N. A. Kutseva[1]*, V. V. Delov[1], N. A. Tolstova, V. S. Larin[2]

[1]*Oles Honchar Dnipro National University, Dnipro, Ukraine*
[2]*MicroFir Tehnologii Industriale, Kishinev, Moldova*
**e-mail: kutseva.natalia@gmail.com*

EFFECT OF ANNEALING ON STRUCTURE AND MAGNETIC PROPERTIES OF FeCo-RICH AMORPHOUS GLASS-COATED MICROWIRES

Thermal evolution of the structure of amorphous glass-coated Fe-rich and FeCo-rich microwires (MW) during crystallization is studied. It is shown that in initial MW the average distance between metal atoms and the average number of Fe neighbors are 0.258 nm and 10, respectively. Heat treatment influenced considerably on the structural parameters of amorphous MW. In both Fe-rich and FeCo-rich microwires, an increase in the height of the first maximum of the structure factor is observed, but in FeCo-rich MW this increasing is 1.5 times higher. Such structure changes indicate the beginning of crystallization processes. In Fe-rich MW the mean grain size of α-Fe nanocrystals and crystallized volume fraction are approxpmately 6nm and 23.5%, respectively. In FeCo-rich MW the size of FeCo nanocrystals remains the same ~6nm, but the crystallized volume fraction increases to 31%. This structure caused a decrease of coercivity from 200 A/m in the initial state to 60 A/m after the annealing at 350 °C.

Keywords: microwire, amorphous and nanocrystalline structure, crystallization, short range order, X-ray diffraction.

1. Introduction

Amorphous and nanocrystalline magnetic wires are very promising for various technical applications. Usually wires obtained by an in-rotating-water quenching technique have typical diameters of about 120 μm. On the other hand, the Taylor-Ulitovski method allows preparing a long homogeneous composite materials consisting of a metallic nucleus with a diameter in the range 1÷50 μm and a glass coating with the thickness of 1÷20 μm. This method consists in drawing a Pyrex-like glass containing the molten metal with further cooling. According to calculations the cooling rate of microwires ranges from 10^5 to 10^6 K/s. Using of this method permits to increase the degree of undercooling of melt and to fix more nonequilibrium metastable states in comparison with those obtained by traditional methods of splat-quenching. It is connected with nonequilibrium crystallization on neutral substrate and deactivation of admixtures by the isolated glass. Fe-rich amorphous microwires with positive magnetostriction constant produced by the Taylor-Ulitovsky method are characterized a good combination of magnetic properties (the large Barkhausen (LBE) effect, giant magnetoimpedance (GMI) effect, low coercivity), enhanced corrosion resistance and small size which are suitable for various applications, such as sensors, transducers, security labels [1, 2]. Magnetic properties of amorphous materials, which are characterized by the absence of long range order, are determined mainly by magnetoelastic anisotropy. But during manufacturing process in the metallic core of the wire both quenching and thermoelastic stresses occur. The thermoelastic stresses induced by the difference in thermal expansion coefficients of the glass and metallic core greatly influence on the structure formation of microwires, and as a result on magnetic characteristics. Excellent magnetic properties of Fe-rich MW characterized by vanishing magnetostriction value are achieved by means of creating of the nanocrystalline structure, which consists of α-Fe nanocrystals (mean size 10-15 nm) embedded in residual amorphous matrix. Partial substitution of Fe for Co improves magnetic properties at high temperatures due to the higher saturation magnetization and

Curie temperature [3, 4]. Appropriate heat treatment, leading to formation of FeCo nanocrystalline phase, can significantly improve physical properties of MW. The aim of this paper is to study influence of Co substitution on crystallization behavior and magnetic properties of Fe-based amorphous microwires.

2. Experimental details

Initial MW of nominal compositions $Fe_{77.5}Si_{7.5}B_{15}$ (sample 1), (metallic nucleus diameter D=20.6 μm and coating thickness Δ=28.4 μm) and $Co_{41.7}Fe_{36.4}Si_{10.1}B_{11.8}$ (sample 2), (D=15.8 μm and Δ=21.6 μm) were obtained by the Taylor-Ulitovski technique. The structure investigations were carried out by using X-ray diffraction (Mo K_α radiation, λ=0.71 nm). The samples were attached to the diffractometer sample holder at which each scan was made over the two theta angular range from 10 to 120 °, step size of 01 °, step time of 100 s for each step. The heat treatments were performed in a conventional furnace. The MW resistivity was measured by four-probe method with continuous heating in a vacuum (~10 mPa) with heating rate 20 K/min. Magnetic properties of microwires were measured by means of a conventional induction method at 50 Hz.

3. Results and discussion

XRD diffraction patterns of both initial MW (sample 1 and 2) are characterized only some broad diffusive halos (fig. 1) and confirm that initial MW have an amorphous structure.

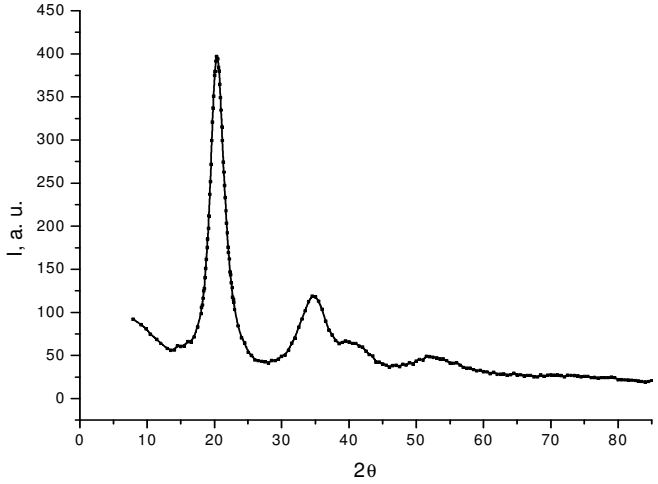

Fig.1. X-ray diffraction patterns of initial MW (sample 2)

The analysis of the structure of disordered systems, which have only short range order, is based on the following equations [5, 6]:

$$I_{kog}^{e.u.}(s) = NF^2 + NF^2 \int_0^\infty 4\pi r^2 [\rho(r) - \rho_o] \frac{\sin sr}{sr} dr \qquad (1)$$

where I_{cog} – the intensity of coherent scattering in electronic units; F – the atomic scattering factor; ρ(r) and ρ_o – the local and average atomic density, respectively; r – the interatomic distance; $s=4\pi\sin\theta/\lambda$;

Using the Fourier transform, from equation (1) is obtained the total radial distribution function of atoms

$$4\pi r^2\rho(r) = 4\pi r^2\rho_o + \frac{2r}{\pi}\int_0^\infty s(a(s)-1)\sin(sr)ds \qquad (2)$$

where $a(s) = \frac{I_{cog}(s)}{NF^2}$ – the structure factor

For multicomponent system

$$F^2 = \sum_i n_i f_i^2\,,\ \rho(r) = \sum_i\sum_j n_i K_i K_j \rho_{ij}(r)\,,\ \rho_o = \left(\sum_i n_i K_i\right)^2,\ K_i^2 = \frac{f_i^2}{F^2} \qquad (3)$$

Scattered intensities obtained from experiment were corrected by polarization factor taking incoherent scattering into account. The corrected intensity values were used to calculate the structure factors (SF) and the total radial distribution functions. The parameters of short range order are presented in Table 1, Fig.2.

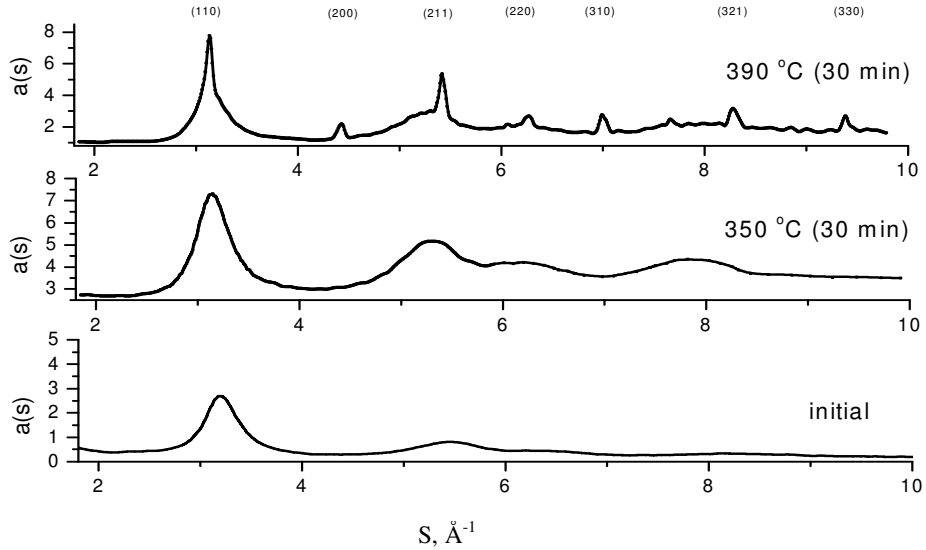

Fig. 2. Structural factors of initial and treated MW (sample 2)

Table 1

The parameters of short range order of initial and treated samples

alloy	*Temperature, °C*	s_1, Å^{-1}	$i(s_1)$	Δs_1	r_1, Å	A_m
Sample 1 $Fe_{77.5}Si_{7.5}B_{15}$	initial	3.13	2.9	0.4	2.58	10.2
	350 (30 min)	3.14	3.8	0.32	2.57	11.3
	390 (30 min)	3.12	4.5	0.29	2.55	11.6
Sample 2 $Co_{41.7}Fe_{36.4}Si_{10.1}B_{11.8}$	initial	3.13	3.0	0.37	2.58	10.6
	350 (30 min)	3.12	4.9	0.3	2.57	10.9
	390 (30 min)	3.13	6.8	0.21	2.57	11.3

here s_1, $i(S_1)$, Δs_1 – the position, height and the full width at half maximum (FWHM) of the first maximum of the structural factor, respectively; r_1-the most probable interatomic distance (the first peak position) ; A_m – coordination number (the area under the first maximum of the total radial distribution function of atoms).

From these data it is clear that the most probable distance between atoms and average number of nearest neighbor atoms in initial MW are approx. 2.58 Å and 10, respectively. These parameters are close to the corresponding one of the Fe-Fe, or Fe-Co interatomic distance (~2.49-2.52 Å). It is worth to note that such structural parameters as height and the FWHM of the first maximum of the structure factor are sensitive to

temperature. Thermal treatment leads to an increase of $i(s_1)$ and an decrease of FWHM of the first maximum of SF, which can be connected with a local change in the short range order and formation of a nanocrystalline structure. The substitution of iron for cobalt causes a greater increase in $i(s_1)$ and indicates acceleration of crystallization processes.

In order to study the thermal stability of amorphous phase and the crystallization behaviour in MW during heating, measurements of electrical resistivity versus temperature were carried out, Fig.3. As can be seen from Fig. 3, the microwire resistivity does not change up to 350 ^{o}C and there is a sharp decrease of the resistivity in the temperature range 350 ^{o}C to 500 ^{o}C. The second interval of irreversible decrease of the resistance is above 600 C.

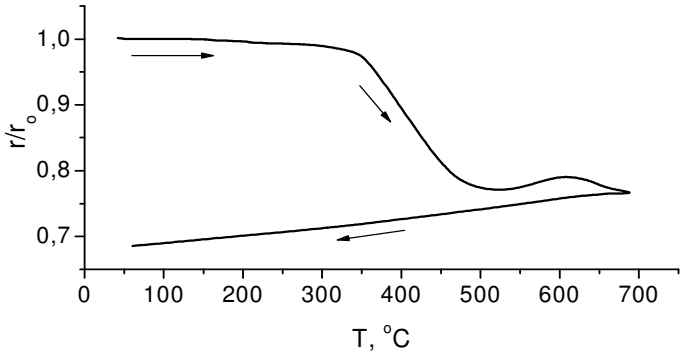

Fig. 3. The temperature dependence of the resistivity of MW (sample 2)

As X-ray results showed, annealing in the temperature range 390 – 400 ^{o}C (30 min) led to the formation of primary BCC α-Fe crystallites in residual amorphous matrix. It should be noted that in sample 1 the lattice parameter of α-Fe (a=0.2865 nm) is close to equilibrium value. At the same time in sample 2 the lattice parameter of α-Fe differs from the equilibrium one (a=0.2838 nm). It means that solid solution α-FeCo(Si) is formed. XRD patterns of treated above 440 ^{o}C MW (sample 2) are characterized by additional reflections (100), (111), (210), that can be interpreted as superlattice peaks of a CsCl (type) chemically ordered FeCo(Si) phase, which is in accordance with the phase diagram. At the second stage of transformation at the temperatures 520 – 550 ^{o}C the decomposition of residual amorphous matrix and formation of metastable phase Fe_3B occurs. In order to evaluate the mean grain size of the formed crystals and crystallized volume fraction (X_c) quantitatively, the separation of contributions to the total intensity coming from the (110) peak of BCC crystalline phase and the residual amorphous matrix was performed. The profile of the main diffraction peak was fitted by pseudo-Voigt function. The mean grain size of the formed crystals is derived from the Scherrer equation. It was found that at the temperature 350 ^{o}C in sample 1 the mean grain size of α-Fe crystalls and Xc were 6 nm and 23.5%, respectively. While for Fe-Co rich MW (sample 2), the mean grain size of α-FeCo crystals had the same value 6nm, but Xc increased to 31.5 %. Annealing in the the temperature range 390 – 400 ^{o}C for sample 1 and 2 resulted in increasing of both grain size and Xc up to 15 nm and 40%, respectively.

The hysteresis loops of both initial MW had rectangular shapes typical for Fe-rich amorphous MW with positive magnetostriction constants. Fig. 4 presents the temperature dependencies of MW coercivity. Annealing at the temperatures below the crystallization one causing the formation of nanocrystalline structure leads to the decrease of coercivity (H_c) from 200 A/m to 60 A/m. With the increase of nanocrystals size and their volume fraction, H_c increases to 400 A/m.

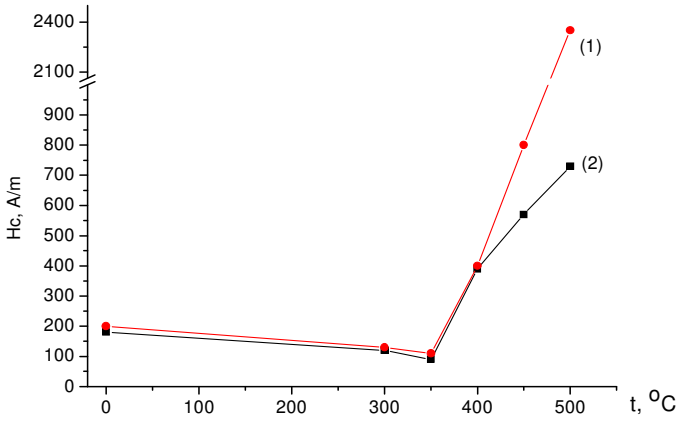

Fig.4. Temperature dependencies of MW coercivity

The second crystallization stage results on differences of up to one order of magnitude in H_c. This can be explained by the formation multiphase structure.

4. Conclusions

In paper was found, that initial Fe-rich and FeCo-rich microwires have amorphous structure. It was shown, that heat treatments lead to the increase of height of the first maximum of structure factors, that it is connected with formation of nanocrystalline structure. It was demonstrated, that magnetic properties can be dramatically changed by an appropriate heat treatment. It was established, that optimal magnetic properties (I_s~1.45 T, H_c~60 A/m) are achieved by annealing at 350 °C (30 min) in FeCo-rich microwires due to the formation of FeCo nanocrystals with the mean grain size ~6 nm and the crystallized volume fraction ~31%.

References

1. **Mohri. K.** Amorphous wire and CMOS IC-basedsensitive micromagnetic sensors utilizing magnetoimpedance (MI) and stress-impedance (SI) effects. [Text] / T. Uchiyama, L. P. Shen, C. M. Cai, L. V. Panina, Y. Honkura, and M. Yamamoto // IEEE Trans. Magn. –2002.– Vol. 38, N 5. – P. 3063–3068.

2. **Zhukov, A.** Development of Thin Magnetic Amorphous Microwires for High Frequency Magnetic Sensors Applications [Text]/ A. Zhukov, M. Ipatov, C. García, J.Gonzalez, L. Panina, J. M. Blanko, V. Zhukova // Progress In Electromagnetics Research Symposium, Hangzhou, China, March, 2008. – p. 650 – 657.

3. **Talaat, A.** Grain size refinement in nanocrystalline Hitperm-type glass-coated microwires [Text]/ A. Talaat, J. J. Del Val, V. Zhukova, M. Ipatov, P. Klein, R. Varga, J. Gonzalez, M. Churyukanova, A. Zhukov // J. of Magnetism and Magnetic Materials. – 2016. – Vol.406. – P. 15 – 21.

4. **Zhukov, A.** Magnetostriction of Co-Fe based Amorphous Soft Magnetic Microwires [Text]/ A. Zhukov, M. Churyukanova, S. Kaloshkin, V. Sudarchikova, S. Gudoshnikov, M. Ipatov, A. Talaat, J. M. Blanko, V. Zhukova // J. of Electronic Materials. – 2016. – Vol. 45, N 1. – p. 226-230.

5. **Skrushevskiy, A. F.** Strukturnjuiy analiz zhidkosteju I amorfnjukh tel. M.: Vjusshaja shkola, 1980. – 328 p. [in Russian]

6. **James, R. W.** The optical Principles of the diffraction of X-rays [Text] / R. W. James. –M: Inostrannaja literatura,1950. – 572 p. [in Russian]

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