UDC 539.213 :539.26

N. A. Kutseva[1], V. F. Bashev[1], A.Y. Derun[1], V. S. Larin[2]

[1]*Oles Honchar Dnipropetrovsk National University*
[2] *MicroFir Tehnologii Industriale, Kishinev, Moldova*

NANOCRYSTALLIZATION PROCESSES IN THE "FINEMET" TYPE MICROWIRES UNDER STRESS ANNEALING

Effect of thermal treatments such as conventional annealing and annealing under tensile stress on nanocrystallization behaviour of $Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$ glass-coated microwire was investigated. Initial microwire obtained by the Taylor-Ulitovski technique had an amorphous structure. It was found that conventional annealing within the temperature interval of 500 – 550 °C during 5 min led to the formation of primary α-Fe(Si) crystals in residual amorphous matrix. The mean grain size of the formed crystals was about of 16 nm and the crystallized volume fraction was 42%. The annealing under tensile stress resulted in changing mechanisms of crystallization, from primary to eutectic crystallization. The structure of microwire annealed within the mentioned temperature interval under stress was the mixture of α-Fe(Si) and Fe_3B crystalline phases. The mean grain size and crystallized volume fraction of the α-Fe(Si) crystals decreased up to 11 nm and 31 %, respectively. The optimal soft magnetic properties of microwires (coercivity was ~ 65 A/m) were achieved by annealing at 520 °C. It was connected with the formation of nanocrystalline structure of microwire.

Keywords: microwire, amorphous state, nanocrystalline structure, heat treatments.

В работе исследовалось влияние различных видов термообработки на процессы кристаллизации в микропроводе состава $Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$ в стеклянной изоляции. Исходный микропровод, полученный методом Улитовского-Тейлора, имел аморфную структуру. При традиционном отжиге в интервале температур 500 – 550 °C (5 мин.) происходило формирование первичных кристаллов α-Fe(Si) в оставшейся аморфной матрице. Средний размер кристаллов составлял ~16 нм и доля кристаллической фазы – 42 %. Отжиг при наличии одноосного растяжения приводил к смене механизма кристаллизации от первичной к эвтектической. Структура микропровода, отожженного в этом же температурном интервале при наличии нагрузки, представляла собой смесь фаз: α-Fe(Si) и Fe_3B. Средний размер и доля закристаллизовавшегося объема кристаллов α-Fe(Si) уменьшались до 11 нм и 31 %, соответственно. Оптимальные магнитные свойства микропровода (коэрцитивная сила ~ 65 А/м) получались отжигом при температуре 520 °C, что связывалось с образованием в нем нанокристаллической структуры.

Ключевые слова: микропровод, аморфное состояние, нанокристаллическая структура, термообработка.

У роботі досліджувався вплив різних видів термообробки на процеси кристалізації у мікродроті складу $Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$ в скляній ізоляції. Вихідний мікродріт, отриманий методом Улітовського-Тейлора, мав аморфну структуру. При відпалі в інтервалі температур 500 – 550 °C протягом 5 хв. спостерігалось утворення первинних кристалів α-Fe(Si) в аморфній матриці. Середній розмір кристалів складав 16 нм та частка кристалічної фази – 42 %. Відпал при прикладенні розтягнення приводив до зміни механізму кристалізації від первинної до евтектичної. Структура микродроту, відпаленого під навантаженням в цьому температурному інтервалі, являла собою суміш фаз: α-Fe(Si) и Fe_3B. Середній розмір та частка кристалічної фази кристалів α-Fe(Si) зменшувались до 11 нм та 31 % відповідно. Оптимальні магнітні властивості мікродроту (коерцитивна сила ~ 65 А/м) були досягнуті відпалом за температури 520 °C, що було пов'язано із формуванням в ньому нанокристалічної структури.

Ключові слова: мікродріт, аморфний стан, нанокристалічна структура, термообробка.

Introduction

The soft ferromagnetic nanocrystalline alloys with trade mark “Finemet” are very promising for technological applications. The enhanced softness of these materials (coercivity less than 5 A/m, high initial permeability values) is usually achieved by the formation of nanocrystalline structure, which consists of an ultrafine α-Fe(Si) grains with typical size 10-15 nm embedded in a residual amorphous matrix. The most reported results are carried out on melt-spun nanocrystalline ribbons. On the other hand, the Taylor-Ulitovsky method allows to fabricate tiny metallic wires (the metallic nucleus diameter 1÷50 μm) covered by an insulating glass coating (the glass coating thickness 1÷20 μm). Nanocrystalline glass-coated microwires (MW) having the excellent combination of soft magnetic properties, stability of nanocrystalline state with small dimensions and their resistance to corrosion are very perspective as sensor elements in a large variety of electronic devices and sensors [1]. During the manufacturing process the large internal stresses (~1GPa) arise as a result of difference between the thermal expansion coefficients of glass and alloy. The presence of such a residual stresses forms a complex domain structure of initial MW [2, 3]. It leads to increasing the coercivity and decreasing the initial permeability. The magnetoelastic anisotropy related to the internal stresses induced during the fabrication as well as the value and sign of the magnetostriction constant play a decisive role in the hysteretic magnetic properties of these thin wires. As well known, thermal treatments allow tailoring the magnetic properties of glass-coated MW [4, 5].

The aim of this work is to investigate the effect of thermal treatments such as conventional annealing and annealing under tensile stress on the structure and physical properties of MW.

Experimental details

Initial $Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$ MW with metallic nucleus diameter 16 μm and total diameter 26 μm have been obtained by the Taylor-Ulitovski technique. The microstructure of initial and heat-treated microwires has been characterized by X-ray diffraction (Mo K_α, Co K_α radiation). The annealing has been performed in conventional furnace at the temperature below crystallization temperature without applied stress (CA) and under applied tensile stress 10 g and 15 g on one microwire (SA). The temperature dependence of the electrical resistivity was used for studying crystallization processes occurring in MW. Thermal analysis for microwires was carried out using a Netzch 404 differential scanning calorimeter (DSC). Studied sample of a few mg weights placed in the alumina crucible and reference sample (empty crucible) were heated with identical thermal program (a heating rate was 20 K/min) while heat flow difference between sample and reference was recorded. Absorbed and released heat values were plotted as a function of temperature. Magnetic properties of microwires were measured by means of a conventional induction method at 50 Hz.

Results and discussion

The X-ray diffraction patterns showed that the initial microwires have amorphous structure (Fig.1). As can be seen, there are some broad diffusive halos, which are an inherent feature of disordered structures. Size of the coherently diffracting domains was approx. 2nm.

In order to study the structure changes and crystallization behaviour in microwires during isochronal heating a DSC test and measurements of electrical resistivity versus temperature were carried out, as shown in Figs. 2, 3.

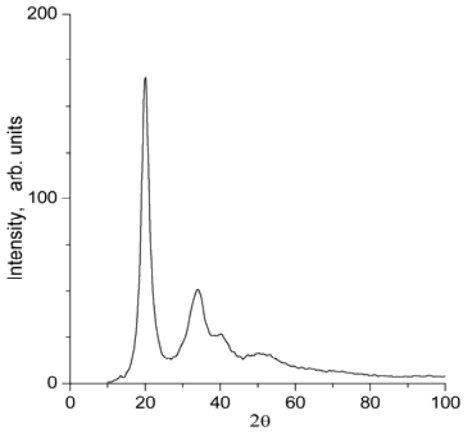

Fig. 1. Mo K_α X-ray diffraction pattern of initial microwire.

The DSC curve shows exothermic effect in the temperature range from 200 °C up to the crystallisation temperature (T_x = 520 °C) and crystallization peak at the temperature 560 °C. The Curie temperature (T_c) was evaluated analysing the curve of magnetisation versus temperature. Its value was 317 °C. It corresponds to the change in the slope of DSC curve. The onset glass transition temperature T_g is 450 °C and the difference (ΔT) between T_x and T_g so called the width of the supercooled region that relates to the stability of amorphous phase, is 70 °C.

The results of the DSC curve correlates with the results of electrical resistance. As can be seen from Fig. 3, the microwire resistivity increases slightly up to 300 °C and there is a sharp decrease of the resistivity from 300 °C to 500°C. The under stress annealing (SA) did not change the character of temperature dependency, but its values slightly increased.

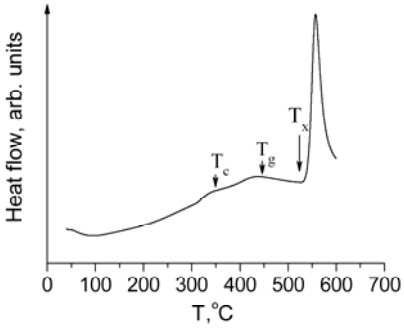

Fig. 2. The differential scanning calorimeter curve for microwires.

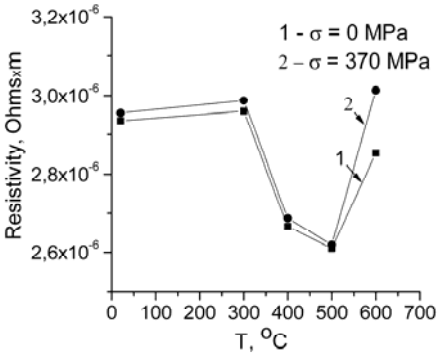

Fig. 3. The temperature dependence o f the resistivity of microwires.

As X-ray results showed, with increasing the annealing temperature (CA) in the range from 500 °C to 550 °C it observed increase of main peak height and its sharpening. It can be explained the formation of the nanocrystalline structure (Fig. 4). As can be seen only a BCC α-Fe(Si) phase appears in residual amorphous matrix. The full width of the peak at half maximum and crystallized volume fraction (X_c) at the final stage of primary crystallization have been evaluated by deconvoluting the total profile of the amorphous halo and the (110) peak of α-Fe(Si) phase [6].

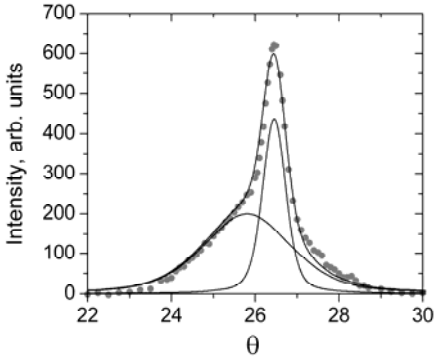

Fig. 4. Co K_α X-ray diffraction pattern of microwires treated at 550 ^{0}C (5 min).

The mean grain size of the formed crystals is derived from the Scherrer equation. It is ~ 16 nm and $X_c \approx 42\%$. Thus, the conventional annealing in range of 500-550 °C leads to the formation nanocrystalline structure through primary crystallization. The other crystallization behavior we have in the case of SA at 110 MPa (Fig. 5).

One can see the width of the main peak does not decrease; moreover, it appears shoulders on the curve. After deconvoluting the total peak on the components it was found, that the structure of stress treated microwires consists of the mixture of α-Fe(Si) and (body tetragonal cubic) Fe_3B crystalline phases [7]. The mean grain size and crystallized volume fraction of α-Fe(Si) phase is 11 nm and 31 %, respectively. The lattice parameter of α-Fe(Si) phase is 0.284 nm and it differs from equilibrium one, likely it connects with the influence of metalloid atoms according to data of phase diagram.

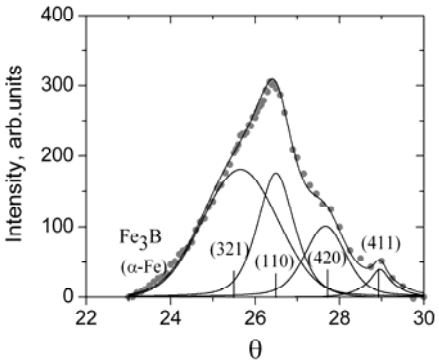

Fig. 5. Co K_α X-ray diffraction pattern of microwires treated at 550 ^{0}C (5 min) under stress 110 MPa.

As well known amorphous structure is very often inhomogeneous and consists of the clusters with different short order. It is possible that stress annealing stimulates the processes of amorphous phase separation into two phases with different compositions and following formation of the mixture of α-Fe(Si) and Fe_3B crystalline phases through eutectic crystallization.

Magnetic characterization of initial and heat treated microwires was performed by conventional method. Coercivity of initial microwires was ~ 100 A/m. It was found that the coercivity values decreased to 62 A/m with increasing annealing temperature up to 520 ^{o}C. As X-ray analysis showed it was connected with formation of nanocrystalline structure.

Conclusions

Initial glass-coated $Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$ microwires have an amorphous structure. Size of the coherently diffracting domains is approx. 2nm. Conventional annealing in temperature range 500 – 550 ^{o}C leads to the formation of nanocrystalline structure consisting of α-Fe(Si) nanograins in residual matrix through primary crystallization.

Annealing under tensile stress in this temperature range leads to the formation of the mixture of α-Fe(Si) and Fe_3B crystalline phases through eutectic crystallization.

The optimal soft magnetic properties of microwires are achieved at the annealing at 520 ^{o}C (coercivity ~ 65 A/m).

References

1. **Zhukov, A.** Glass-coated magnetic microwires for technical applications/ A. Zhukov // J. Magn. and Magn. Materials. – 2002. – V. 242-245 – P. 216-223.

2. **Chiriac, H.** Amorphous glass-covered magnetic wires: preparation, properties, applications / H. Chiriac, A.Ovari // Progress in Materials Science. – 1996. – V. 40. – P. 333-407.

3. **Hernando, B.** Magnetic domain structure of amorphous $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ wires under torsional stress/ B. Hernando, M.L. Sanchez, V.M. Prida, J.D. Santos, J. Olivera, F.J. Belzunce, G. Badini, M. Vazguez // J.Appl.Phys. – 2008. – N 103. – 07E716.

4. **Miguel, C.** Coercivity and induced magnetic anisotropy by stress and/or field annealing in Fe- and Co- based (Finemet - type) amorphous alloys/ C. Miguel, A. Zhukov, J.J. del Val, J. Gonzalez // J. Magn. Magn. Mater. – 2005. – N 294. – P.245-251.

5. **Di, Y.** Magnetic and microwave properties of glass-coated amorphous ferromagnetic microwires/ Y. Di, J. Jiang, G. Du, B. Tian, S. Bie, H. He// J. Trans. Nonferrous Met. Soc. China. – 2007. – N 17. – P.1352-1357.

6. **Blazguez, J.** Microstructure and magnetic properties of $Fe_{78-x}Co_xNb_6B_{15}Cu_1$ (x=18, 39, 60) alloys / J. Blazguez, V. Franco, C. Conde, A. Conde //J. Magn. Magn. Mater. - 2003. - N254-255. - P.460-462.

7. **Walter, J.L.** Crystallization of the amorphous alloys $Fe_{50}Ni_{30}B_{20}$ and $Fe_{80}B_{20}$ / J.L. Walter, S.F. Bartram, R.R. Russell // Met. Trans. – 1978. – V. 9A, N6 – P.803-814.

Received 13.07.2013.