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The effect of heat treatment on the magnetic properties of $Fe_{82}Zr_7Nb_2Cu_1B_8$ amorphous alloy

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Properties

ABSTRACT

Purpose: This paper presents the results of investigations into the: microstructure, magnetic properties and thermal stability of amorphous $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy in the state prevailing after solidification and a multi-stage heat treatment process.
Design/methodology/approach: The investigated alloy was obtained in the form of thin ribbons of width 3 mm and thickness approximately 20 μm. The required ingots of alloy were obtained by arc-melting high-purity component elements. The structure and microstructure were examined using Mössbauer spectroscopy and transmission electron microscopy. The microstructure study confirmed the amorphicity of the investigated alloy. The thermal stability was determined on the basis of DSC (Differential Scanning Calorimetry) plots. Also measurements were taken of the magnetic properties, such as magnetic susceptibility and magnetization as a function of temperature and magnetizing field.
Findings: Samples of the investigated $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy were found to be amorphous, both in the as-quenched state and after a multistage thermal annealing process. The sample with the lowest value of hyperfine field induction on the 57Fe was found to possess the lowest value of Curie temperature, it is related to the so-called invar effect. The sample of the investigated alloy that had been subjected to the annealing process, at temperatures of 573 K and 600 K for 15 minutes exhibits the biggest change in the magnetic entropy.
Practical implications: The paper disscus the effect of heat treatment on the magnetic properties of $Fe_{82}Zr_7Nb_2Cu_1B_8$ amorphous alloy.
Originality/value: The paper presents some researches of the Fe-based amorphous alloys obtained by arc-melting high-purity component elements.
Keywords: Amorphous alloys; Mössbauer spectroscopy; Magnetic properties; Differential scanning calorimetry
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1. Introduction

In order to obtain an alloy with a required set of magnetic properties, it is important to choose appropriate chemical components and thermal treatment as both have major influences on the magnetic structure of the resulting alloy [1-3].

The iron-based soft magnetic materials make up an interesting group, from both the scientific and industrial applications points of view. A particularly interesting subset of this group comprises of materials which feature Curie temperatures that are close to room temperature [4,5]; these materials could be utilized in production of magnetic fridges. Moreover, through the use of appropriate heat treatment, nanocrystalline alloys can be obtained. These alloys consist of nanometric grains of the α-Fe phase and amorphous matrix [6].

Typically, amorphous alloys are produced by quenching of liquid alloy on a rotating, copper wheel; this process forms a ribbon of alloy with a thickness of about 30 μm. Alloys such as these are obtained when the cooling speed exceeds 10^4 K/s.

In this paper, the results are presented of investigations into the: microstructure, magnetic properties and thermal stability of amorphous $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy. Measurements were performed on samples in the as-quenched state, as well as after a multistep thermal treatment process.

2. Materials and methodology

The samples studied in the investigations were produced in the form of ribbons with approximate dimensions of width 3 mm and thickness 20 μm. The required ingots of alloy were obtained by arc-melting high-purity component elements. Ribbons, with the nominal composition $Fe_{82}Zr_7Nb_2Cu_1B_8$, were fabricated from the ingots, using a rapid-quenching method (i.e. quenching of the molten alloy on a rotating wheel). The production process was carried out under a protective atmosphere of an inert gas. The investigations were performed on the resulting samples, which were subjected to a multistep thermal treatment; eventually, this thermal treatment facilitated the elimination of fluctuations in the chemical composition along the length of the ribbon.

The samples were placed in a quartz tube from which the air then was removed using a vacuum pump. The tube was placed in a preheated resistance furnace, and subjected to subsequent thermal treatment. After thermal treatment, the samples in the tube were cooled down to room temperature. The conditions of the thermal treatment are presented in Table 1.

The microstructure and magnetic properties of the aforementioned samples were investigated, both in the as-quenched state and after the multistep thermal treatment. This was achieved by means of a 'POLON' Mössbauer spectrometer, equipped with a ^{57}Co (Rh) source with an activity of 50 mCi, at room temperature. Transmission Mössbauer spectra were analysed using 'NORMOS' software [7].

The amorphicity of the investigated samples was confirmed by investigations using a transmission electron microscope (TEM). The thermal stability of the alloys was measured by means of differential scanning calorimetry (DSC).

The measurements of the magnetic susceptibility were performed on toroid-shaped samples, with two windings: magnetizing and measuring (transformer method) using a computerized automatic test set-up. A magnetic field of amplitude 0.26 A/m and frequency of 2 kHz was used (low-field magnetic susceptibility). The temperature range for the magnetic susceptibility measurements was chosen by taking into account the Curie temperature of the investigated alloy. In the case of the investigated alloy, the temperature range was extended from 160 K to 340 K. In order to obtain temperatures of lower than room temperature, a flow thermostat was used; higher temperatures were obtained using a vacuum and resistance furnace with a bifilar spiral.

Measurement of isothermal magnetization $\sigma(\mu_0 H)$ curves was performed by means of a Faraday magnetic balance over the magnetic field range of: 0 to 0.75 T. Analysis of these curves facilitated the calculation of values of the system's magnetic entropy, which is an indirect measure of the magnetocalorific effect.

3. Results and discussion

On the basis of DSC investigations, the temperatures for the multistage thermal treatment were well-below the crystallization temperature of the alloy. The isothermal treatment, under vacuum within the resistance furnace, should only lead to changes in the magnetic structure of the alloy. Fig. 1 presents the thermal curve recorded at the heating rate of 10 K/min for the alloy in the as-quenched state.

Table 1.
The experimental conditions of the multistep thermal treatment performed on the investigated alloy samples ('+' denotes 'next step of the thermal treatment')

Alloy composition	Thermal treatment Temperature/time
$Fe_{82}Zr_7Nb_2Cu_1B_8$	573 K/15 min +600 K/15 min +650 K /15 min +700 K/15 min +750 K/15 min

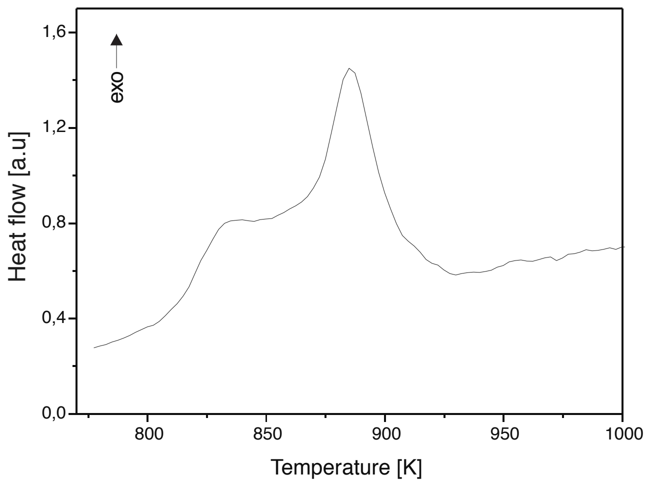

Fig. 1. The DCS curve for the $Fe_{82}Zr_7Nb_2Cu_1B_8$ sample of the amorphous alloy in the as-quenched state

The clear, single, peak on the DCS curve, at a temperature of approximately 825 K, is attributed to the crystallization temperature of the alloy.

The distributions of the hyperfine fields for the amorphous samples of $Fe_{82}Zr_7Nb_2Cu_1B_8$ are presented in Fig. 2; marked low- and high-field components can be observed. The data obtained from the analysis of the Mössbauer spectra are gathered in Table 2. The observed transmission Mössbauer spectra exhibit the shape of the Zeeman sextet, characteristic of magnetically-soft amorphous materials. In the hyperfine field distributions, two components could be distinguished: low- and high-field, which is linked with the presence of areas of differing iron content. The bimodal shape of the hyperfine field distribution for the sample in the as-quenched state, as well as that after initial stages of the thermal treatment, confirms the existence of two different local distribution patterns of the iron atoms in the sample volume. The low-field component corresponds to areas with high concentrations of iron atoms with small distances between them. The second component, observed in the higher fields of the hyperfine field distribution, is associated with areas in which the Fe atoms are closely interspersed with Zr and B atoms [8].

An increase of the low-field component in the distribution of the hyperfine fields on the ^{57}Fe nuclei leads to a decrease in the average induction of the hyperfine field. This is accompanied by a change in the standard deviation of the induction (Table 2).

This change could be treated as a measure of the heterogeneous surroundings of the iron atoms.

Table 2.
Average i nduction of the hyperfine field $(B_{hf})_{ef}$, standard deviation of the hyperfine field distributions (ΔD_s), relative intensity of the $A_{2,5}$ line in the Mössbauer spectra; the measurement uncertainties are included in brackets

The thermal treatment of $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy in 15 mins.	$(B_{hf})_{ef}$ [T]	ΔD_s [T]
As-quenched	9.86(2)	4.17(2)
573 K	9.20(2)	4.01(2)
+ 600 K	8.93(3)	4.00(3)
+ 650 K	9.27(2)	4.14(2)
+ 700 K	9.76(3)	4.19(4)
+ 750 K	9.91(2)	4.23(3)

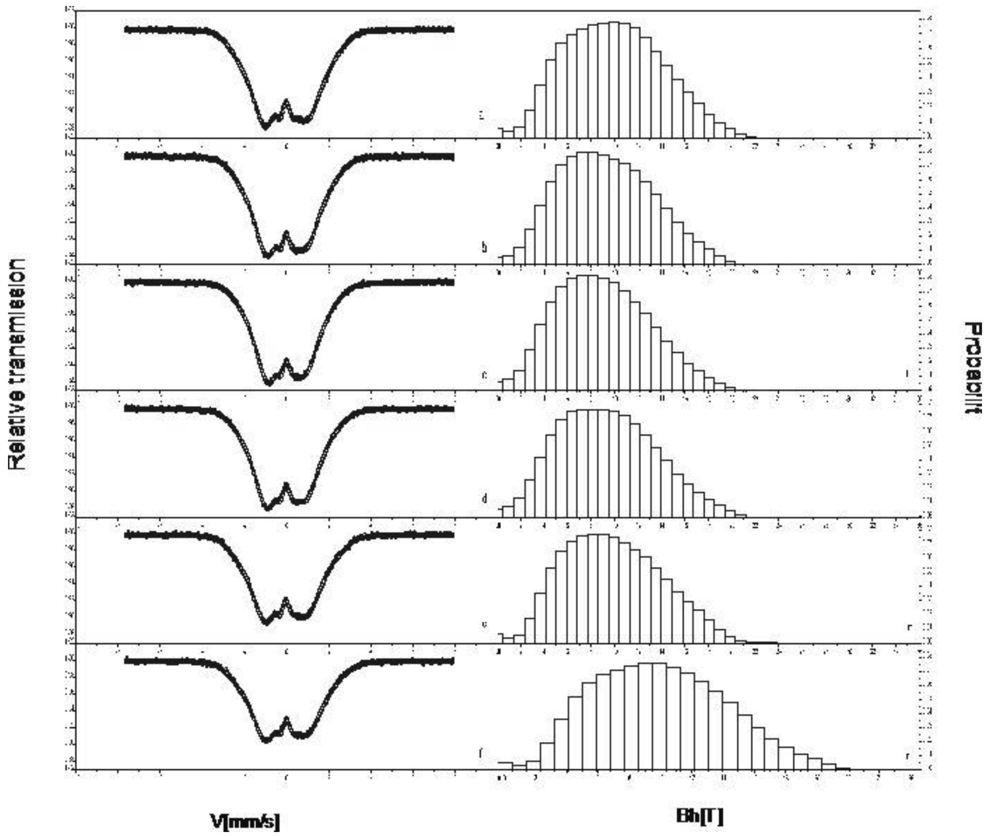

Fig. 2. Transmission Mössbauer spectra (a, b, c, d, e, f) and derived hyperfine field distributions (g, h, i, j, k, l) for the $Fe_{82}Zr_7Nb_2Cu_1B_8$ amorphous alloys in the: as-quenched state (a, g) and after multistage thermal treatment (b, c, d, e, f, h, i, j, k, l)

On the basis of the data presented in Table 2, it could be stated that, the sample after annealing at the temperature of 600 K for 15 minutes, is characterized by the highest atomic packing density. An increase in the average hyperfine field induction observed in samples after annealing at the temperatures of: 650 K, 700 K and then 750 K may be related to diffusion processes, which could lead to the creation of atomic arrangements similar to the embryos of the preferentially-related crystalline phases [9]. The thermal annealing (undertaken below the crystallization temperature) in comparison to the as-quenched state, causes an increase in the tendency to arrange the magnetization vector in the plane of the ribbon; this is connected to structural relaxation of the sample. The lack of crystalline grains in the investigated alloy, both in the as-quenched state and after thermal treatment at a temperature of 600 K for 5 minutes, was confirmed by the microstructure images, obtained by means of a high resolution transmission electron microscope (Fig. 3a).

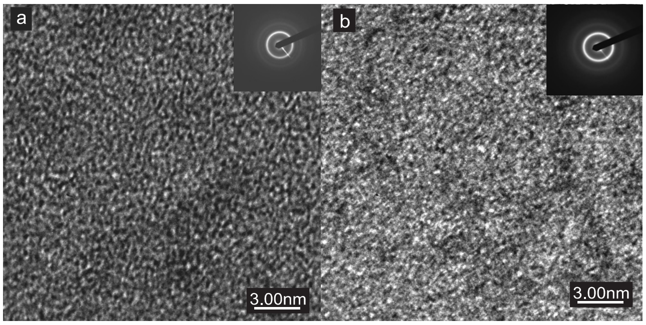

Fig. 3. The microstructure and corresponding electronogram for the amorphous $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy in the as-quenched state (a) and after thermal treatment at 600 K/15min (b)

The microstructure images and corresponding electronograms are characteristic for materials which feature amorphous structure.

Fig. 4 shows the dependence of low-field magnetic susceptibility (χ) on temperature for the investigated alloys. After the initial stages of the thermal treatment, the value of the average hyperfine field on the ^{57}Fe nuclei was seen to decrease (Table 2); this phenomenon could be connected with one of the invar effect anomalies which is also accompanied by a decrease in the value of the Curie temperature, in comparison to that observed for the sample in the as-quenched state. This is visible as a shift in the Hopkinson's [10] maximum values on the χ(T) curves. The magnetic susceptibility for the sample in the as-quenched stat increases slightly with an temperature increase, and at a temperature of approximately T = 340 K on the χ(T) curve, a rapid decrease in the maxima values is observed, associated with a ferromagnetic-paramagnetic phase transition. The observed shape of the χ(T) curve is different after multistage thermal treatment at the temperatures of 573 K and then at 600 K (both for 15 minutes). It is strongly believed that this difference is connected with the inhomogeneous distribution of magnetic atoms in the sample volume. The observed shift in the peak value, towards lower temperature, can be explained in a similar way to observed changes in the average value of the hyperfine field induction (Table 2). During the annealing process, structural relaxation of the sample is taking place and a distinct increase in the magnetic susceptibility is observed (Fig. 4).

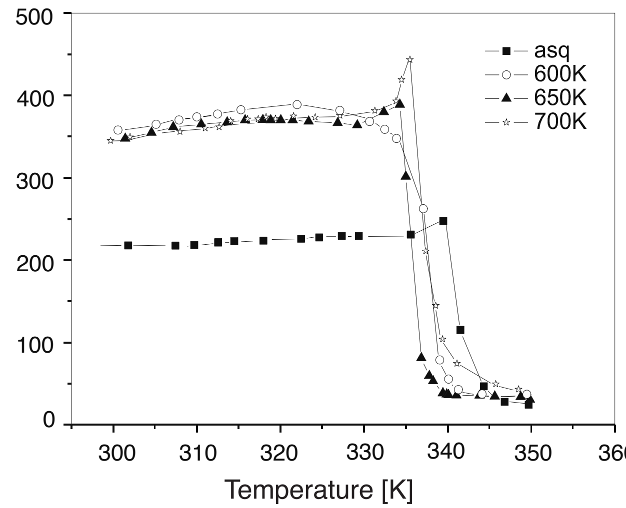

Fig. 4. Temperature dependence of the low-field magnetic susceptibility (χ) for the samples of $Fe_{82}Zr_7Nb_2Cu_1B_8$ amorphous alloy in the as-quenched state (asq) and after multistep thermal treatment for 15 minutes

On the basis of the magnetization measurements, as a function of the induction of the magnetizing field at the different temperatures, the changes in magnetic entropy $\Delta S_M(T)_{\Delta H}$ were calculated, according to relationship [11]:

$$\Delta S = \mu_0 \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T} \right)_H dH \qquad (1),$$

Where: H_1 and H_2 are the lowest and the highest values of the magnetizing field, respectively.

The changes in the magnetic entropy (equation 1), with the temperature of the $Fe_{82}Zr_7Nb_1Cu_1B_8$ alloy, are presented in Fig. 5. On the $-\Delta S_M(T)$ curves, obtained for the sample of the investigated alloy in the as-quenched state and after the multistep annealing, distinctive maxima can be observed in the temperature range from 330 K to 345 K. It is well known, that thermal annealing of amorphous alloys causes re-configuration of the magnetic atoms within the volume of the sample and can lead both to a simultaneous improvement and deterioration in the magnetic parameters.

This improvement in the magnetic characteristics is characterized by: increases in the magnetic susceptibility and saturation magnetization, and decreases in the coercivity and hysteresis-loss values. The deterioration in the magnetic characteristics is represented by the presence of the invar effect, which explains the anomaly of the magnetic parameters.

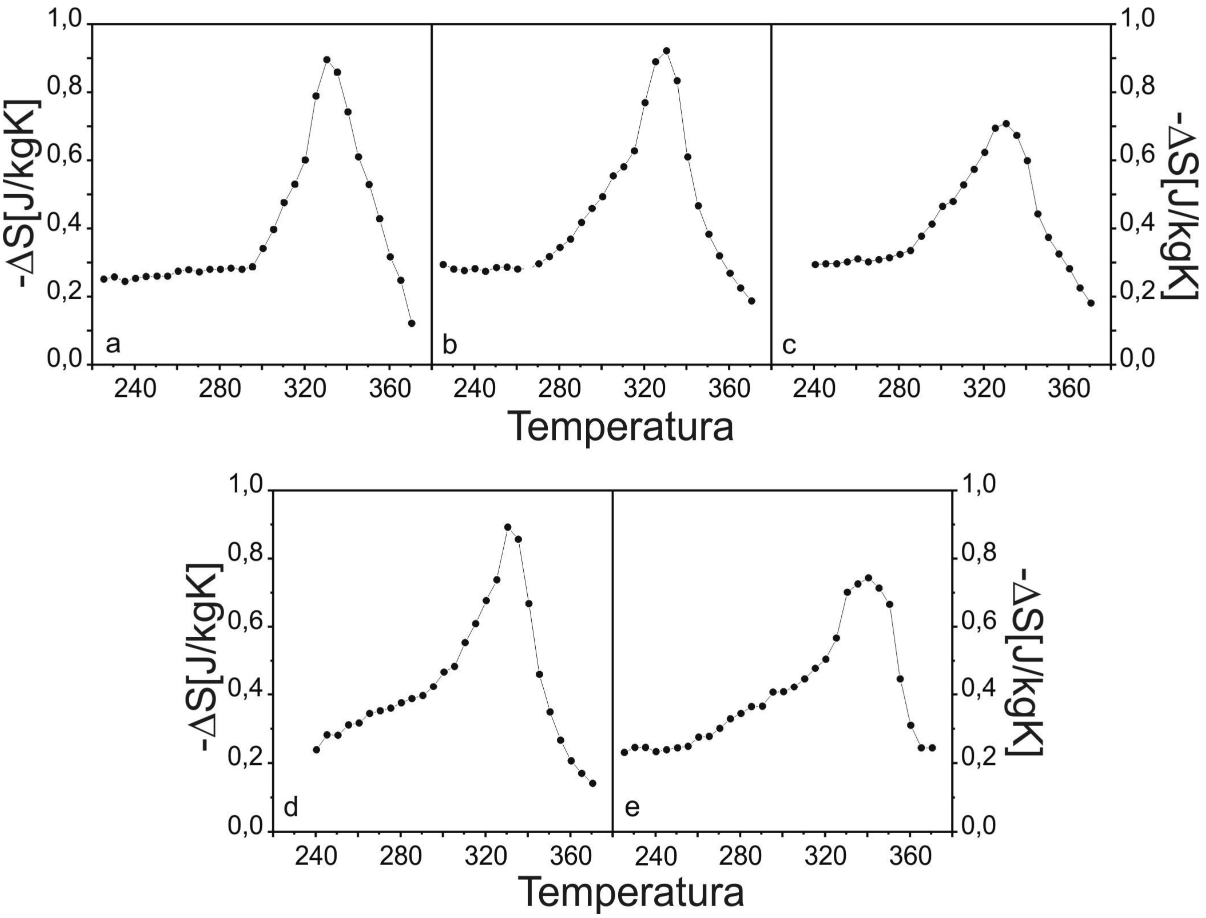

Fig. 5. The relationship of magnetic entropy (-ΔS_M) with changing temperature, for the Fe82Zr7Nb2Cu1B8 alloy in the as-quenched state (a), and after thermal treatment over 15 minutes at the temperatures of: 573 K and then 600 K (b), 650 K (c),700 K (d) and 750 K (e)

4. Conclusions

On the basis of the performed investigations, it has been stated that:

- Samples of the investigated $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy were found to be amorphous, both in the as-quenched state and after a multistage thermal annealing process;
- In the hyperfine field distributions, obtained from analysis of the transmission Mössbauer spectra, an increase in the low-field component was observed; this component is related to the so-called invar effect, and an associated decrease in the average hyperfine field induction on the ^{57}Fe (in comparison to the as-quenched state);
- The sample with the lowest value of hyperfine field induction on the ^{57}Fe was found to possess the lowest value of Curie temperature;
- The biggest change in the magnetic entropy was observed for the sample of the investigated alloy that had been subjected to the annealing process, at temperatures of 573K and 600 K for 15 minutes each.

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