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Crystallization kinetics of an amorphous $Co_{77}Si_{11.5}B_{11.5}$ alloy

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Materials

ABSTRACT

Purpose: This paper describes crystallization kinetics and changes magnetic properties involved by process of crystallization Co-Si-B amorphous 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: In this work has been performed influence of thermal annealing on crystallization kinetics and magnetic properties amorphous $Co_{77}Si_{11.5}B_{11.5}$ alloy.
Practical implications: The attractive properties of Co-Si-B alloy are of special interest for basic research on the materials as well as for their potential applications, like magnetic sensors. The Co soft magnetic material is used in noise filters, saturable reactors, miniature inductance elements for abating spike noise, mains transformers, choke coils, zero-phase current transformers, and magnetic heads etc., i.e., devices which are expected to exhibit high levels of permeability at high frequencies.
Originality/value: It has been shown that thermal annealing at temperature close to the crystallization temperature leads to a significant increase of the initial magnetic permeability.
Keywords: Amorphous materials; Electrical properties and magnetic properties; Heat treatment annealing; X-ray diffraction method

1. Introduction

During the last years interest is raised to the study of amorphous magnetic alloys due to their combination of magnetic properties applications in the field of high performance electro-magnetic devices [1]. Amorphous and nanocrystalline alloys based on iron form one of the most interesting groups of soft magnetic materials. We can exchange Fe-, Ni- or Co-based amorphous magnetic alloys. The attractive properties of Co-Si-B alloy are of special interest for basic research on the materials as well as for their potential applications, like magnetic sensors. For example Co soft magnetic material may be used in power electronics, telecommunication equipment, sensing devices [2,3] Amorphous alloys can be prepared by a number of different techniques, e.g. thermal decomposition, mechanical alloying, melt-spinning. Compared to other techniques, rapid solidification processing can form metastable crystalline, qusiccrystalline or glassy phases and an extend solid solubility above the equilibrium limit [4,5].

Amorphous alloys for soft magnetic applications are usually given a stress relief annealing treatment to optimize their magnetic properties for low frequency applications [6]. It is know that amorphous alloys are not in thermodynamic equilibrium. This is a simple consequence of a rapid cooling from liquid phase. In fact, physical properties of these materials exhibit relatively high instability with respect to both time and temperature. Obviously such instabilities hinder their practical applications. In general, the thermodynamic equilibrium can be induced by structural relaxation and crystallization [7]. It is know that amorphous materials annealing below the crystallization temperature relaxes the residual internal stresses induced during the preparation process, improving the magnetic response of the material. Higher temperatures of annealing initiate the crystallization process, in the amorphous material [8]. The primary crystallization of Co-Si-B alloys (without Fe additions) is known to result only h.c.p.-Co phase [9÷11]. DSC technique is the most frequently used method to study the crystallization behavior. However, it needs the reaction to occur with a relatively large heat of crystallization and is not very useful when the reaction rate is slow or small heat transfer is involved. Electrical resistivity, in such situations, has a number of advantages. It is not only related to the phase type and volume fraction, but also the distribution of different phases. Therefore, it can give more detailed information on the crystallization [12÷13]. The crystallization behavior of metallic glasses has been studied by many researchers. It interesting because is connected with the changes involved in physical and chemical properties which determine most applications [14]. It has been reported that either the magnetic properties may deteriorate after crystallization or they may be improved nanocrystalline phases are formed [15]. In this paper we present and discuss crystallization kinetics and magnetic properties of Co-based amorphous alloy. Changes magnetic properties involved by process of crystallization was measured using X-ray diffraction (XRD), electrical resistivity in situ measurements (four - point probe) and initial relative magnetic permeability measurements (Maxwell - Wien bridge).

2. Experiments

Experiments were curried out on the $Co_{77}Si_{11.5}B_{11.5}$ group of amorphous alloy. Tapes obtained by planar-flow casting method were 0.020 mm thickness and 10.0 mm width. The samples of 110 mm long were annealed in argon atmosphere in temperature range from 373÷873 K with step of 50 K. The annealing time was constant and equal to 1 hour.

In order to study the structural changes taking place during structural relaxation and crystallization X- ray diffraction analysis (XRD7 SEIFERT – FPM) using cobalt K_α radiation have been used.

Magnetic properties were determined by making use of static and dynamic measurements of samples in as quenched state and after annealing in temperature range T_a= 373÷873 K, have been done (magnetic balance, fluxometer, Maxwell – Wien bridge; frequency=1 kHz and magnetic field=0.5 A/m.). Measurements of saturation magnetization M 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 annealing. The kinetic of the crystallization was examined by applying electrical resistivity measurements with continuous heating rate 4.7 K/min (so called in situ measurements) [7]. The Curie temperature of the examined alloy was determined (with the precision of about ±2 K by applying magnetic balance, i.e. saturation magnetization was measured as a function of temperature.

3. Results and discussion

The examinations made by applying X – ray diffraction technique show that in as quenched state the $Co_{77}Si_{11.5}B_{11.5}$ alloy has amorphous structure (Fig. 1).

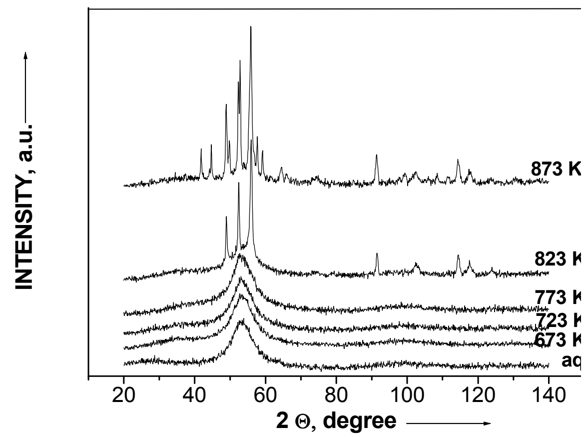

Fig. 1. X –ray diffraction pattern of the $Co_{77}Si_{11.5}B_{11.5}$ alloy in as quenched state and after annealing in temperature range 673÷ 873 K

The investigated $Co_{77}Si_{11.5}B_{11.5}$ alloy in as quenched state has a following magnetic properties like saturation magnetization M≅0.6 T (Fig.2), initial relative magnetic permeability μ_r=600 (Fig.3), and μ_{max}= 4500 (Fig. 6). The obtained physical properties: M, μ_r and μ_{max} allow to classify the $Co_{77}Si_{11.5}B_{11.5}$ alloy in as quenched state as a soft magnetic material [12].

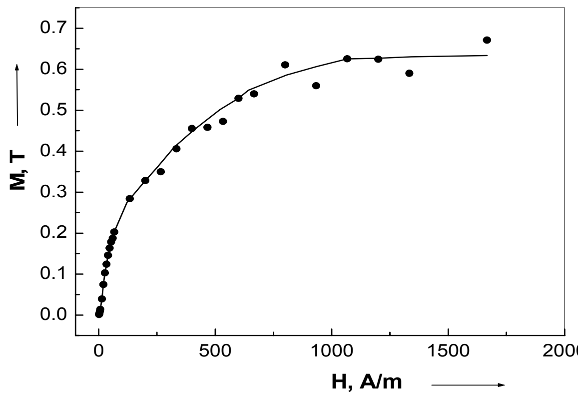

Fig. 2. Magnetization M versus magnetic field H for $Co_{77}Si_{11.5}B_{11.5}$ alloy obtained by fluxmeter

First stage of crystallization in $Co_{77}Si_{11.5}B_{11.5}$ alloy was found in the temperature range 773 ÷ 823 K (Fig. 1). Fig. 1 shows the XRD data obtained from the $Co_{77}Si_{11.5}B_{11.5}$ alloy ribbons annealing in temperature range from 673 ÷ 773 K can be seen that almost the same structure which in as quenched state. Increase of the annealing temperature above 773 K leads to changes of structure of the investigated alloy (Fig. 1). As can be seen from Fig. 1 at 823 K the crystallization of the amorphous alloy proceeds trough nucleation of the hexagonal (h.c.p.) α – Co phase in the amorphous matrix. Further increase of the annealing temperature leads to changes in X – ray diffraction pattern (Fig. 1) and at annealing temperature 873 K the existence Co_2B, Co_3B and Co_2Si phases were observed (Fig.1) besides to the α-Co phase.

Fig. 3 shows initial relative magnetic permeability μ_r measured at room temperature plotted versus 1 h annealing temperature. The changes of magnetic properties have been observed with increasing the temperature annealing of investigated alloy. From Fig. 3, it can be recognized that μ_r passes by a distinct maximum (at annealing temperature 723 K) related to formation of nanocrystalline phase α –Co, or annealing out of free volumes (microvoids) formed into during fabrication is observed [16]. The last stage of annealing, in the temperature range from 730 K up to 850 K, is characterized by decrease of magnetic permeability (Fig. 3) of investigated alloy. Existence of borides Co_2B and Co_3B observed leads to decrease of magnetic permeability (Fig. 3). This phenomenon (at temperature above 730 K) can be explained by formation of the equilibrium phases as well as the grain coarsening.

The ageing changes of electrical resistivity of ribbons after 1 h isothermal heating present Fig.3. In Fig.4 presented $\rho(T)$ curve obtained for $Co_{77}Si_{11.5}B_{11.5}$ alloy with linear heating rate 4.7 K/min. The observed strong decrease of ρ is due to crystallization of the amorphous alloy. The appearance of a long – range order leads to decrease of ρ value [7]. The resistivity behavior is typical for the usual crystallization from the amorphous phase, where the resistivity continuously decrees because the resistivity of the order alloy is lower than disordered one of the some composition (Fig. 3) [12]. Fig.5 shows a family of normalized curves $M(T)/M(300\text{ K})$ measured for $Co_{77}Si_{11.5}B_{11.5}$ alloy.

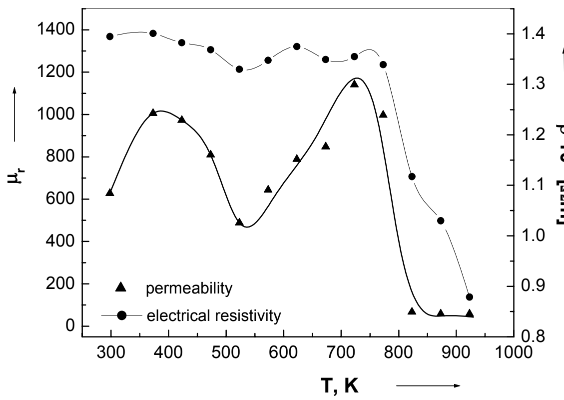

Fig. 3. Initial relative permeability μ_r and electrical resistivity ρ measured at room temperature for $Co_{77}Si_{11.5}B_{11.5}$ alloy after 1 h annealing

Measurement was done at magnetic balance with two heating rates: v=5 K/min and v=10 K/min. From this data, the Curie temperatures of the amorphous phase T_c can be determined by applying the condition $dM(T)/dT$=minimum. For v=5 K/min T_c equal 725 K and for v=10 K/min T_c equal 736 K.

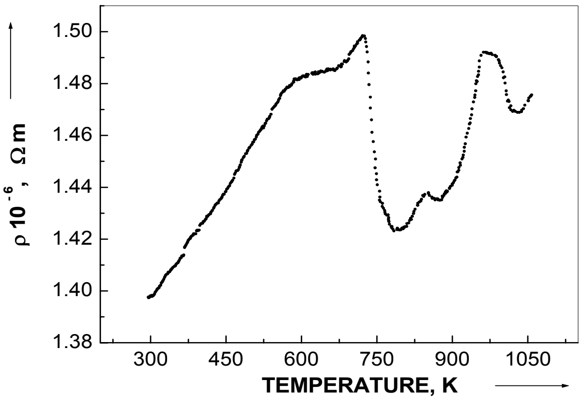

Fig. 4. The in situ isochronal resistivity curves for $Co_{77}Si_{11.5}B_{11.5}$ alloy obtained with heating rate 4.7 K/min

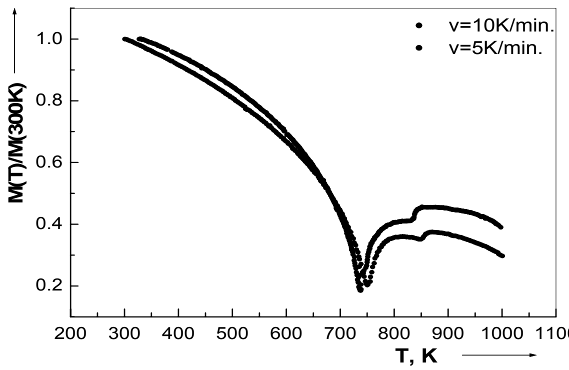

Fig. 5. Normalized magnetization versus temperature T of $Co_{77}Si_{11.5}B_{11.5}$ alloy

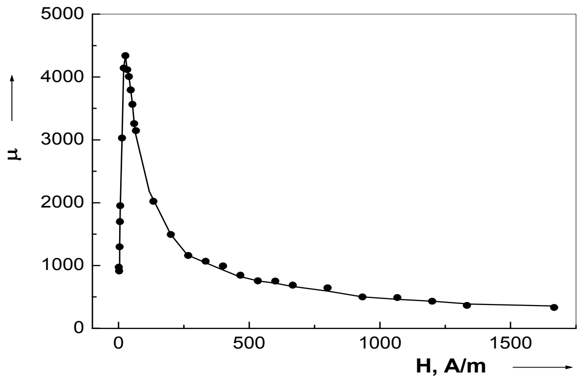

Fig. 6. The maximum permeability μ_{max} achieved from the primary curves of magnetization for $Co_{77}Si_{11.5}B_{11.5}$ alloy in as quenched state

4. Conclusions

The crystallization behaviour of the $Co_{77}Si_{11.5}B_{11.5}$ metallic glass is studied using different methods. The main conclusions of the present paper can be summarized as follows:

- the research results showed that $Co_{77}Si_{11.5}B_{11.5}$ alloy in as quenched state has an amorphous structure and physical properties like: initial relative magnetic permeability $\mu_r = 600$, saturation magnetization M=0.6 T, electrical resistivity ρ near 1.70μΩm, and classify the $Co_{77}Si_{11.5}B_{11.5}$ alloy in as quenched state as a soft magnetic material.
- the investigations proved that thermal annealing of amorphous $Co_{77}Si_{11,5}B_{11,5}$ alloy within the temperature range 373 ÷ 873 K leads to crystallization process and changes of magnetic properties.
- - the crystallization process leads to increase of initial relative permeability from 600 for ribbons in as quenched state to 1200 for ribbons heat treated at temperature 723 K. This phenomenon is connected with the formation of the hexagonal α–Co phase in an amorphous matrix at the temperature T = 823 K and this is the first stage of the crystallization process, what have been showed on X –ray diffraction.
- in the temperature T = 873 K appearance of boride phase Co_2B, Co_3B and silicide phase Co_2Si was state. It is the second stage of crystallization. The existence of boride phases was confirmed by a decrease of initial magnetic permeability μ_r after annealing. The secondary crystallization is known to cause grain coarsening of phases and the degradation of the soft magnetic properties [16].

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