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The effect of annealing on magnetic properties, phase structure and evolution of free volumes in Pr-Fe-B-W metallic glasses

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ABSTRACT

In the present work magnetic properties, phase structure and evolution of free volumes in the rapidly solidified $Fe_{65}Pr_9B_{22}W_4$ alloy ribbons in as-cast state and those subjected to short-time annealing were investigated. The base alloy was prepared by arc-melting of the high purity elements under an Ar atmosphere. The ribbon samples were obtained by melt-spinning technique under reduced pressure of Ar. As-cast samples were fully amorphous and have shown soft magnetic properties. In order to develop nanocrystalline microstructure, the specimens were annealed at temperatures ranging from 929 K to 1003 K for 5 min. Heat treatment caused the increase of volume fractions of hard magnetic phase, which was accompanied by significant changes of hysteresis loops. XRD studies revealed evolution of phase constitution of annealed ribbons. All annealed specimens contained hard magnetic $Pr_2Fe_{14}B$ and paramagnetic $Pr_{1+x}Fe_4B_4$ phases. Positron annihilation lifetime spectroscopy (PALS) has been applied for detection of vacancy defects and positron-trapping voids.

1. Introduction

Currently, RE-Fe-B alloys are the most frequently used permanent magnets allowing reduction of size of electromagnetic devices, while maintaining their performance. A big disadvantage of this type of magnets is rather high cost of their production, that is generated by use of large quantity of rare-earth elements as well as energy consumption in processing route. Therefore current studies are focused on development of alloys containing low fraction of RE in their chemical composition [1–4] and on improvement of their glass forming abilities that would allow application of rapid solidification techniques [5].

An interesting group of RE-based magnets are Pr-Fe-B-type alloys, in which $Pr_2Fe_{14}B$ phase is responsible for the high coercivity [6]. The $Pr_2Fe_{14}B$ phase does not undergo a spin reorientation down to 4.2 K [7], thus resulting in superior magnetic properties at low temperatures. In addition it has high value of magnetocrystalline anisotropy field [8]. These factors cause that the Pr-Fe-B magnets are attractive for applications in a wide range of temperatures [9]. Admixture of refractory elements, such as: Zr, Nb or W is frequently used in tailoring glass forming abilities as well as magnetic properties [10–14]. Attaining optimal magnetic parameters is closely related to the technological process in which the proper phase composition and microstructure are obtained. Frequently used method of processing hard magnetic materials is the melt-spinning of induction molten alloy under controlled atmosphere of Ar [15,16]. To obtain good magnetic properties, suitable annealing conditions are also crucial [17]. Application of rapid solidification processes allows cutting the manufacturing costs due to reduction of time and energy needed for development of the nanocrystalline microstructure.

Positron annihilation lifetime spectroscopy [18–20] is an interesting method to provide information about characteristic positron annihilation sites – typically atomic-sized lattice defects, such as vacancies, dislocations, grain boundaries. Therefore, it could be useful technique for material characterization [21] and deeper understanding of microstructural changes [22]. This method allows examining relaxation and crystallization processes of metallic glasses. For amorphous alloys the information provided by PALS essentially comes from the atomic-size or a vacancy-like free volumes (small sub-vacancy-sized free volume or excess of free volume) inside the structure. PALS also can provide information about sub microscopic defects and therefore can be useful for studies of

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the interfacial structure of amorphous and nanocrystalline materials [23–25].

The aim of the present paper was the study of the influence of annealing conditions on the vacancy defects, phase constitution and magnetic properties of the rapidly solidified $Fe_{65}Pr_9B_{22}W_4$ alloy ribbons.

2. Sample preparation and experimental methods

The ingot samples of the nominal composition of $Fe_{65}Pr_9B_{22}W_4$ were obtained by arc-melting of the high purity elements under low pressure of Ar. In order to homogenize the alloy, the ingot sample was re-melted several times. Subsequently, the ribbon specimens were produced by melt-spinning technique under the Ar atmosphere at linear speed of the copper roll surface of 25 m/s. Nanocrystalline microstructure was obtained by annealing of ribbons at temperatures ranging from 929 K to 1003 K for 5 min and quenching in water. The range of annealing temperatures was chosen base on analysis of crystallization behavior using DSC studies. In order to maintain the purity of the atmosphere during heat treatment, the ribbon samples were sealed-off in a quartz tube under low pressure of argon. Room temperature hysteresis loops were measured by LakeShore VSM 7307 vibrating sample magnetometer at external magnetic field up to 2 T. The phase structure was studied using Bruker D8 Advance diffractometer with CuKα radiation equipped with LynxEye detector (linear focus of 25 mm, primary beam divergent slit − 0.6 mm) with Soller slits on primary and diffracted beam. The measurements were performed in Bragg-Brentano configuration with K_β filter on detector side. The 2θ step size was 0.02 deg. and step time 5 s. Rietveld refinement of XRD patterns was performed using DIFFRAC Plus TOPAS 4.2 software in 2θ range from 30 deg. to 90 deg. to obtain the weight fractions of constituent phases, crystallite sizes and unit cell parameters. Mössbauer spectra were measured using transmission mode Mössbauer spectrometer with ^{57}Co source within the Rh matrix and subsequently analyzed using WinNormos for the Igor 3.0. The ribbons were crushed to powder in order to obtain a specimens representative for the entire volume of the material. Positron lifetime measurements (PALS) were performed at room temperature using a ORTEC spectrometer, based on a “start-stop” method [26,27]. The spectrometer with a lifetime resolution (FWHM) of 270 ps was monitored with a ^{60}Co source and used to record all PALS spectra. The sample, along with the source of positrons (^{22}Na isotope of an activity 4×10^5 Bq) and Kapton foil (with thickness of 6 μm), formed so-called “sandwich” system. Positron lifetime spectra were analysed using the LT computer program [28].

3. Results and discussion

The XRD scans were measured for $Fe_{65}Pr_9B_{22}W_4$ alloy ribbons in as-cast state and for those subjected to annealing. For the as-cast sample, a wide bump on XRD pattern in the range of 2Θ from 30 to 50 deg is characteristic for the amorphous phase. Short-time heat treatment resulted in significant changes of the phase constitution. The sample annealed at 929 K for 5 min was not fully amorphous, however the appearance of just one diffraction peak did not allowed the clear identification of the present crystalline phases (Fig. 1). Heat treatment at the 948 K and higher temperatures for 5 min resulted in decrease of volume fraction of the amorphous phase and allowed to obtain a nanocrystalline structure consisting of the hard magnetic $Pr_2Fe_{14}B$ and the paramagnetic $Pr_{1+x}Fe_4B_4$ phases (Fig. 2).

In order to determine the weight fraction of constituent phases as well as the crystallite sizes and unit cell parameters, the Rietveld refinement was performed (Fig. 2). The results were summarized in Table 1. A presence of paramagnetic $Pr_{1+x}Fe_4B_4$ and hard magnetic $Pr_2Fe_{14}B$ crystalline phases, has been taken into account in the refinement. Furthermore, for obtaining the best fit, an existence of heterogeneous microstructure was considered. Therefore in the refinement procedure, two components representing $Pr_2Fe_{14}B$ crystal structure were taken into account. The argument for considering two different crystallographic representation of the hard magnetic phase in the Rietveld refinement was based on analysis of Mössbauer spectra (Fig. 3), where presence of large fractions of highly disordered phases was observed in annealed ribbons. The lattice parameters of the constituent phases changed slightly with annealing temperature. The crystallite sizes of identified phases are of the nanometer size for all phase components. However, the hard magnetic phase form nanocrystals of various sizes. Furthermore, calculated differences in the unit cell parameters for components representing the $Pr_2Fe_{14}B$ phase significantly differ. In case of one component (denoted as the ordered $Pr_2Fe_{14}B$ phase in Table 1) the unit cell parameters remain close to the starting values (a = 8.775 Å and b = 12.1218 Å), while those for the disordered one significantly differ. This indicates that the second component of this phase is not fully ordered. This observation was supported by a complementary Mössbauer studies of annealed ribbons (Fig. 3). The reason for that is a possibility of replacement of Fe positions by W in the disordered $Pr_2Fe_{14}B$ phase. The weight fraction of the disordered representation of the $Pr_2Fe_{14}B$ phase decreases with the rise of the annealing temperature. Furthermore crystallite sizes calculated for the ordered component of this phase do not change significantly with the annealing temperature, while in case of disordered one, slight increase of crystallites from 11.5 nm to 23.5 nm was shown. Moreover, the weight fraction of $Pr_{1+x}Fe_4B_4$ phase increases from 39.2 wt % to 48.8 wt % with the increase of the annealing temperature.

Analysis of Mössbauer spectrum for the as-cast sample confirmed its amorphous structure, where large broadening of the Mössbauer line, typical for glassy alloys, was measured. In the fitting procedure, the hyperfine field distribution was calculated and experimental spectrum was fitted by broad line corresponding to this distribution. In case of annealed samples a presence of paramagnetic $Pr_{1+x}Fe_4B_4$ phase was represented by doublet line. Furthermore, the existence of $Pr_2Fe_{14}B$ phase was defined by six Zeeman lines corresponding to the magnetically nonequivalent positions of the Fe atoms in the unit cell of $Pr_2Fe_{14}B$ phase. In the

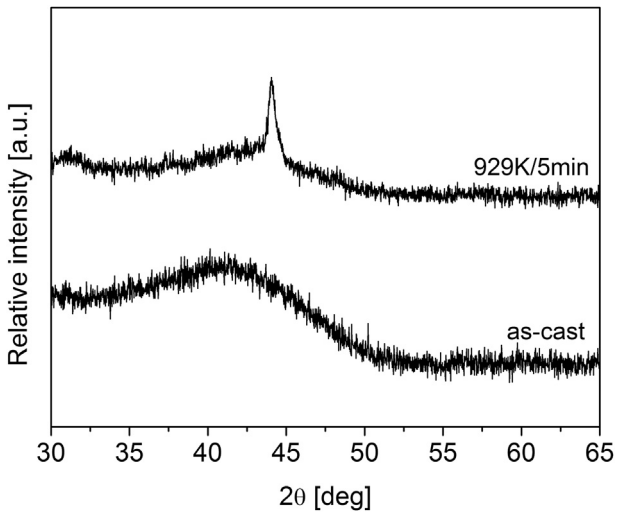

Fig. 1. X-ray diffraction patterns of rapidly solidified $Fe_{65}Pr_9B_{22}W_4$ alloy ribbons in as-cast and annealed at 929 K for 5 min.