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Structure and magnetic properties of the amorphous $Co_{80}Si_9B_{11}$ alloy

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Materials

ABSTRACT

Purpose: The main aim of the paper was to study the influence of heat treatment on changes of structure and magnetic properties of the amorphous $Co_{80}Si_9B_{11}$ alloy.
Design/methodology/approach: The following experimental techniques were used: X-ray diffraction (XRD), electrical resistivity in situ measurements (four-point probe), static and dynamic measurements of magnetic properties (magnetic balance, fluxmeter, Maxwell-Wien bridge).
Findings: The crystallization process involved by heat treatment leads to significant changes of phase composition and magnetic properties of amorphous $Co_{80}Si_9B_{11}$ alloy. The activation energy of this process was determined by Kissinger method, which yields Ec=3.0±0.2 eV.
Practical implications: According to the results presented in the present paper the examined $Co_{80}Si_9B_{11}$ alloy as a soft ferromagnetic material with high permeability may be utilized in construction of more inductive components and is of great technological interest.
Originality/value: The maximum permeability for examined alloy in as quenched state is about 11300.
Keywords: Amorphous materials; Nanomaterials; Heat treatment; Magnetic properties

1. Introduction

The Co-rich amorphous alloys have attracted great interest for a basic research on the materials as well as for a variety of applications including electronics, magnetic recording and magnetic sensors due to its near-zero magnetostriction, high permeability and saturation magnetization [1,2].

In the last decade, some nanocrystalline Co-based soft magnetic alloys have been obtained on the way of crystallization of amorphous alloys involved by heat treatment process. The crystallization process of amorphous alloys is the complex phenomenon, depending on chemical composition of alloy and conditions of heat treatment process [3÷5]. The heat treatment can be realized by conventional or impulse methods [6,7]. The method most often used is isothermal heating in constant time, for instance 0.5, 1.0, 1.5, 4.0, 8.0 hour [8÷12]. It is known that result of heat treatment process of amorphous alloys below the crystallization temperatures relaxes the residual internal stresses induced during the preparation process, improving the magnetic response of the material. Higher temperatures of heat treatment initiate the crystallization process in the amorphous materials [4,10,11,13]. Depending on the alloy chemical composition, transition from metastable amorphous structure to crystalline state (equilibrium or metastable) can proceeds in one stage (polymorphic or eutectic crystallization) or as a multistage process (primary crystallization) [4,5,14,15]. The primary crystallization of Co-Si-B alloys (without Fe additions) is known to result only hcp-Co phase [16,17]. The crystallization process of amorphous alloys is interesting because it is connected with the changes involved in chemical and physical (e.g. magnetic) properties which determine most applications [1,18÷23]. For that reason a few resent researches have focused on systematically studies of this process. The kinetics of crystallization of amorphous alloys is often described by the well-known phenomenological Johnson-Mehl-Avrami equation for isothermal experiments [24,25]. The activation energy of the crystallization process can be obtained from the temperature dependence of the reaction-rate constant, which is known as Kissinger's method [22,24,26].

The main of the present paper is to study the influence of heat treatment parameters on changes of structure and magnetic properties of the amorphous $Co_{80}Si_9B_{11}$ alloy involved by heat treatment.

2. Experiments

Amorphous alloy ribbons of composition $Co_{80}Si_9B_{11}$ were prepared by a planar flow casting method. Typical samples produced were 0.014 mm thick and 7 mm wide. Composition of samples was verified by X-ray fluorescence (XRF) using the SUPERPROBE 733 JEOL.

Sections of ribbons of 110 mm length were annealed in electric chamber furnace THERMOLYNE type F6020C with protective argon atmosphere in the temperature range from 373÷873 K with step of 50 K. The annealing time was constant and equal to 0.5 and 1 h.

The structure investigations have been performed by X-ray diffraction (XRD) method using diffractometer XRD7, SEIFERT-FPM. Crystalline phases were identified by XRD using filtered Co-K_α radiation.

Static and dynamic magnetic measurements of samples in as quenched state and after annealing in temperature range T_a= 373÷873 K, have been done. The following magnetic properties were measured: magnetic permeability μ_r (Maxwell-Wien bridge at frequency about 1 kHz and magnetic field =0.5 A/m; open coil, demagnetization factor was numerically and experimentally determined), saturation magnetization M and maximum permeability μ_{max}, (fluxmeter). Measurements of saturation magnetization M and maximum permeability μ_{max} were performed for the samples in as quenched state however initial relative magnetic permeability μ_r was performed for samples in as quenched state as well as after heat treatment.

Kinetics of the crystallization process was examined by applying two experimental techniques: electrical resistivity measurements in situ with different heating rates in the range 0.5÷4.4 K/min and measurements of saturation magnetization as a function of temperature $M(T)$. From the isochronous resistivity curve of the investigated alloy the crystallization temperature T_{x1} of the amorphous alloy and the effective activation energy for the crystallization E_c were determined. The crystallization temperature T_{x1} of samples can be obtained from the condition $d\rho/dT$=0. The effective activation energy for the crystallization E_c was evaluated by the Kissinger method [24,26], which is written as Eq. (1):

$$\ln \frac{V_l}{T_h^2} + \ln const = -\frac{E_c}{k_B} \cdot \frac{1}{T_h} \qquad (1)$$

where: E_c, is the effective activation energy for the crystallization processes, V_l , is linear heating rate, T_h – is the so-called temperature of an homological point determined for the heating rate V_l, i.e. temperature which the rate of crystallization process is maximum [24,27], and k_B is the Boltzman constant.

Measurements of saturation magnetization of samples were used. Samples in as quenched state were heated with heating rates: 5 and 10 K/min up to 1000 K, and simultaneously, $M(T)$ curves were recorded by applying magnetic balance technique. The results were presented as normalized curves $M(T)/M$(300 K).

3. Results and discussion

It was found from the obtained results of structural studies performed by X-ray diffraction that in as quenched state the $Co_{80}Si_9B_{11}$ alloy has amorphous structure (Fig. 1). Only a broad diffraction peak at about $2\Theta\cong52°$ can be observed from Fig. 1, indicating that obtained ribbon had amorphous structure.

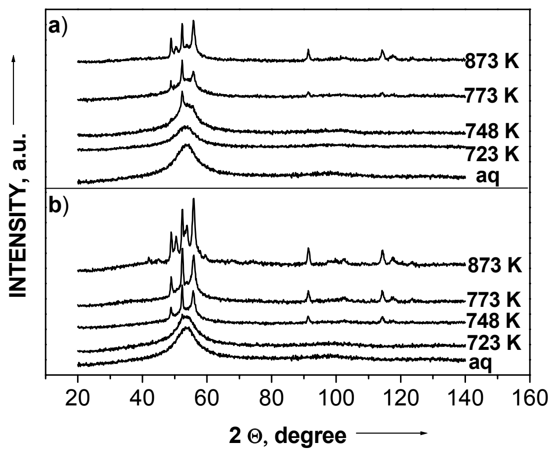

Fig. 1. X-ray diffraction pattern of the $Co_{80}Si_9B_{11}$ alloy in as quenched state and after annealing in temperature range 723÷873K for 0.5 h (a) and 1.0 h (b)

The investigated $Co_{80}Si_9B_{11}$ alloy in as quenched state has a high value of resistivity ρ equal 1.15 μΩm [22] and the following magnetic properties: saturation magnetization M= 0.8 T [22], initial relative magnetic permeability μ_r=1090 (Table 1) and μ_{max}=11300 (Fig. 2). The obtained physical properties, i.e. ρ, M, μ_r and μ_{max} allow to classify the $Co_{80}Si_9B_{11}$ alloy in as quenched state as a soft magnetic material.

There are three types of crystallization transformations for amorphous alloys: primary, polymorphous and eutectic [5].

The primary crystallization temperature - T_{x1} of $Co_{80}Si_9B_{11}$ alloy has been determined using different methods (both isothermal and non-isothermal).

From [22] shows that value of the crystallization temperature T_{x1} is dependent of the heating rate and is in the range of 655÷681 K for the heating rate 0.5÷4.4 K/min, respectively. Using the Kissinger method the effective activation energy of crystallization E_c was determined. The effective activation energy of the crystallization process determined, according to equation (1) is 3.0±0.2 eV [22].

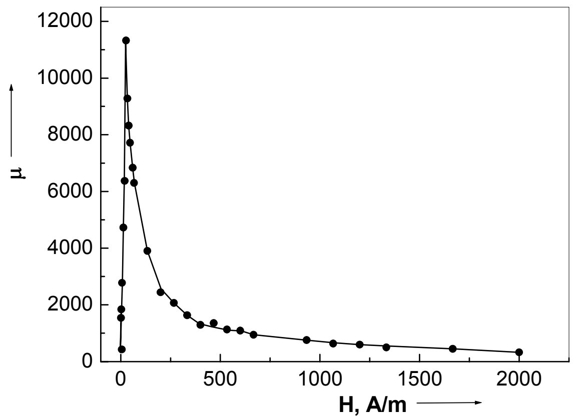

Fig. 2. The maximum permeability μ_{max} for amorphous $Co_{80}Si_9B_{11}$ alloy in as quenched state

Table 1
The parameters of heat treatment (temperature and time) and initial relative magnetic permeability μ_r of the $Co_{80}Si_9B_{11}$ alloy

Annealing temperature	The initial relative magnetic permeability μ_r of $Co_{80}Si_9B_{11}$ alloy after	
T_a, K	0.5 h annealing	1.0 h anneling
aq[1)]	1090	1090
373	1049	1056
423	916	1361
473	850	942
523	875	611
573	528	1073
623	531	445
673	361	581
723	589	798
748	120	145
773	65	69
823	58	56
873	57	56

[1)] - as quenched state

The crystallization temperature T_{x1} of $Co_{80}Si_9B_{11}$, determined from normalized in situ curves of magnetization is about 725÷730 K for the heating rate 5÷10 K/min [22].

The XRD analysis shows that the first stage of crystallization is above 723 K for the $Co_{80}Si_9B_{11}$ alloy heat-treated for 0.5 and 1.0 h (Fig. 1). The phases formed in different heat treatment conditions were identified using XRD, as in Fig. 1 and in [22]. From Fig. 1 it can be seen that three phases α-Co, Co_2Si and Co_3B are formed at lower temperatures while Co_2B formed at higher temperatures. The phases formed in primary and secondary crystallization have been determined using XRD. As can be seen from Fig. 1, samples heat-treated at 748 and 773 K for 0.5 and 1.0 h has similar phases. At 748 K the bulk crystallization of the amorphous alloy proceeds through nucleation of the hexagonal (h.c.p.) α-Co phase in the amorphous matrix, while at 773 K the α-Co, Co_2Si and Co_3B phases was identified. But for the samples heat-treated at 873 K for 0.5 and 1.0 h Co_2B phase appear. There are sharp changes in the intensity of the phases formed at higher temperature and longer time.

The detailed analysis of our experimental data shows that the values of crystallization temperature T_{x1} obtained from resistivity curves are always higher than the temperature T_{x1} deduced from magnetization measurements [22]. This difference cannot be explained neither by the unavoidable temperature gradient existing in both apparatuses nor by the natural dependence of magnetization on temperature [28].

Based on investigation results, it seems reasonable to conclude that the value of the crystallization temperature T_{x1} of an amorphous $Co_{80}Si_9B_{11}$ is strongly depend on the heat treatment conditions (linear heating or isothermal heating) and on the using methods. To compare the value of the crystallization temperature T_{x1} can take place only under a constant heating rate using different methods.

The worked out investigations at temperature annealing in range 373÷873 K by 1 h of the investigated alloy have showed that in mentioned temperature range, the changes of structure and magnetic properties took place (Fig. 1, Fig. 2, Table 1) [22].

From Table 1 it can be recognized that for the $Co_{80}Si_9B_{11}$ alloy annealed in temperature range from 373÷723 K for 0.5 and 1.0 h the initial magnetic permeability μ_r has high value i.e. 1049÷589 and 1056÷798, respectively. The heat treatment for annealing temperature – $T_a<T_{x1}$ connecting with annealing out of microvoids of $Co_{80}Si_9B_{11}$ alloy does not play a dominant role in significantly improve of initial relative magnetic permeability μ_r (Table 1) [27]. Heat treatment of $Co_{80}Si_9B_{11}$ alloy at temperature $T_a>T_{x1}$ involved decrease of initial relative magnetic permeability μ_r (Table 1) due to formation of Co_3B and Co_2Si besides α-Co phase (Fig.1) [22]. Increase of annealing temperature leads to further decrease of initial relative magnetic permeability μ_r (Table 1) which can be related to the formation of boride Co_2B besides mentioned phases [22].

4. Conclusions

The experimental results show that amorphous $Co_{80}Si_9B_{11}$ alloy in as quenched state is not in thermodynamic equilibrium. This is a consequence of rapid cooling from liquid phase. In fact, physical properties (e.g. electric and magnetic) of this materials exhibit relatively high instability with respect to both time and temperature. The thermodynamic equilibrium can induced by structural relaxation and crystallization involved by heat treatment. The activation energy of the crystallization process was determined by Kissinger method, which yields E_c=3.0±0.2 eV.

In $Co_{80}Si_9B_{11}$ alloy annealing out of microvoids taking place at lower temperature than the crystallization temperature T_{x1} does not lead to significant increase of initial relative magnetic permeability μ_r.

The initial relative magnetic permeability μ_r of $Co_{80}Si_9B_{11}$ alloy heat-treated at temperature above T_{x1} for 0.5 and 1.0 h rapidly decreases due to formation of phases like Co_3B and Co_2Si beside α-Co phase.

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