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Influence of crystallisation anamorphous $Co_{77}Si_{11.5}B_{11.5}$ alloy on corrosion behavior

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Materials

ABSTRACT

Purpose: This paper describes crystallization kinetics and its influence on changes of electrochemical behavior of amorphous, amorphous relaxed and nanocrysalline $Co_{77}Si_{11.5}B_{11.5}$ alloy.

Design/methodology/approach: The following experimental techniques were used: structural research – X-ray diffraction (XRD) and electrochemical investigations were carried out by means of an electrochemical impedance spectroscopy method.

Findings: Heat treatment of amorphous $Co_{77}Si_{11.5}B_{11.5}$ alloy leads to the formation of the hexagonal α–Co phase in an amorphous matrix at the temperature T = 798 K and this is the first stage of the crystallization process. At the temperature T = 873 K appearance of boride phase Co_2B, Co_3B and silicates phase Co_2Si was state. It is the second stage of crystallization. The existence of boride phases was confirmed by after annealing in the temperature range from 730 K up to 873 K. The secondary crystallization is known to cause grain coarsening of phases and the electrochemical properties. The analysis leads to the conclusion that in view of data obtained from electrochemical tests in 3% NaCl solution, the crystallization process begins at lower temperatures than resulting from XRD data $Co_{77}Si_{11.5}B_{11.5}$ 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. Due to their numerous potential application nanocrystalline cobalt based alloys could be work in a wet industrial and marine atmosphere containing sulphide and chloride ions. Electrochemical corrosion can changes structure and magnetic properties of Co-based alloys.

Originality/value: It has been shown that thermal annealing at temperature lower than the crystallization temperature leads to a significant changes of the initial electrochemical behavior in 3% NaCl solution.

Keywords: Metallic Alloys; Amorphous materials; X-ray diffraction method; Electrochemical impedance method

1. Introduction

Amorphous and nanocrystalline alloys based on cobalt 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. When bulk amorphous alloys for their good static and dynamic mechanical properties are used as structural materials, it is essential for the bulk amorphous alloys to have good corrosion resistance in various kinds of corrosive solutions [1 – 6].

Nanocrystalline soft magnetic materials with low coercivity, high saturation magnetisation and high permeability are commonly used as cores in transformers and generators in stress and field sensors. Due to their numerous application nanocrystalline iron based alloys often work in a wet industrial and marine atmosphere containing sulphide and chloride ions. The influence of factors connected with corrosion is almost impossible to eliminate.

It is well known that amorphous alloys are non stable materials. This is a consequence of a rapid cooling from liquid phase. In general, the thermodynamic equilibrium can be induced by structural relaxation and crystallization [7]. Suitable high 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]. The crystallization behavior of metallic glasses has been studied by many researchers. The physical properties, such a corrosion resistance, in amorphous metallic materials mostly depends on their structure and phase compositions [12 – 15].

There have been a few data published on the electrochemical behavior of Co – based bulk amorphous alloys in corrosive solution. That is why we decided to examined the corrosion resistance of melt-spun amorphous $Co_{77}Si_{11.5}B_{11.5}$ alloy in 3% NaCl solutions In this paper we present and discuss crystallization kinetics and corrosion properties of Co-based amorphous alloy. Changes involved by process of crystallization was measured using X-ray diffraction (XRD) and electrochemical behavior measured using an electrochemical impedance spectroscopy (EIS).

2. Experiments

Experiments were carried out on the $Co_{77}Si_{11.5}B_{11.5}$ 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 (Table 1). Electrochemical properties were determined by using an Eco Chemie B.V PGSTAT30 Potentiostat and accompanying software FRA (Frequency Response Analyzer System).

The electrochemical impedance experiment were performed at open circuit potential. The measurements were made in the frequency range between 20kHz and 1Hz. with perturbation amplitude of 0.05 mV. Impedance spectra have been presented as Bode phase and Bode magnitude plots. The Bode plots are used because it has been argued that they are more informative than the conventionally popular Nyquist plots. The tests were carried out in 3% NaCl solution.

3. Results and discussion

The examinations of structure performed by X-ray diffraction (XRD) technique show that in as quenched state the $Co_{77}Si_{11.5}B_{11.5}$ alloy has amorphous structure.

In Figure 1 the X –ray diffraction pattern of the $Co_{77}Si_{11.5}B_{11.5}$ alloy in as quenched state is presented

First stage of crystallization of $Co_{77}Si_{11.5}B_{11.5}$ alloy was found in the temperature range 773 ÷ 823 K. Figure 1 shows the XRD data obtained from the $Co_{77}Si_{11.5}B_{11.5}$ alloy ribbons annealing in the 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 798 K the crystallization of the amorphous alloy proceeds trough nucleation of the hexagonal (h.c.p.) α – Co phase in the amorphous matrix [16]. 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 besides to the α-Co phase [16].

The results of XRD – method proved that β - Co phase (bcc) did not indicate in the samples of $Co_{77}Si_{11.5}B_{11.5}$ alloy annealed at 873 K for 1 h (see Fig. 2).

Table 1.
The diffractometer's parameters used in XRD method for samples of $Co_{77}Si_{11.5}B_{11.5}$ alloy

Diffractometer's parameters	Diffractometer XRD 7, SEIFERT - FPM firm	
	a	**b**
Current intensity of X – ray tube	40 mA	40 mA
Voltage of X – ray tube	35 kV	35 kV
The time of counting in one measurement's point	7s	20s
Step between measurement's points	0.05°Θ	0.01°Θ

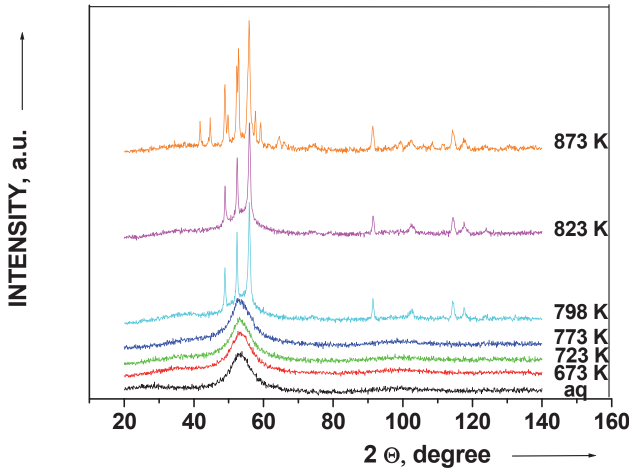

Fig. 1. X –ray diffraction pattern of the $Co_{77}Si_{11.5}B_{11.5}$ alloy in as quenched state and after annealing in temperature range T_a=673÷ 873 K

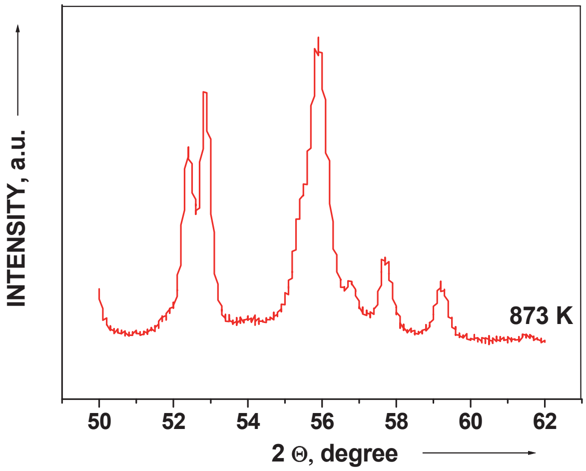

Fig. 2. X – ray diffraction pattern of the $Co_{77}Si_{11.5}B_{11.5}$ alloy after annealing at temperature 798 K for 1 h. The parameters of diffractometer – see Table 1

The EIS method does not accelerate the corrosion reaction and is nondestructive technique due to the low magnitude of applied voltage signal. And it is quite sensitive to changes in the resistive – capacitive nature of electrochemical interface [17 – 19].

Impedance spectra usually are present as Bode phase and Bode magnitude as a function of frequency plots. In this paper impedance spectra have been presented as Bode phase and Bode magnitude plots for heat treated samples in a rage of temperatures from 373K to 673K in Fig. 3, and in Fig. 4 impedance spectra for heat treated samples in a rage of temperatures from 723K to 923K. Bode plots are used because it has been argued that they are more informative than the conventionally popular Nyquist plots [21].

Comparison of impedance spectra recorded on annealed samples at temperature lower than 723K and annealed samples at temperature upper than 723K, differences may be observed in their shape as in the Θ vs. log f plots, see Fig 3 and Fig 4. Thermal annealing of amorphous $Co_{77}Si_{11,5}B_{11,5}$ alloy is connecting with the formation of the hexagonal α–Co phase in an amorphous matrix at the temperature T = 798 K. But in view of data obtained from electrochemical research, the crystallization process begins earlier, at lower temperatures.

The impedance spectrum obtained for amorphous and amorphous relaxed ribbons is presented in Figure 3. As can be seen, there were little differences between recorded data. The phase angle maximum is near – 75º and it is narrow. At a medium and low frequencies, the phase angle abruptly decreases and approach constant value between – 15º and – 30º.

At the temperature T = 873 K appearance of boride phase Co_2B, Co_3B and silicate phase Co_2Si was state. But we recorded differences in the electrochemical behavior for lower temperature of annealing (already at a temperature 723K). It points that the crystallization process could starts first at a surface of amorphous ribbons.

Capacitive behavior of $Co_{77}Si_{11.5}B_{11.5}$ alloy after annealing temperature range of 723ºC to 923ºC dominates in the wider range of frequencies in comparison to the earlier discussed samples.

The phase angle maximum is significantly higher. It points to the presence of thinner and more homogeneous films. At lower frequencies, the phase angle decreases and approach constant value between – 5º and – 45º.

In Our opinion results indicates that changes of electrochemical behavior in 3% NaCl of the heat treated amorphous alloy was attributed to a larger rate of silicon diffusion. Probably it leads to a larger rate of silicon deposition on the surface and growth of a continuous and protective SiO_2 film [14, 20].

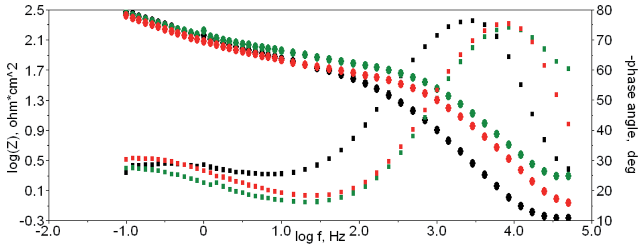

Fig. 3. Bode plots of impedance spectra for amorphous (black), heat treatment at 523K (red) and heat treatment at 673K (green) samples recorded in 3% NaCl solution

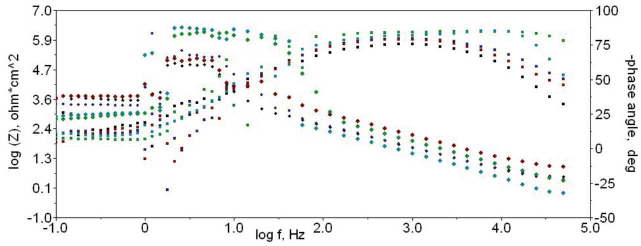

Fig. 4. Bode plots of impedance spectra for: heat treatment at 723K (black), heat treatment at 773K (red), heat treatment at 823K (green), heat treatment at 873K (blue), heat treatment at 923K (cyan) samples recorded in 3% NaCl solution

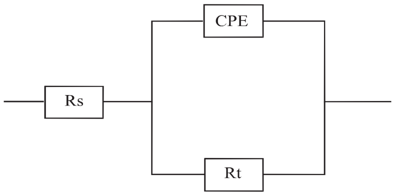

Fig. 5 An equivalent circuit model of heat treatment $Co_{77}Si_{11,5}B_{11,5}$ samples in temperature range 723K to 923K at corrosion potential in 3% NaCl solution, where Rs – solution resistance, Rt - charge transfer resistance, CPE – capacitance of constat phase element

The best fitting for impedance spectrum heat treatment $Co_{77}Si_{11,5}B_{11,5}$ samples in temperature range 723K to 923K was obtained using the equivalent shown in Figure 5.

This behavior can be interpreted according to this simple equivalent circuit model. Here Rt is the metal charge – transfer resistance of bare alloy, Rs is the resistance of the solution and CPE is the Faradic capacitance.

4. Conclusions

The influence of crystallization on electrochemical behavior of the $Co_{77}Si_{11.5}B_{11.5}$ metallic glass is studied using XRD and EIS 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,
- 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. This phenomenon is connecting with the formation of the hexagonal α–Co phase in an amorphous matrix at the temperature T = 798 K and this is the first stage of the crystallization process,
- 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 secondary crystallization is known to cause grain coarsening of phases and changes of electrochemical properties in 3% NaCl corrosive solution,
- In view of results from the electrochemical measurements, it could affirm the crystallization process starts first at a surface of amorphous ribbons. There were recorded differences in the electrochemical behavior for lower temperature of annealing (already at a temperature 723K).

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