distribution function of relaxation times was usually used [20–22]. In this paper, a
Gaussian distribution in ln τ is used [23, 24] which is more likely to describe real processes in
the amorphous materials. A Gaussian distribution function is given by:

\[ \varphi(\ln \tau) = \frac{1}{\sqrt{\pi \beta}} \exp \left[ - \left( \frac{\ln \tau / \tau_m}{\beta} \right)^2 \right] \]  

(8)

where \( \tau_m \) is an average value of relaxation times (τ) which fulfils the Arrhenius law [25] and \( \beta \)
is a distribution parameter. Furthermore, the observed relaxation spectra may be described by
a superposition of individual processes. Under these assumptions [24], an isochronal relaxation
spectrum may be expressed as:

\[ \Delta \left( \frac{1}{\lambda} \right) = \sum_{i=1}^{n} \frac{1}{\sqrt{\beta_i}} \int_{-\beta_i}^{+3\beta_i} \frac{I_p(T_p)}{T} \times \left\{ \exp \left[ -\left( \frac{t_1}{\tau_{m_i}} \right) \right] - \exp \left[ -\left( \frac{t_2}{\tau_{m_i}} \right) \right] \right\} \exp \left[ -\left( \frac{Z}{\beta_i} \right)^2 \right] \, dz \]  

(9)

where \( Z = \ln \tau / \tau_{m_i} \), \( I = I_p T_p / T \) denotes the disaccommodation intensity of elementary
processes, \( I_p \) is the disaccommodation intensity at \( T_p \) (peak temperature) and \( \tau_{m_i} \) is an
average relaxation time for individual processes. The limit values for \( Z \) are assumed to be
equal to ±3\( \beta \) which approximately correspond to ±∞.

From the numerical analysis of the relaxation spectrum the following parameters for individu-
als processes are determined: the disaccommodation intensity \( I_p \) at \( T_p \) (peak temperature),
the average activation energy \( (E_{m_i}) \) and the distribution parameter \( \beta_i \). Furthermore, the
pre-exponential factor \( \tau_0m_i \), is given by the Arrhenius law:

\[ \tau_0m_i = \tau_p \exp \left( \frac{-E_{m_i}}{kT_p} \right) \]  

(10)

where \( k \) is the Boltzmann constant and \( \tau_p \) the relaxation time at the peak temperature. The
distribution of relaxation times corresponds to the distribution of activation energies \( E_i \):

\[ E_{m_i} - \beta_i kT_p \leq E_i \leq E_{m_i} + \beta_i kT_p. \]  

(11)

The results obtained from decomposition of the isochronal disaccommodation curves into ele-
mentary processes for the investigated samples annealed at 823 K for 5 s are listed in Table IV.
The fitted curves and experimental points for these samples are presented in Figures 9a, b. It is seen
(Tab. IV) that the average values of activation energies of the individual processes for the
Fe_{66.5}Co_{7}Cu_{1}Nb_{3}Si_{13.5}B_{9} alloy are higher than for the Fe_{73.5}Cu_{1}Nb_{3}Si_{13.5}B_{9} alloy.

It is worth noticing that the distinct decrease of the disaccommodation intensity occurs
(Figs. 3 and 4) after the subsequent annealing of the samples at 823 K for 10 and 60 min. This
is connected with annealing out more and more free volumes during these treatments.

Although the volume fraction of the crystalline phase increases up to about 55%, the con-
tribution of this phase to the magnetic after-effect is not evident (Tab. I, Figs. 3–6). The
rapid increase of the disaccommodation intensity above 600 K (Figs. 3–6) is observed for both
conventionally and accumulatively annealed samples. It is known that the disaccommodation
intensity is proportional to 1/d (where d is the domain wall width) [26] and the domain wall
Table IV. — Peak temperature ($T_p$), intensity of the process ($I_p$) at $T_p$, average activation energy ($E_m$), pre-exponential factor ($\tau_{0m}$), activation energy ($E$) from (12) obtained for the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ and Fe$_{66.5}$Co$_7$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloys after annealing at 823 K for 5 s.

<table>
<thead>
<tr>
<th>Sample</th>
<th>process</th>
<th>$T_p$(K)</th>
<th>$10^{-7}I_p$</th>
<th>$E_m$(eV)</th>
<th>$10^{-15}\tau_0$(s)</th>
<th>$E$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{73.5}$Cu$_1$Nb$<em>3$Si$</em>{13.5}$B$_9$</td>
<td>I</td>
<td>395</td>
<td>62</td>
<td>1.23</td>
<td>5.5</td>
<td>1.08 $\leq E \leq 1.38$</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>445</td>
<td>35</td>
<td>1.39</td>
<td>4.9</td>
<td>1.32 $\leq E \leq 1.46$</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>502</td>
<td>59</td>
<td>1.58</td>
<td>3.8</td>
<td>1.52 $\leq E \leq 1.64$</td>
</tr>
<tr>
<td>Fe$_{66.5}$Co$_7$Cu$_1$Nb$<em>3$Si$</em>{13.5}$B$_9$</td>
<td>I</td>
<td>415</td>
<td>3</td>
<td>1.34</td>
<td>1.5</td>
<td>1.26 $\leq E \leq 1.42$</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>477</td>
<td>9</td>
<td>1.50</td>
<td>3.6</td>
<td>1.44 $\leq E \leq 1.56$</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>533</td>
<td>40</td>
<td>1.66</td>
<td>5.2</td>
<td>1.62 $\leq E \leq 1.70$</td>
</tr>
</tbody>
</table>

Fig. 9. — Fitted isochronal $\Delta(1/\chi) = f(T)$ curves and experimental points: (a) for the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ and (b) Fe$_{66.5}$Co$_7$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloys annealed at 823 K for 5 s.

width is inversely proportional to the square root of the anisotropy constant. Moreover, from the random anisotropy model [6] it was found that near the Curie temperature of the amorphous matrix the average anisotropy $\langle K_1 \rangle$ distinctly increases with temperature. Thus, these effects lead to the rapid increase of the disaccommodation intensity near the Curie temperature of the amorphous matrix.

5. Conclusions

It is found that the volume fraction of the crystalline phase in the nanocrystalline Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ and Fe$_{66.5}$Co$_7$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ alloys increases with the annealing time. This causes the increase of the initial susceptibility and decrease of the coercivity.

The nanocrystalline Fe$_{66.5}$Co$_7$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ samples (obtained by the conventional annealing at 823 K for 1 h) exhibit better soft magnetic properties (e.g. higher initial susceptibility and lower coercivity) than the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ ones.

It is worth noticing that the crystalline phase of conventionally annealed samples exhibits D0$_3$-type order.

In spite of the increase of the volume fraction of the crystalline phase up to about 55%, its contribution to the magnetic after-effect is not evident.
References