UDC 539.213+ 539.26

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

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

CRYSTALLIZATION PROCESSES IN Co-BASED AMORPHOUS MICROWIRES

Investigations of the effect of thermal treatments such as conventional annealing and annealing under tensile stress on crystallization behavior of $Co_{57}Fe_{6.1}Ni_{10}Si_{11}B_{15.9}$ glass-coated microwire are carried out. It is shown that the crystallization of amorphous microwires occurs in two stages. At the first stage of crystallization primary α- and β-Co crystallites are formed in residual amorphous matrix at the temperature 480 °C. At the second stage the residual B and Si enriched amorphous phase transforms into Co_2Si phase and the metastable phase Co_3B through eutectic crystallization in the temperature range 520 – 550 °C. The mean grain size and crystallized volume fraction of Co crystals increase from 4 nm to 20 nm and from 10% to 25%, respectively. Stress annealing in this temperature range stimulates the crystal grain nucleation (crystallized volume fraction of Co crystals increases up to 40%, however the crystalline grain size increases weakly to 10 nm). It is found that stress annealing accelerates the nucleation of new grains rather than existing grain growth.

Keywords: microwire, amorphous and nanocrystalline structure, crystallization, stress annealing, X-ray diffraction.

Досліджувався вплив різних видів термообробки на процеси кристалізації в мікродроті складу $Co_{57}Fe_{6.1}Ni_{10}Si_{11}B_{15.9}$ в скляній ізоляції. Встановлено, що кристалізація микродроту відбувається в дві стадії. На перший стадії кристалізації при температурі 480 °C утворюються первинні кристали α-, β-Co в залишковій аморфній матриці. На другій стадії збагачена B и Si аморфна фаза розпадається на Co_2Si и метастабільну фазу Co_3B внаслідок евтектичної кристалізації в температурному інтервалі 520 – 550 °C. Середній розмір зерна та частина закристалізованого об'єму зростають від 4 нм до 20 нм та від 10% до 25%, відповідно. Відпал за наявності одноосного розтягування в цьому температурному інтервалі стимулює утворення кристалів (частина закристалізованого об'єму зросла до 40 %, але розмір кристалів збільшився незначно – до 10 нм). Встановлено, що відпал за наявності розтягування більше прискорює формування зародків нової фази, а не швидкість зростання існуючих кристалів.

Ключові слова: мікродріт, аморфна та нанокристалічна структура, кристалізація, відпал при наявності одноосного розтягування, дифракція рентгенівських променів.

Исследовалось влияние различных видов термообработки на процессы кристаллизации в микропроводе состава $Co_{57}Fe_{6.1}Ni_{10}Si_{11}B_{15.9}$ в стеклянной изоляции. Показано, что кристаллизация аморфного микропровода проходит в две стадии. На первой стадии кристаллизации при температуре 480 °C образуются первичные кристаллы α-, β-Co в оставшейся аморфной матрице. На второй стадии обогащенная B и Si аморфная фаза распадается на фазу Co_2Si и метастабильную фазу Co_3B в результате эвтектической кристаллизации в температурном интервале 520 – 550 °C. Средний размер зерна и доля закристаллизованного объема кристаллов Co увеличились от 4 нм до 20 нм и от 10% до 25%, соответственно. Отжиг при наличии одноосного растяжения в этом температурном интервале стимулирует образование кристаллов (доля закристаллизованного объема Co возросла до 40%, однако размер кристаллов увеличился незначительно до 10 нм). Установлено, что наличие одноосного растяжения при термообработке ускоряет больше образование зародышей новой фазы, а не скорость роста уже возникших кристаллов.

Ключевые слова: микропровод, аморфная и нанокристаллическая структура, кристаллизация, отжиг при наличии одноосного растяжения, дифракция рентгеновских лучей.

1. Introduction

Amorphous and nanocrystalline glass-coated microwires (MW) have attracted a great interest due to their good combination of unique physical properties and thermal stability of amorphous or nanocrystalline state with small dimension. Nanocrystalline wires present a number of excellent magnetic properties which are suitable for various applications, such as sensors, transducers, security labels [1, 2]. 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. During the manufacturing process in the metallic nucleus of the wire both quenching and thermoelastic stresses occur and as a result initial microwires are characterized by great values of internal stress. Magnetic properties of amorphous materials, which are no crystalline structure, are controlled most of all magnetoelastic and shape anisotropies, as well as the value and sign of the magnetostriction constant. Recently some studies have indicated that annealing and stress annealing change the magnetic anisotropy and promote the crystallization processes in Fe-rich materials with positive magnetostriction [3-6]. Magnetic behavior of nearly zero magnetostrictive microwires is controlled by the surface anisotropy that can be changed by glass removal or thermal treatments [7]. However the most studies focused only on magnetic characteristics of such wires and there is a little information about the influence of stress annealing on phase transformation from an amorphous state to the crystalline one. The aim of this paper is to investigate the effect of thermal treatments such as conventional annealing and annealing under tensile stress on the crystallization processes and magnetic properties of Co-based amorphous microwires.

2. Experimental details

Initial MW of nominal composition $Co_{57}Fe_{6.1}Ni_{10}Si_{11}B_{15.9}$ (metallic nucleus diameter 14 μm and coating thickness 12 μm) was obtained by the Taylor-Ulitovski technique. The structure investigations were carried out by X-ray diffraction (Mo K_α, Co K_α radiation). The heat treatments were performed in a conventional furnace without applied stress (CA) and under applied tensile stress 15 g on one microwire (SA). Thermal analysis for microwires was carried out with using a Netzch 404 differential scanning calorimeter (DSC) with a heating rate 20 K/min.

3. Results and discussion

The structure examinations show that initial MW has amorphous structure. The X-ray diffraction patterns are characterized only some broad diffusive halos, which indicate an amorphous state of the MW (Fig. 1).

In order to study the crystallization processes in MW during heating, a DSC test was performed (Fig. 2). DSC curve shows several exothermal peaks at the temperatures 480 ^oC, 540 ^oC, and 590 ^oC demonstrating that devitrification occurs in a multistage manner. As X-ray results shows, on the first stage of crystallization at the temperature 480 ^oC primary α-, β-Co crystallites are formed in residual amorphous matrix. It is worth to note that according to the phase diagram, adding of 10 at. % Ni leads to the nucleation of crystallites of both modifications: the hexagonal closed- packed (hcp) α-Co (space group $P6_3/mmc$) and cubic face-centered (fcc) β-Co (space group Fm3m). The lattice parameters of α-Co (a = 0.2503 nm, c = 0.4223 nm) are close to equilibrium values, this proves that B does not dissolve in lattice of (hcp) α-Co. At the same time the lattice parameter of β-Co (a=0.3531 nm) differs from the equilibrium one (a=0.3544 nm). It means that solid solution β-Co(B) is formed.

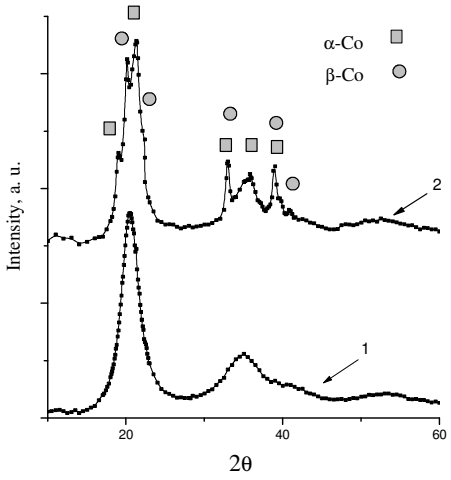

Fig. 1. Mo K_α X-ray diffraction patterns of MW: 1 – initial; 2 – treated at 480 °C (30 min)

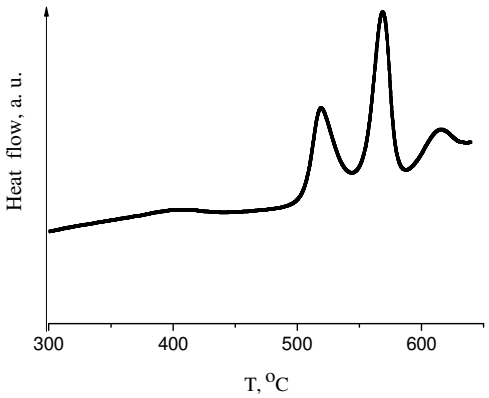

Fig. 2. The differential scanning calorimeter

At the second stage of transformation at the temperatures 520 – 550 °C the decomposition of residual amorphous matrix and formation of multiphase structure: α-, β-Co, Co_2Si, and metastable phase Co_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 crystalline phases 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. Fig. 3 presents Co Kα X-ray diffraction patterns of microwire treated at 520 °C for 30 min.

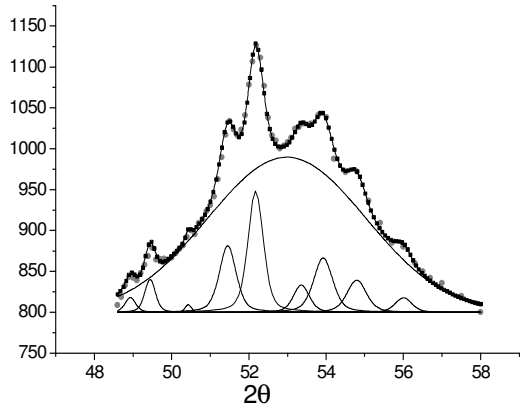

Fig. 3. Co K_α X-ray diffraction pattern of MW treated at 520 °C (30 min)

It was found that in the temperature range 520 – 550 °C the mean grain size of Co crystalls and Xc increased from 4 nm to 20 nm and from 10% to 25%, respectively.

The annealing in the temperature range 600 – 650 °C leads to the decomposition of metastable phase Co_3B with formation of equilibrium phases: β-Co (a=0.3544 nm), Co_2B (I4/mcm, a=0.503 nm, c=0.424 nm), and Co_2Si. Alloying elements such as Ni, Fe, B are known as (fcc) β-Co stabilizers because of sluggishness of the α-Co ↔ β-Co transformation in alloy.

Stress annealing (σ = 280 MPa) in the temperature range 520 – 550 °C stimulates crystallization processes. Fig. 4 presents Co Kα X-ray diffraction patterns of microwire treated at 520 °C (30 min.) under stress. After the total peak decomposition into components it was found that the structure of stress treated microwires consisted of the

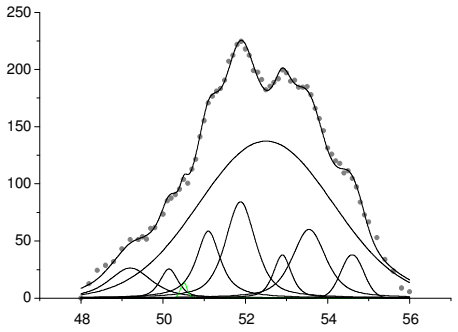

Fig. 4 Co K_α X-ray diffraction pattern of MW treated at 520 ^oC, σ=280 MPa

mixture of α-, β-Co, Co_2Si, and metastable phase Co_3B. The mean grain size of Co crystallites increased only to 10 nm that was almost two times smaller than the grain size at the traditional annealing. At the same time the crystallized volume fraction increased up to 40 %. As well known, amorphous structure is inhomogeneous and consist of the clusters with different short order. The inhomogeneties can act as nucleation sites of nanocrystallites to promote the crystallization under stress annealing.

4. Conclusions

It was found that initial $Co_{57}Fe_{6.1}Ni_{10}Si_{11}B_{15.9}$ microwires have amorphous structure. Crystallization of amorphous MW occurs into two stages. Annealing at the temperature 480 ^oC leads to the formation primary crystals of Co (B) solid solution embedded in amorphous matrix. At the second stage of crystallization the B-enriched Si amorphous phase transforms into the Co_2Si and metastable Co_3B phases, which decompose to the equilibrium phases: β-Co, Co_2B, and Co_2Si.The mean grain size and crystallized volume fraction of Co crystals increase from 4 nm to 20 nm and from 10% to 25%, respectively. The annealing stress promotes the crystallization processes and accelerates the nucleation of new grains rather than existing grain growth.

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Received 20.05.2016