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Structural and magnetic transformations in amorphous ferromagnetic microwires during thermomagnetic treatment under conditions of directional crystallization

A.T. Morchenko [a, *], L.V. Panina [a], V.S. Larin [b], M.N. Churyukanova [a], M.M. Salem [a, c], H. Hashim [a], A.V. Trukhanov [a], V.V. Korovushkin [a], V.G. Kostishyn [a]

[a] National University of Science and Technology MISiS, Moscow, Russia
[b] MFTI Ltd, Kishinev, Republic of Moldova
[c] Physics Department, Faculty of Science, Tanta University, Tanta 31527, Egypt

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ABSTRACT

As produced glass-coated ferromagnetic microwires typically have an amorphous state and demonstrate ultra-soft magnetic properties. For many applications, microwires with strong hard magnetic properties are of interest. A giant increase in coercivity has been recently reported for microwires subjected to directed crystallization. This paper confirms the coercivity increase up to 42 kA/m for wires of composition $Fe_{4.3}Co_{67.7}Si_{11}B_{14}Cr_3$ after magnetic-field assistant directed crystallization. To understand the effect of the directional crystallization on wire magnetic properties and to develop the reliable annealing technology the structural and mechanical transformation occurring during various stages of the annealing processes were investigated.

1. Introduction

Thin metallic wires of diameter 1–50 microns find a large number of applications owing to their electromagnetic and mechanical properties. Periodic arrangements of thin metallic wires are also of high interest for metamaterial design [1,2]. Considering the wire shape and micron size they do not conflict with structural integrity when used in fiber reinforced composites to introduce electromagnetic functionality [3]. Progress in developing applications of thin wires has been made possible by the current techniques for the fabrication and processing of materials with controlled characteristics on the nano and micro scale (i.e. rapid solidification, nanocrystallization, directional crystallization, nanolithography, sputtering, chemical methods).

Ferromagnetic microwires offer many more functionalities. Being produced in amorphous or nanocrystalline state [4,5] they exhibit outstanding soft magnetic properties and magnetic bistability with very low switching fields, which makes them attractive as miniature sensing elements and tunable microwave absorbers. Recently the method of directional crystallization of amorphous microwires in glass coating was proposed with the aim to establish a hard magnetic state [6]. A giant increase in coercivity was reported for microwires of Co-rich composition after a directional crystallization. For applications, combining the functional wire with the hard magnetic wire serving as a bias can provide additional tuning. Hard magnetic microwires are also of interest as micromagnets which provide passive contactless manipulation of small particles including biological objects. Many techniques for obtaining miniature magnets have been developed, such as thermomagnetic patterning [7], however, there are limitations. The established alternative technology will be in high demand.

As-prepared magnetic microwires are typically in amorphous state due to rapid cooling and solidification of the molten alloy. This process results in occurring of a large frozen-in stress which to a

* Corresponding author.
E-mail address: dratm@mail.ru (A.T. Morchenko).

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great extent determines the magnetic structure [8,9]. Various annealing treatments were proposed to modify the magnetic structure [10,11]. In particular, annealing treatment can result in a complete change of the magnetization curve from almost linear to a bistable type [12,13]. Furthermore, it is possible to obtain various intermediate magnetization behaviors similar to the changes produced by the wire composition [14]. However, in all these cases the annealing temperature is well below the crystallization temperature and does not produce structural transformations. In amorphous wires the magnetization behaviour is characterized by a narrow magnetization loop with the coercivity of no more than few hundred A/m. The largest increase in coercivity was recently discovered in microwires undergone the directional crystallization from the amorphous state with the formation of ordered micro crystals such as hexagonal α-Co [6].

This paper further advances the directional crystallization technique of producing hard-magnetic microwires with the aim to understand the mechanism of coercivity increase. The wire microstructure after different stages of the crystallization process was investigated using differential scanning calorimetry (DSC), X-ray diffraction (XRD) and Mössbauer spectroscopy. Our analysis has demonstrated that predominantly face-centered cubic cobalt (fcc-Co) crystals are formed with <111> easy anisotropy axis. The easy-axis of magnetization is not random as for a polycrystalline state but oriented nearly along the wire. The combination of crystal texture and predominant easy anisotropy direction is believed to be responsible for a giant coercivity increase.

A process of crystal growth in a certain direction and at a constant speed is known as directional crystallization. Typically, this process is realised from a liquid state and a number of methods are established such as Bridgman–Stockbarger technique, Czochralski method, zone melting, etc. [15,16]. In this work, a directional crystallization from amorphous state is realised in a glass-coated microwire of Co-rich composition by the propagation of thermally activated crystallization boundary. The directional crystallization was also assisted by the application of a magnetic field. The efficiency of the process was confirmed by giant increase in the coercivity.

The method of directional crystallization can be opposed to partial crystallization of an amorphous matrix to produce a nanocrystalline state with soft magnetic properties [17,18]. Changing the temperature regimes makes it possible to control the extent of crystallization which occupies 20–40% of the total volume. The crystallites of a size of 10–30 nm are randomly distributed in the amorphous matrix and a record low coercivity can be achieved as in Fe–Si–B alloy systems with addition of Cu and Nb (known as Finemet).

2. Experimental details

We have investigated a number of annealing regimes to realize a directional crystallization in glass-coated $Fe_{4.3}Co_{67.7}Si_{11}B_{14}Cr_3$ amorphous microwires. Two types of wire samples were used with different total (D) and metal core (d) diameters: $D = 39\ \mu m, d = 31\ \mu m$ (wire label 2323) and $D = 20.5\ \mu m,\ d = 15.5\ \mu m$ (wire label 2328). With the aim to realize a directional crystallization from amorphous state the samples were undergone annealing with a positive temperature gradient as described in Ref. [6]. The sample consisting of 10–15 wires of 7–10 cm long was placed in a long narrow oven with a uniform temperature distribution which was controlled by thermocouples located along the oven. The oven temperature could be raised up to 600 °C which is sufficient for normal crystallization. Local overheating (ignition) was realised with an additional coil located at one end of the oven which provides additional increase in temperature by up to 180 °C uniformly in radial direction. The oven could be placed inside a solenoid of 250 mm long to generate a dc magnetic field up to 10 kA/m during the crystallization process.

The characteristic temperatures and the extent of crystallization were found from differential scanning calorimetry (DSC) using standard IT applications. The DSC measurements were performed using DSC 204 F1 Netzsch calorimeter in Ar atmosphere at a heating rate of 10 K/min. The mass of the samples was 3–10 mg.

The presence of crystalline phases was investigated by XRD with CoK_α radiation using DRON-3M diffractometer in the angle range of 10–100° with a step of 0.03°. The time of exposition was 5 s. X-ray tube parameters were 30 kV and 20 mA. Microwires were crushed, ground and then separated from glass shell by an external magnetic field.

Mössbauer spectroscopy of $Fe^{57}$was performed to evaluate the magnetization orientation in both amorphous and crystalline microwires. The spectrometer (Ms-1104 Em) with Co^{57} as a source of $\gamma-$ rays was operating in the regime of constant acceleration. The mathematical treatment of spectra was performed with the use of Univerm Ms software. Isomeric shift was calculated relative to $\alpha - Fe$. The microwires were placed in the absorber holder so that the $\gamma-$ rays were perpendicular to the wires. The powdered wire samples were also studied.

Young's moduli were measured by an optical strain gauge method.

The hysteresis loops of microwires were measured by a vibrating sample magnetometer producing a maximum magnetic field of 10^7 A/m. The sample was comprised of 15 microwire pieces of 1.5 mm in length. The coercivity was also measured by a standard inductive method using narrow differential detection coils (with the inner diameter of 3 mm and the length of 60 mm) placed in the Helmholtz coils generating an ac field up to 100 kA/m. For a quick check of a possible structural change the coercivity could be controlled for a wire sample inside the oven. In this case the maximum field is 5 kA/m.

3. Directional crystallization procedure

The wires are heated to the temperature slightly below by 5–7° of the primary crystallization temperature ($T_{cr} = 521 - 528.5$ °C as found from DSC measurements) during several minutes to reach the thermal equilibrium. At this stage, the wires can be taken out of the oven for magnetic/structural investigation. The local ignition applied for 20–30 s initiates the crystallization process by producing a positive temperature gradient. Overheating well above T_{cr} creates the crystallization phase boundary with the latent heat release. The speed of crystallization depends on many factors and in each case the temperatures should be carefully chosen so that the propagation of the crystallization front could be self-maintained.

For ferromagnetic microwires the increase in coercivity could be used as a quick indicator of the structural change. The annealing setup allows such coercivity measurement to be made locally, for example in the area of ignition and after this area.

The effect of a magnetic field applied during the crystallization front propagation was also investigated. The oven temperature and the local heating temperature were the same as in the experiments without a magnetic field.

The Curie temperature of microwires in amorphous state is lower than T_{cr}, therefore, before the crystallization takes place the wires are in a paramagnetic state. The crystalline phases have much larger Curie temperatures exciding the crystallization temperatures. Upon crystallization the ferromagnetic state is restored so the applied magnetic field can assist the formation of some texture along the wire.

Considering the annealing regimes and achieved results for