EFFECT OF THERMOMECHANICAL TREATMENTS ON CRYSTALLIZATION BEHAVIOR AND MAGNETIC PROPERTIES OF Co-Si-B MICROWIRES

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The influence of heat treatments under tensile stresses on the thermal stability of the amorphous phase, crystallization processes and magnetic properties of glass-coated Co-Si-B microwires is investigated. It is found that conventional annealing leads to relaxation of internal stresses and the formation of primary α-Co crystals in the residual amorphous matrix. Annealing under tensile stress increases the thermal stability of amorphous phase by 50 – 60 °C and expands the temperature range for practical application of soft magnetic microwires.

Keywords: microwire, nanocrystalline structure, stresses, magnetic properties, X-ray diffraction.

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1. Introduction

Amorphous and nanocrystalline glass-coated microwires (MW) have become a new type of magnetic materials due to their good combination of excellent magnetic properties (the large Barkhausen effect (LBE), giant magnetoimpedance (GMI), magnetic bistability, high permeability, low coercivity) with small dimension and allow to use microwires in high-sensitivity magnetic field sensors [1-3]. Glass-coated MW is a composite material, which consists of a metal nucleus (amorphous alloy) covered with a glass coating. High cooling rates (~ 10^6 -10^7 K/s) that occur during the manufacture of MW with the presence of glass insulation cause large quenching and thermoelastic stresses in the metal core of the wire. The thermoelastic stresses occur during solidification due to the difference in thermal expansion coefficients of the glass and metallic core (more than 10 times), which is responsible for high radial stresses that are maximal at the metal core surface and decrease toward the wire axis. Magnetic properties of amorphous materials, which have no crystalline structure, are determined to the greatest extent by magnetoelasticity and shape anisotropy, as well as the value and sign of the magnetostriction constant. The great residual stresses arising at the manufacturing processes give rise to noticeable magnetoelastic energy that can deteriorate the magnetic softness of initial MW. The magnitude of internal stresses depends on the geometrical parameters of the wire (the diameter of metallic core, the glass coating thickness and their correlation), technological parameters. The magnetic domain structure of MW with a positive saturation magnetostriction consists of a large single domain magnetized along the microwire axis and surrounded by an outer shell with the magnetization oriented in the radial direction. Magnetoelastic anisotropy of amorphous MW can be tailored by appropriate thermal treatment. In [4-6], the influence of conventional and thermal annealing on the magnetic properties and the GMI effect in Co-rich amorphous MW was investigated. It was found that heat treatments under tensile stresses lead to the development of a transverse magnetic anisotropy in the outer shell due to magnetoelastic effects. However, most studies are focused solely on the magnetic properties of such wires and there is a little information about the effect of thermomechanical treatments on the phase transformation from an amorphous state to the crystalline one. The aim of this paper is to study the influence of heat treatments under tensile stress on the thermal stability of amorphous phase and crystallization behavior of MW.

2. Experimental details

Initial glass-coated microwires of nominal composition $Co_{67,7}Cr_3Fe_{4.3}Si_{10}B_{15}$ (metallic nucleus diameter 20 μm and coating thickness 10 μm) were obtained by the Taylor-Ulitovski technique. This method consists of drawing a Pyrex-like glass containing the molten metal with further cooling. The structure investigations of MW were carried out by using X-ray diffraction (Mo K_α radiation, λ=0.071 nm). The samples were attached to the diffractometer sample holder at which each scan was made over the 2θ angular range from 10^o to 120^o, step size of 01^o, step time of 100 s for each step. The annealing was performed in a conventional furnace. The heat treatments under tensile stresses were carried out in a conventional furnace where a mechanical load was attached to one end of microwire. Values of the applied stresses were calculated based on Young moduli of the metal core and the glass coating, as well as the microwire cross sectional area:

$$\sigma = \frac{mg}{S_{\mathrm{m}} + \dfrac{E_{\mathrm{gl}}}{E_{\mathrm{m}}} S_{\mathrm{gl}}}$$

where E_{m}, E_{gl} and S_{m}, S_{gl} – Young moduli and cross section area of the metal core and the glass coating, respectively; *m* – load mass.

The hysteresis loops of the MW were measured by conventional method (ferro-tester TR-9801/A).

3. Results and discussion

The structure examination shows that the initial MW has amorphous structure. The X-ray diffraction patterns are characterized by only a few broad diffuse halos (Fig.1).

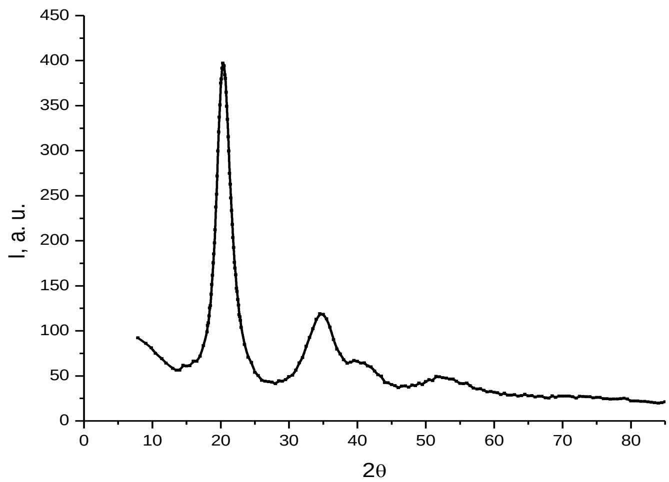

Fig. 1. X-ray diffraction patterns of the initial MW.

To analyse the structure of disordered systems, which have only short-range order in the arrangement of atoms and its changes during different types of heat treatments, structural factors and radial distribution functions of atoms were calculated by the method described in [7]. The parameters of short-range order of initial and treated MW are presented in Table 1.

Table 1

Structure parameters of as-prepared and treated MW: 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 (SF), 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)

Temperature, °C	s_1, nm^{-1}	$i(s_1)$	Δs_1	r_1, nm	A_m
initial	31.3	3.3	0.49	0.254	10.2
350 (30 min)	31.4	3.5	0.42	0.253	11.3
450 (30 min)	3.12	4.9	0.35	2.53	11.6
350 (30 min), σ=130 MPa	31.1	3.04	0.50	0.257	9.65
450 (30 min), σ=130 MPa	31.4	3.0	0.51	0.256	9.7
500 (30 min), σ=130 MPa	31.2	3.1	0.49	0.256	10.14
520 (30 min), σ=130 MPa	30.8	3.3	0.48	0.255	10.2

From these data it is clear, that the average distance between metal atoms and the average number of nearest neighboring atoms in initial MW were 0.254 nm and 10, respectively, which corresponds to the short-range order parameters of Co metal atoms (Co-Co interatomic distance ~ 0.25 – 0.252 nm).

Results of differential scanning calorimetry (DSC) analysis showed [8, 9] that crystallization of Co-Si-B microwires occurred in a multistage manner in the temperature range 480 °C – 600 °C. Therefore, to study the thermal stability of the amorphous phase, conventional annealing and annealing under tensile stress were carried out at the temperatures 350 °C, 450 °C, 500 °C. Conventional annealing at the temperatures 350 °C, 450 °C leads to an increase in $i(s_1)$ from 3.3 to 4.9 units, a decrease in the FWHM of the first SF maximum from 0.49 to 0.35 and decrease of the average interatomic distance (Table 1). Such changes are characteristic features of the local rearrangements of atoms and formation of a nanocrystalline structure, which determines the crystallization mechanism. Crystallization of MW occurs in the temperature range 480 °C – 500 °C with the formation of primary hexagonal closed-packed (hcp) α-Co crystals in a residual amorphous matrix. At the second stage of transformation at the temperatures 500 °C – 550 °C the decomposition of residual amorphous matrix and formation of multiphase structure: α-, β-Co, Co_2Si, and metastable phase Co_3B occur.

The other crystallization behaviour was observed at the annealing under tensile stress. One can see (Table 1) the values of $i(s_1)$, FWHM, the average interatomic distance change slightly during annealing under tensile stress up to the temperature 520 °C. Crystallization of treated under tensile stress MW begun in the temperature range 540 °C – 550 °C with the formation of multiphase structure: α-, β-Co, and metastable phase $(Co,Si)_3B$. Conventional annealing leads to the relaxation of significant quenching stresses, rearrangements of atoms through the diffusive process and formation of more ordered configurations, which reduces the amount of excess free volume. Stress annealing, however, involves a counterbalance between the relaxation of internal stresses and the formation of new ones under the action of an applied tensile load. As is well known, during crystallization a decrease in free volume occurs. Applying external tensile stress can oppose this process and as a result increases the Gibbs free energy required to form a critical nucleus of the new phase. Annealing under tensile stress increases the thermal stability of the amorphous phase in MW by suppressing the nucleation rate of crystallites, shifts the onset of crystallization to higher temperatures.

The magnetic characterization of initial and heat treated microwires was performed by conventional method. Coercivity of initial MW was ~ 125 A/m, saturation magnetization was 0.6 T. Such value of coercivity can be connected, as already mentioned, with significant internal stresses during fabrication. The temperature dependence of coercivity is presented in Fig. 2.

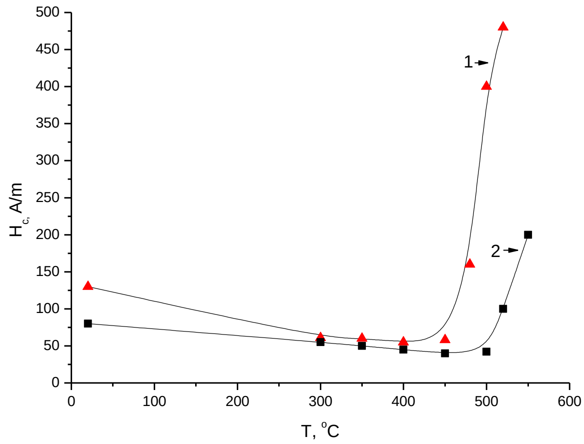

Fig. 2. Temperature dependencies of MW coercivity:
1 – conventional annealing; 2 –annealing under tensile stress 130 MPa.

As can be seen, the coercivity values of treated MW without stress slightly decreased to 55 – 60 A/m with increasing annealing temperature up to 450 °C, which can be connected with relaxation processes and the formation of nanocrystalline structure. Annealing at temperatures above 480 °C leads to an increase in coercivity, which, as shown by X-Ray analysis, is due to the formation of a multiphase structure. Annealing under tensile stress expands the temperature interval of good soft magnetic properties due to an increasing of thermal stability of amorphous phase up to 500 °C.

4. Conclusions

It was found that initial $Co_{67,7}Fe_{4,3}Cr_3B_{15}Si_{10}$ microwires have amorphous structure. It was found that conventional annealing leads to the formation of a nanocrystalline structure, which determines the subsequent primary crystallization of α-Co crystals in residual amorphous matrix. Annealing under tensile stress increases the thermal stability of amorphous phase and shifts the onset of crystallization towards higher temperatures.

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