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Medium range ordering and some magnetic properties of amorphous $Fe_{90}Zr_7B_3$ alloy

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ABSTRACT

High-resolution electron microscopy (HREM) reveals in the as-quenched $Fe_{90}Zr_7B_3$ alloy the existence of medium range ordered (MRO) regions 1–2 nm in size. Transmission Mössbauer spectroscopy confirms that these regions are α-Fe MRO ones. Above the Curie point of the amorphous phase (T_C=(257 ± 2)K) they behave like non-interacting superparamagnetic particles with the magnetization decreasing linearly with the temperature. For these particles the average magnetic moment of 390μ_B and the average size of 1.7 nm, in excellent agreement with HREM observations, were estimated. The maximum of the isothermal magnetic entropy change at the maximum magnetizing field induction of 2 T occurs at the Curie temperature of the amorphous phase and equals to 1.05 Jkg^{-1} K^{-1}. The magnetic entropy changes exhibit the linear dependence on the maximum magnetizing field induction in the range 0.5–2 T below, near and above T_C. Such correlations are attributed to superparamagnetic behavior of α-Fe MRO regions.

1. Introduction

Amorphous structures are characterized by the lack of the long range translational symmetry and angle correlations in atoms arrangement. For an individual atom, a short range ordering involving the nearest neighbor atoms can be considered. If the space configuration of atoms is taken into account, one can speak about topological short range ordering (TSRO). When kinds of atoms are under consideration, one deals with chemical short range ordering (CSRO). The changes in TSRO and CSRO, which usually take place at elevated temperatures, are commonly known as amorphous structure relaxations [1].

Modern experimental techniques, such as high-resolution electron transmission microscopy and Mössbauer spectroscopy, reveal the existence of fringe like structures in amorphous alloys [2–5], which correspond to the medium range ordered (MRO) regions 1–2 nm in size. These regions grow during annealing at temperatures lower than the crystallization ones and become the nuclei of the crystalline grains [3,5].

Magnetic properties of iron rich amorphous $Fe_{100-x}Zr_x$ alloys ($7 \le x \le 12$) were intensively investigated in the two last decades of the twentieth century. Ryan et al. [6] proposed the magnetic structure of these alloys as a "wandering axis ferromagnet" with moments aligned over domains of dimension 2–3 nm. Below a temperature $T_{xy} < T_C$ (T_C—the Curie point), the spins freeze randomly to asperomagnetic order. Moreover, Kaul et al. [7–9] in order to elucidate the low temperature magnetic properties and small angle neutron scattering experiments in $Fe_{100-x}Zr_x$ ($7 \le x \le 12$) amorphous alloys proposed the model of magnetically ordered finite clusters embedded in the ferromagnetic infinite matrix, but both clusters and matrix remain in the amorphous state. It is believed that the ferromagnetic matrix is responsible for both the invar effect and weak itinerant ferromagnetism, while the ferromagnetic clusters cause the reentrant magnetism. It is in contrast with the results obtained by Ghafari et al. [10] because they observed that the vast majority of Fe moments, not only from the inclusions, participate in the spin freezing process. They proposed the model in which the whole Fe–Zr system consists of exchange–coupled spin clusters with an average cluster moment, which is mainly determined by competitive antiferromagnetic and ferromagnetic exchange interactions [10]. It is also shown that Fe-rich Fe–Zr alloys can be treated as Heisenberg ferromagnets. Read et al. [11] introduced the model of clusters containing the antiferromagneticaly coupled Fe moments embedded in ferromagnetic matrix in order to explain the temperature dependence of the coercivity in Fe-rich Fe–Zr amorphous alloys. Despite the controversy, it is widely believed that Fe atoms in amorphous Fe-rich Fe–Zr alloys are in low and high spin state giving rise to the bimodal hyperfine magnetic induction distribution and that their magnetic structure depends on preparation conditions.

Replacement of Zr by B atoms in $Fe_{100-x}Zr_x$ amorphous alloys in Fe-rich zone ($x < 14$) increases their Curie temperature [12]. The classical amorphous $Fe_{90}Zr_7B_3$ alloy in the form of thin

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ribbons is a precursor of a well known NANOPERM-type magnetically soft nanocrystalline material obtained by conventional heat treatment [13]. The as-quenched samples of this alloy exhibit the existence of α-Fe type MRO regions [3], which grow after annealing at temperature lower than the onset of the primary crystallization, but high enough to cause effective structure relaxations within the amorphous state [5].

Till date the influence of MRO regions on magnetic properties of amorphous ferromagnets at temperatures lower than room ones has been reported only in few papers. In this paper, the presence of the medium range ordering regions, revealed by the HREM and the Mössbauer spectroscopy, in the as-quenched state of the $Fe_{90}Zr_7B_3$ alloy and their effect on some magnetic properties, such as thermal demagnetization and isothermal magnetic entropy changes in the temperature range 77–300 K, are discussed.

2. Experimental procedure

Classical amorphous $Fe_{90}Zr_7B_3$ alloy ribbons, 20 μm thick and 1.5 cm wide, were prepared by a melt spinning method. The microstructure of the as-quenched samples was studied by the transmission electron microscopy and the Mössbauer spectroscopy. A JEM 3010 microscope working in high-resolution regime was used. The transmission Mössbauer spectra were recorded at liquid nitrogen (77 K) and at room temperature (300 K) by means of a conventional constant acceleration spectrometer with a ^{57}Co(Rh) radioactive source. The spectrometer was calibrated and the isomer shift (IS) was determined with respect to the α-Fe polycrystalline foil. To improve the resolution, the spectra for specimens exhibiting only quadrupole splitting (QS) were recorded also at narrow velocity range. Spectra fittings were carried out using the NORMOS package written by Brand [14]. The magnetization versus temperature at the magnetizing field of 1.2 T was measured at the temperature range 77–300 K by a force Sucksmith's type magnetometer for samples consisting of 5 discs, 3 mm in diameter arranged along the rolling direction of the ribbon. The isothermal magnetization curves as a function of the external magnetizing field induction were recorded for the same samples in the temperature range 77–300 K and magnetizing field induction range 0–2 T by means of a vibrating sample magnetometer (VSM).

The average density of the material at the ambient temperature was measured using the Archimedes method by weighing the samples in air and in toluene.

3. Results and discussion

The high-resolution transmission electron microscope image of the as-cast $Fe_{90}Zr_7B_3$ ribbons is shown in Fig. 1. As an inset in the top right corner, the selected area diffraction pattern is also depicted. The broad, concentric rings typical of amorphous structure occur. The microstructure is also a characteristic of the amorphous state but fringe like regions (indicated by white arrows) can be visible. These regions are MRO ones with 1–2 nm in size. The fringe spacing is estimated to be about 0.2 nm and may correspond to the atomic plane distances in BCC or FCC iron. The MRO regions are randomly distributed in the amorphous matrix and no sharp boundaries between them and the matrix are seen. It is worth noticing that the second inner diffraction ring is partially broken (Fig. 1). It may be connected with the presence of the MRO regions in the samples.

The transmission Mössbauer spectrum obtained at room temperature for the as-quenched $Fe_{90}Zr_7B_3$ alloy is presented in

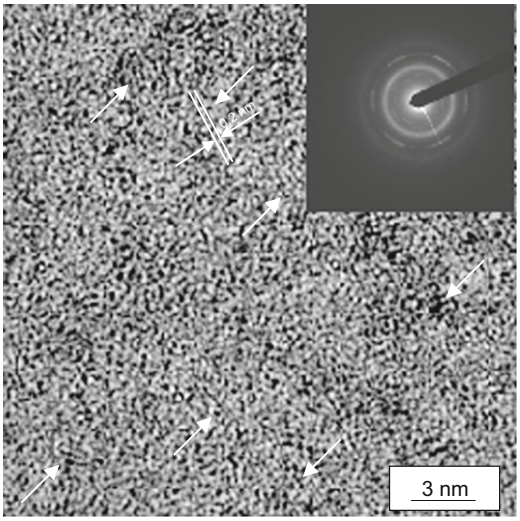

Fig. 1. High-resolution electron microscope image and selected area diffraction pattern for the as-quenched $Fe_{90}Zr_7B_3$ alloy.

Fig. 2a. The spectrum typical of amorphous paramagnetic material is asymmetric indicating the correlation between the isomer shift (IS) and quadrupole splitting (QS). The quadrupole splitting distribution, P(QS), shown in Fig. 2b is derived assuming a linear relation between IS and QS. The distribution block is composed of individual symmetric doublets with the same line width, which value was the same as that of an α-Fe calibration foil (FWHM = 0.31 mms^{-1}) and QS ranging from 0 to 0.85 mms^{-1}. It can be seen that P(QS) distribution has three characteristic features; not vanishing value of probability for QS = 0 and two local well resolved maxima for different values of QS. According to this, the as-quenched Mössbauer spectrum at 300 K can be decomposed into three subspectra: a single line, two broad doublets with two blocks of symmetric quadrupole doublets distributions D_1 and D_2 and QS ranging from 0 to 0.6 mms^{-1} and from 0.2 to 0.85 mms^{-1}, respectively. The linear correlation IS(QS) is independently applied in both blocks. Such a decomposition is shown in Fig. 2c. The distributions P(QS) for each quadrupole subspectrum are depicted in Fig. 2d. The main hyperfine parameters of the subspectra are listed in Table 1. The asymmetric doublet of $\overline{QS_1} = (0.30 \pm 0.05)$ mm/s may be ascribed to Fe atoms having only iron atoms as the nearest neighbors but with the atomic arrangement symmetry lower than cubic. The average value of QS in this block is larger than that for ε-Fe (hexagonal close packing iron) phase, which equals to (0.17 ± 0.03) mm/s [15]. In this distribution block, the Fe sites with the local symmetry of the nearest neighborhood different from cubic and hexagonal are mostly presented. The asymmetric doublet with the average $\overline{QS_2} = (0.53 \pm 0.05)$ mm/s may correspond to the Fe sites in amorphous structure with Zr or B atoms in the nearest neighborhood. Cubic symmetry in the arrangement of Fe atoms (FCC or BCC) gives QS = 0 due to vanishing of electric field gradient at Fe nuclei. The IS value of the single line (Table 1) indicates that this line can be rather ascribed to α-Fe (BCC) than to γ-Fe (FCC) phase because IS of the latter amounts to −0.09 mm/s [16,17]. MRO regions seem to be magnetically ordered Fe regions with BCC structure in atomic arrangement. However, they do not contribute to the Mössbauer spectra at room temperature (Fig. 2a and c) in the form of a Zeeman sextet.

The transmission Mössbauer spectrum for the as-quenched $Fe_{90}Zr_7B_3$ alloy recorded at 77 K is depicted in Fig. 3a. The hyperfine field induction distribution, $P(B_{hf})$, presented in Fig. 3b