Changes of magnetic properties of Co$_{78}$Si$_{9}$B$_{13}$ metallic glass in the crystallization process

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Abstract. The crystallization process of Co$_{78}$Si$_{9}$B$_{13}$ metallic glass starts at 648 K and as a result of this the ε-Co(Si) phase with needle morphology is formed. The second stage of the crystallization follows after annealing at 773 K and as a consequence of this the main phases: α-Co(Si) and (Co,Si)$_3$B, (Co,Si)$_2$B are created. Crystallites of the α-Co(Si) phase have layer morphology. The coercivity increases after the both stages of the crystallization.

1. Introduction

As-quenched metallic glasses are in the metastable state. This metastability is understandable, because the solid state is obtained as a result of rapid solidification. Therefore, the as-quenched metallic glasses possess the structure characteristic of the liquid with short range ordering (SRO). The as-received metallic glasses are in a higher energetic state because atoms during the quick transition from the liquid to the solid state do not take up an equilibrium position, in which they would have lower energy. So, the metallic glasses undergo structural changes first through the structural relaxations of type chemical and/or topological short range ordering (CSRO, TSRO) and next medium (MRO) and finally to long range ordering (crystallization) [1,2]. Under the influence of different stimulating factors (e.g. annealing at different temperatures or isothermal annealing during different time intervals and annealing by contribution of additional conditions as magnetic field, and stress) they evolve with different rate to the stable polycrystalline state [3-6]. Depending on their composition the process of the crystallization proceeds through one or many stages and various types of transformation are possible: primary, eutectic, polymorphic or peritectic [7,8]. The process of structural changes is accompanied by changes in the physical properties. The magnetic properties (coercivity, saturation magnetization, remanence, Curie temperature) are particularly sensitive to the structural changes [9]. Considering the application of the ferromagnetic metallic glasses, it is important problem to specify the conditions in which the amorphous structure is satisfactorily stable in a given time and temperature range.

In this paper are presented the results of the structural changes of the Co$_{78}$Si$_{9}$B$_{13}$ metallic glass on the magnetic properties, which are important applicational parameters, i.e. saturation magnetization, remanence and coercivity. Progressive process of crystallization was stimulated by a controlled
annealing. By means of X-ray diffraction and transmission electron microscopy (TEM) the sequence of the creation of the crystalline phases from the amorphous matrix was stated.

2. Experimental

The Co$_{78}$Si$_9$B$_{13}$ metallic glass was prepared by the melt spinning technique in Faculty of Materials Science and Engineering of Warsaw University of Technology in Poland. X-ray diffraction was done at the room temperature for the non-annealed as well as isochronally (4 h) annealed samples at various temperatures (573 K - 823 K) and for the isothermally (648 K) annealed samples during different time intervals ($10^4$ s - $2 \cdot 10^4$ s). The annealing was always made for the as-received samples in an inert argon atmosphere. The X-ray studies were performed using a DRON-2.0 diffractometer with a horizontal goniometer of GUR-5 type. The X-ray tube had a molybdenium target ($\lambda_{K\alpha} = 0.71069 \cdot 10^{-10} \text{m}$) and a graphite monochromator in the primary beam.

The microstructure and phase composition were studied by transmission electron microscopy (TEM) using JEOL-JEM 3010 microscope with EDS detector. Thin foils for transmission electron microscopy were prepared by ion polishing. Partially the investigations of the microstructure and phase composition were studied also by the high resolution transmission electron microscopy (HRTEM) using Philips CM 20 Super Twin microscope. For these studies fine powder sample was prepared by grinding the sample in mortar and dispersing in methanol with ultrasonic agitation. A droplet of suspension was deposited on a microscope grid covered with holey carbon film.

The magnetic properties were determined from the measured hysteresis loops at room temperature using a vibration sample magnetometer (VSM-Lake Shore) operating in a magnetic field up to 2 T. From the hysteresis loops for non-annealed samples as well as annealed at 648 K and 823 K the values of magnetic parameters like coercivity, remanence and specific saturation magnetization were determined.

3. Results and discussion

The values of the magnetic parameters: coercivity $H_c$, remanence $M_r$ and specific saturation magnetization $M_s$ [10,11] for non-annealed samples as well as annealed at 648 K and 823 K were obtained from the hysteresis loops (Fig.1) and are listed in table 1.

| sample           | $H_c$ [kA/m] | $M_s$ [Am$^2$/kg] | $M_r$ [Am$^2$/kg] |
|------------------|--------------|-------------------|-------------------|
| non-annealed     | 0,15         | 104,14            | 0,48              |
| annealed at 648 K| 7,34         | 82,88             | 6,99              |
| annealed at 823 K| 40,43        | 90,23             | 19,92             |

The increase of the coercivity after annealing at 648 K and 823 K correspond to Herzer diagram for the nanocrystallites, according to which: $H_c \propto D^6$ ($D$ – average grain diameter) [12].
The obtained values of coercivity and the average grain diameters show the following dependences:

\[
\left( \frac{H_{c,823K}}{H_{c,648K}} \right)^{1/6} = 1.33 \quad \text{and} \quad \frac{D_{823K}}{D_{648K}} \approx 1.31.
\]

It agrees with Herzer diagram [12]. The increase of coercivity (49 and 270 times bigger after the first and second stages of crystallization, respectively, than in the non-annealed state) is caused by the characteristic morphology of the created crystallites during crystallization, the needle one after the first stage (Fig.2) and the layer one after the second stage (Fig.3). The pictures of the microstructure obtained by the electron microscopy for the samples after the annealing at the 648 K and 823 K show different morphology of the crystallites. These are crystallites with needle morphology (Fig.2) and a numerous group with layer morphology (Fig.3). The second ones are polycrystallites of fused crystallites from the early stage of crystallization and the ones growing in the second stage of crystallization.

In order to analyse of the structural changes and identify the crystalline phases formed in the transformation of Co$_{78}$Si$_{9}$B$_{13}$ metallic glass from the parent amorphous matrix to the crystalline state besides TEM study the X-ray investigations were performed. The X-ray diffraction made for the non-annealed as well as annealed samples (Fig.4a). The X-ray diffraction performed for the samples annealed at different temperatures (573 K - 823 K) during 4 h allowed to observe the occurring structural changes. It was stated that after the annealing at the temperature 648 K the metallic glass starts the primary crystallization, and the crystallizing phase is the hexagonal $\varepsilon$-Co(Si) [13]. This was proved by the X-ray diffraction patterns (Fig.4b) obtained for the samples annealed isothermally at this temperature in different times ($10^3$ s - $2 \cdot 10^4$ s).

The phase identification proved the existence of the crystalline metallic phase of type $\alpha$-Co(Si) as well as the boron phases: (Co,Si)$_2$B (Co,Si)$_3$B and a small part of the metallic phase of type $\varepsilon$-Co(Si) after the final annealing (823 K) [13, 14]. The creation of the metallic phase $\alpha$-Co(Si) and boron phases is a result of the eutectic crystallization, which occurs after the annealing at the temperature 773K. The trace amount of the phase $\varepsilon$-Co(Si) can be explained by the polymorphous reaction, which results in transformation of the phase $\varepsilon$-Co(Si) into $\alpha$-Co(Si) phase. This transformation correlates with the phase diagram Co-Si, which shows that 693 K is the temperature of transformation:

$$\varepsilon$$-Co(Si) $\rightarrow$ $\alpha$-Co(Si) [15].

The typical microstructure of the Co$_{78}$Si$_{9}$B$_{13}$ alloy after annealing at 823 K is presented in the Fig.3. and this characteristic image proves that the alloy possesses of the full crystallization. However, the
investigations by means of the high resolution transmission electron microscope (HRTEM) point that in the volume of the alloy the rest of the amorphous phase exist (Fig.5).

**Figure 2.** TEM micrograph for the sample of the Co$_{78}$Si$_{9}$B$_{13}$ alloy annealed at 648 K for 4 h and grain size distribution, a – the electron diffraction pattern for ε-Co(Si).

**Figure 3.** TEM micrograph for the sample of the Co$_{78}$Si$_{9}$B$_{13}$ alloy annealed at 823 K for 4 h and grain size distribution, a – the electron diffraction pattern for Co$_{2}$Si.
Figure 4. X-ray diffraction patterns for samples of the Co$_{78}$Si$_9$B$_{13}$ alloy annealed: at different temperatures (a), during different time intervals at 648 K (b).

Figure 5. HRTEM image for the sample of the Co$_{78}$Si$_9$B$_{13}$ alloy annealed at 823 K for 4 h.

In the Fig.5, in the amorphous background are the visible nanocrystallites between 2.5 and 25 nm sizes. The phase analysis of them was carried out by FFT (Fast Fourier Transform) patterns obtained from the HRTEM image of the nanocrystallites proves that these are CoB compounds [16].
4. Conclusions  
- The crystallization process of Co$_{78}$Si$_9$B$_{13}$ metallic glass proceeds through two main stages at 648 K and 773 K.  
- The hexagonal metallic phase ε-Co(Si) formed during the first stage of crystallization transforms through the polymorphous reaction into regular phase α-Co(Si).  
- Both stages of the crystallization are accompanied by different morphologies of the crystallites: needle and layer in the first and the second stages of crystallization, respectively.  
- The characteristic morphology of the crystallites is responsible for the increase of coercivity after the first and the second stages of crystallization.  
- HRTEM study for the samples of the alloy annealed at 823 K for 4 h proves that in the volume of the alloy the rest of the amorphous phase exists.

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