Mössbauer Studies and Soft Magnetic Properties of $\text{Fe}_{85.4-x}\text{Co}_x\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ ($x = 0$ or 42.7) Alloys

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The phase composition, magnetic susceptibility and its disaccommodation of the amorphous and nanocrystalline $\text{Fe}_{85.4-x}\text{Co}_x\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ ($x = 0$ or 42.7) alloys were studied. We have found that in the nanocrystalline $\text{Fe}_{42.7}\text{Co}_{42.7}\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ alloy the ordered α -FeCo phase is present. Moreover, that alloy exhibits the higher susceptibility at elevated temperatures than the $\text{Fe}_{85.4}\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ one. The disaccommodation phenomenon in both investigated alloys is connected with relaxation processes occurring in the amorphous matrix.

Keywords: magnetic susceptibility, disaccommodation, Mössbauer spectroscopy, amorphous and nanocrystalline alloys.

1. Introduction

Nanocrystalline materials have found a broad interest in the last few years because of the superior magnetic properties and promising application potentials. The nanocrystalline very soft magnetic materials are usually produced by utilizing the first step of crystallization of amorphous alloys. These materials can be divided into two groups: Fe-Si-B-Nb-Cu and Fe-Zr-B-Cu-(Nb) alloys [1, 2]. The excellent soft magnetic properties of those alloys (low coercivity and high permeability) are related to formation of nanosized grains (α -Fe or α -FeSi) in amorphous ribbons resulting from a proper heat treatment [3]. Such structure leads to a significant decrease in anisotropy and magnetostriction of those materials [4]. However, the magnetic properties of Fe-based nanocrystalline alloys drastically deteriorate near the Curie temperature of an amorphous matrix [4] due to the decrease of magnetic coupling between crystalline grains. Recently, the nanocrystalline (FeCo)-Zr-B-Cu alloys have been developed [5]. Those nanocrystalline alloys exhibit significantly improved high temperature magnetic properties.

In this paper we present the results of investigations of the microstructure and soft magnetic properties i.e. susceptibility and its disaccommodation of $\text{Fe}_{85.4-x}\text{Co}_x\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ ($x = 0$ or 42.7) alloys subjected to the accumulative annealing at different temperatures.

2. Experimental procedure

Amorphous $\text{Fe}_{85.4-x}\text{Co}_x\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ ($x = 0$ or 42.7) ribbons, 0.02 mm thick and 3 mm wide were prepared by a single roller melt spinning technique in an argon atmosphere. The amorphicity of the as-quenched ribbons was checked by Mössbauer spectroscopy and X-ray diffractometry. The crystallization temperature of the as-quenched samples was determined from the thermomagnetic curves measured by means of a force magnetometer. The as-quenched ribbons were subjected to the accumulative annealing at 573 K for 1 h, then at 723 K for 10, 40 and 70 min and at 800 K for 5 min. The phase composition of the annealed samples was determined from transmission Mössbauer spectra analysis [6]. The magnetic susceptibility was investigated for toroidal samples in the temperature range from 160 up to 500 K. The amplitude and frequency of the magnetizing field were equal to $H = 0.16$ A/m and 2 kHz, respectively. From these results the isochronal disaccommodation curves were constructed [6].

3. Results

Mössbauer spectra and corresponding hyperfine field distributions of the amorphous and nanocrystalline samples are presented in Figs 1 and 2.

The Mössbauer spectra of the as-quenched alloys (Figs 1a and 2a) consist of broad and overlapped lines. The similar spectra are observed after annealing the samples at 573 K for 1 h (Fig 1b). The hyperfine field distribution of the as-quenched and annealed at 575 K samples are asymmetric. However, in the Mössbauer spectra of the samples annealed at 723 K and 800 K the additional sextet with sharp lines superimposed on broad line feature is observed.

The magnetic susceptibility versus temperature of the $\text{Fe}_{85.4-x}\text{Co}_x\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ ($x = 0$ or 42.7) alloys annealed at 573 K for 1 h and subsequently at 723 K for 40 min, as an example, are presented in Fig. 3.

As can be seen from this figure, the magnetic susceptibility of the investigated alloys distinctly increases after annealing at 723 K for 40 min. Moreover, one can notice that the magnetic susceptibility of the

Fig. 1 Mössbauer spectra and corresponding hyperfine field distributions of the $\text{Fe}_{85.4}\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ alloy in the as-quenched state (a) and annealed at: 573 K for 1 h (b) and then at 723 K for 40 min (c) and 70 min plus at 800 K for 5 min (d).

$\text{Fe}_{85.4}\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ alloy strongly depends on temperature. However, the magnetic susceptibility of the

Fig. 2 Mössbauer spectra and corresponding hyperfine field distributions of the $\text{Fe}_{42.7}\text{Co}_{42.7}\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ alloy in the as-quenched state (a) and annealed at 573 K for 1 h and then at 723 K for 10 min (b), 40 min (c), and 70 min plus at 800 K for 5 min (d).

Fig. 3 The dependence of the magnetic susceptibility on temperature for the $\text{Fe}_{85.4-x}\text{Co}_x\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ alloys: $x = 0$ (a, c), $x = 42.7$ (b, d) annealed at 573 K (a, b) and then at 723 K for 40 min (c, d).

$\text{Fe}_{42.7}\text{Co}_{42.7}\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ alloy in the temperature range from 100 up to about 550 K is almost temperature independent.

Fig. 4 shows the isochronal disaccommodation curves $\Delta(1/\chi) = f(T)$ of the $\text{Fe}_{85.4-x}\text{Co}_x\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ ($x = 0$ or 42.7) alloys annealed at 573 K for 1 h and then at 723 K for 40 min. One can see (Fig. 5) that the alloys annealed at 573 K for 1 h show the broad disaccommodation spectrum ranging from 150 to 340 K and from 120 to 500 K for the $\text{Fe}_{85.4}\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ and $\text{Fe}_{42.7}\text{Co}_{42.7}\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ alloys, respectively. After the annealing of the samples at 723 K for 40 min the decrease of the disaccommodation intensity is observed. Moreover, only temperature independent background in disaccommodation curves from 100 K to 300 K is seen.

Fig. 4 Isochronal disaccommodation curves of the $\text{Fe}_{85.4-x}\text{Co}_x\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ alloys: $x = 0$ (a, c), $x = 42.7$ (b, d) annealed at 573 K for 1 h (a, b) and then at 723 K for 40 min (c, d).

4. Discussion

Some fitted Mössbauer parameters of the amorphous and nanocrystalline alloys are presented in Table 1.

Table 1 The average hyperfine field (B_{eff}) and hyperfine field (B_{cr}), composition and volume fraction (V_{cr}) of the crystalline phase for the $Fe_{85.4-x}Co_xZr_{5.8}Nb_1B_{6.8}Cu_1$ ($x = 0$ or 42.7) alloys in the as-quenched state (as-q) and after heat treatments.

Treatment	B_{eff} (T)	B_{cr} (T)	V_{cr}	Crystalline phase
$Fe_{85.4}Zr_{5.8}Nb_1B_{6.8}Cu_1$				
as-q	12.15			
573K/1h	11.05			
723K/10min	13.82	32.81	0.035	98at% Fe
723K/40min	16.31	32.80	0.10	98at% Fe
723K/70min	18.88	32.94	0.17	99at% Fe
800K/5min	25.35	33.04	0.40	100at% Fe
$Fe_{42.7}Co_{42.7}Zr_{5.8}Nb_1B_{6.8}Cu_1$				
as-q	28.56			
573K/1h	29.32			
723K/10min	31.03	35.32	0.36	$Fe_{62}Co_{38}$
723K/40min	31.52	35.30	0.42	$Fe_{62}Co_{38}$
723K/70min	31.80	35.23	0.47	$Fe_{60}Co_{40}$
800K/5min	32.36	35.12	0.48	$Fe_{59}Co_{41}$

The results obtained from Mössbauer studies (Figs 1a, 1b and 2a, Table 1) indicate that the as-quenched and annealed at 573 K for 1 h alloys are completely amorphous. However, from the hyperfine field distributions (Figs 1a, b) one can conclude that the $Fe_{85.4}Zr_{5.8}Nb_1B_{6.8}Cu_1$ alloy after that treatment is more inhomogenous. Moreover, the decrease of the average hyperfine field of the $Fe_{85.4}Zr_{5.8}Nb_1B_{6.8}Cu_1$ alloy after annealing at 573 K for 1 h due to invar effect [7] is observed (Table 1).

After the annealing of the $Fe_{85.4}Zr_{5.8}Nb_1B_{6.8}Cu_1$ alloy at 723 K for 10 min the crystalline α -Fe phase appears (Fig. 1c, Table 2). Moreover, in the hyperfine field distribution of the amorphous matrix of that alloy low and high components are apparent. These components correspond to regions poor and rich in iron. The additional high field component in the hyperfine field distribution is also observed after the further heat treatment of the sample. That component we ascribe to the interfacial zone [8] between the crystalline grains and the amorphous matrix.

In the partially crystallized $Fe_{42.7}Co_{42.7}Zr_{5.8}Nb_1B_{6.8}Cu_1$ alloy the ordered α -FeCo phase was found (Fig. 2, Table 1). The volume fraction of the crystalline phase in both investigated alloys increases with annealing time and temperature. Moreover, the increase of Fe content in α -Fe phase and Co content in α -FeCo grains with annealing time and temperature is observed.

The microstructure of the investigated alloys highly influences their magnetic properties. Both investigated alloys exhibit not so high value of magnetic susceptibility after annealing at 575 K for 1 h (Fig. 3). However, the magnetic susceptibility distinctly increases after the additional annealing those alloys at 723 K for 40 min. It is worth noticing that the magnetic susceptibility of the $Fe_{42.7}Co_{42.7}Zr_{5.8}Nb_1B_{6.8}Cu_1$ alloy is almost temperature independent in both amorphous and nanocrystalline states. Moreover, the magnetic susceptibility of this alloy in the nanocrystalline state at temperatures above 450 K is higher than that for the $Fe_{85.4}Zr_{5.8}Nb_1B_{6.8}Cu_1$ alloy. This is connected with the presence in the nanocrystalline $Fe_{42.7}Co_{42.7}Zr_{5.8}Nb_1B_{6.8}Cu_1$ alloy of both the amorphous matrix (containing Co atoms) and α -FeCo phase, which exhibit the high Curie temperatures [5].

The highest value (8000) of the magnetic susceptibility of the $Fe_{85.4}Zr_{5.8}Nb_1B_{6.8}Cu_1$ alloy was obtained after annealing the sample at 800 K for 5 min. As for the $Fe_{42.7}Co_{42.7}Zr_{5.8}Nb_1B_{6.8}Cu_1$ alloy after that treatment, the magnetic susceptibility slightly decreases.

The isochronal disaccommodation curves $\Delta(1/\chi) = f(T)$ of the investigated alloys annealed at 573 K for 1 h were decomposed into three elementary processes assuming the gaussian distribution of relaxation times [9] (Table 2).

The values of the preexponential factor and activation energies of the elementary processes indicate that the disaccommodation phenomenon in these alloys are connected with directional ordering of the atom pairs near the free volumes [10]. The low intensity of the disaccommodation of nanocrystalline samples (Fig. 4) in the temperature range 160–400 K is caused by the annealing out of the free volumes in the amorphous matrix. The increase of the disaccommodation intensity at higher temperature is caused by the transition of the amorphous matrix from the ferro- to the paramagnetic state.

The “bell shape” of the $\Delta(1/\chi) = f(H_m)$ curves (Fig. 5) indicates that the disaccommodation phenomenon in these alloys is mainly connected with migration process of atoms inside 180° domain walls [11].

Table 2 The intensity (I_p) at the peak temperature T_p , pre-exponential factor of the Arrhenius law (t_0) and average activation energy (Q) of elementary processes obtained for the $Fe_{85.4}Zr_{5.8}Nb_1B_{6.8}Cu_1$ and $Fe_{42.7}Co_{42.7}Zr_{5.8}Nb_1B_{6.8}Cu_1$ alloys annealed at 573 K for 1 h.

Processes	$I_p \cdot 10^6$	T_p (K)	$\tau_0 \cdot 10^{15}$ (s)	Q (eV)
$Fe_{85.4}Zr_{5.8}Nb_1B_{6.8}Cu_1$				
I	3	258	3.3	0.81
II	11	280	1.9	0.90
III	11	309	2.95	0.98
$Fe_{42.7}Co_{42.7}Zr_{5.8}Nb_1B_{6.8}Cu_1$				
I	75	284	2.1	0.91
II	170	347	3.2	1.10
III	164	400	2.8	1.29

Fig. 5 Disaccommodation $\Delta(1/\chi) = f(H_m)$ of the $\text{Fe}_{85.4-x}\text{Co}_x\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ alloy annealed at 573 K for 1 h: $x = 0$ (a), $x = 42.7$ (b).

5. Conclusion

Annealing the amorphous $\text{Fe}_{85.4}\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ alloy below the crystallization temperature leads to the decrease of the average hyperfine field due to the invar effect.

The replacement of 42.7 % of Fe atoms by Co atoms in the $\text{Fe}_{85.4}\text{Zr}_{5.8}\text{Nb}_1\text{B}_{6.8}\text{Cu}_1$ alloy enhances the magnetic susceptibility at high temperatures of both amorphous and nanocrystalline samples.

The relaxation processes occurring in the amorphous matrix are the main source of the magnetic susceptibility disaccommodation in the investigated alloys.

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