The Effect of Isothermal Annealing on the Structural and Magnetic Properties of the Bulk Amorphous Alloy: FeCoTiYB

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The aim of this paper was to conduct studies concerning the magnetization of bulk amorphous $Fe_{61}Co_{10}Ti_4Y_5B_{20}$ alloy when subjected to strong magnetic felds in the area known as the approach to ferromagnetic saturation. The samples were produced using the suction-casting method. The amorphicity of the investigated alloy, in the as-quenched state and after annealing process in a temperature below the crystallization temperature was verified using X-ray diffractometry. The magnetization was measured using a vibrating sample magnetometer. On the basis of the obtained results, the type of structural defects having influence on magnetization in high magnetic fields were determined. Analysis of the high-field magnetization curves has facilitated the calculation of the spin wave stiffness parameter. From this parameter, the range and strength of the exchange interactions could be determined.

Keywords: Approach to ferromagnetic saturation, amorphous materials, bulk metallic glasses, structural defects, spin wave stiffness parameter

Modern materials with improved properties are highly sought after, due to the rapid development of civilisation. At present, the main medium is electric current, and electrical and electronic devices are driving the economy. Therefore it is imperative, for both fundamental research and applications, to develop new manufacturing methods for the production of functional materials; in particular, for applications in the electronics, electrical or energy industries.

Research into metallic ferromagnetic materials which feature an amorphous structure has been carried out for more than half a century. One of the subjects of this research has been that of amorphous ribbons, obtained using quenching speeds of $10^4 – 10^6$ K/s [1]. Unfortunately, these values of quenching speed only allowed the production of materials with thicknesses ranging from 30 – 80 μm, which restricted their resulting applications. Therefore, intensive studies have been undertaken to improve on this manufacturing method, in order to obtain amorphous materials with greater thicknesses. However, little major progress has been made in this specific area. One related major breakthrough came in the year 1989, when A. Inoue presented three criteria for the selection of alloy components suitable for systematic production of the so-called bulk amorphous alloys [2]. More than ever, there are now sound reasons for pursuing and classifying these alloys in terms of 'thickness', which is directly connected to the quenching speed of the alloy [3]. During the solidification process, diffusion of atoms occurs. The distance of the diffusion is correlated strongly with the solidification time and the chemical composition of the alloy [4-5]. In the case of the ferromagnetic alloys with soft magnetic properties, the distances between the atoms represent the main factor influencing their application parameters, (i.e. the values of: coercivity, saturation magnetisation and core losses). Moreover, the internal stresses present in the alloy, and affecting its properties, are also related to the solidification time [6].

These relaxations could be minimised using various techniques, e.g.: impulse annealing, long-term annealing above the Curie temperature for the alloy but below its crystallisation temperature, or by a combination of these methods. According to many authors, short-term isothermal annealing, at below the crystallisation temperature, enhances the structural relaxations of the sample and yields the best results [7, 8].

In this work, the results of investigations concerning the amorphous alloy of $Fe_{61}Co_{10}Ti_4Y_5B_2$ are presented.

Experimental part

The investigated alloy, $Fe_{61}Co_{10}Ti_4Y_5B_{20}$, was produced using a suction-casting method; the molten alloy was sucked into a water-cooled, copper die. Samples were produced in the form of rods with the following approximate dimensions: length 2 cm and diameter 1 mm. Investigations into the structure and the magnetic properties were carried out on samples in both the as-quenched state and also after isothermal annealing at a temperature of 720 K for 20 min.

The structure of the samples was studied by means of a Bruker D8 Advance X-ray spectrometer, equipped with a lamp with a cobalt anode. The investigations were carried out over a 2Θ range of 30 to 120° with a measurement step of 0.02° and a time per step of 5 s.

The thermal stability of the obtained alloy was studied by means of a differential scanning calorimeter (DSC). On the basis of analysis of the DSC curves, the onset of crystallisation and crystallisation temperatures were determined. The DSC curves were recorded at a heating rate of 5K/min. The DSC investigations allowed the determination of an optimal annealing temperature for the alloy. Isothermal magnetisation curves were recorded using a vibrating sample magnetometer (VSM). These measurements were performed on open samples in the form of rods with a length of 5 mm and a diameter of 1 mm. The effect of the demagnetising field was taken into account when analysing the magnetisation curves. The reduced magnetisation M / M_s was presented as a function of: $1/(\mu_o H)^{1/2}$, $1/(\mu_o H)$, $1/(\mu_o H)^2$ and $(\mu_o H)^{1/2}$; linear relationships were obtained over the relevant range of the magnetic field. Using the least squares method, the line

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parameters: $a_{1/2}$, a_1 , a_2 and b were calculated. Through analysis of the initial magnetisation curve within the Holstein-Primakoff region, the spin-wave stiffness parameter (D_{sp}) was determined. The D_{sp} parameter is described by the following equation [9]:

$$D_{sp} = \frac{1}{3} S J_{ex}(a) a^2 z_m \qquad (1)$$

where:

S – the spin value at the distance from the central atom,

J_{ex} – the local exchange integral,

a – the distance to the nearest–neighbour atoms,

z_m – the quantity of magnetic atoms in the nearest neighbourhood.

The value of the spin-wave stiffness parameter D_{sp} is related with the changes within the nearest neighbourhood of an iron atom [9, 10].

Results and discussions

Figure 1 shows the DSC curve, recorded at a heating rate of 5 K/min, for the investigated alloy in the as-cast state.

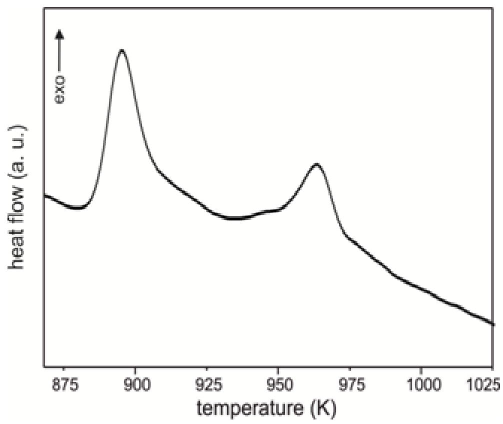

Fig. 1. The DSC curve, recorded at heating rate of 5 K/min, for the bulk amorphous alloy$Fe_{61}Co_{10}Ti_4Y_5B_{20}$ in the as-quenched state

On the DSC curve, two exothermic peaks are visible: the first peak is at a temperature of 895 K and the second is at 963 K.

A sample was subjected to an annealing process, at a temperature of 720 K for 20 min. The aim of this thermal treatment was solely to relax the structure, and not to induce crystallisation within the alloy. Therefore the investigated material was annealed at a temperature well below the crystallisation temperature.

Figure 2 shows X-ray diffraction patterns for the investigated alloy in the form of rods of length 2 cm and diameter 1 mm; results are shown both for the as-cast state and after isothermal annealing at a temperature of 720K for 20 min.

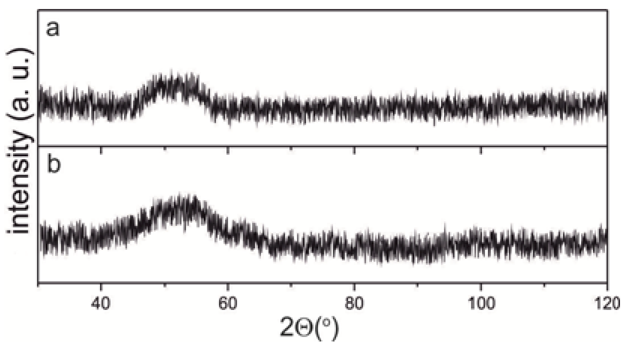

Fig. 2. X-ray diffraction patterns for the bulk amorphous alloy $Fe_{61}Co_{10}Ti_4Y_5B_{20}$: (a) – in the as-cast state, and (b) – after isothermal annealing at a temperature of 720 K for 20 min

The X-ray diffraction patterns obtained for the as-cast and isothermally annealed samples are both typical of those for amorphous alloys. There is an absence of the narrow maxima that would be typical for crystalline materials. Only one broad maximum is visible at $2\theta \approx 50^o$.

Figure 3 presents static hysteresis loops, measured for the bulk amorphous alloy $Fe_{61}Co_{10}Ti_4Y_5B_{20}$ in the as-cast state and after isothermal annealing at a temperature of 720 K for 20 min.

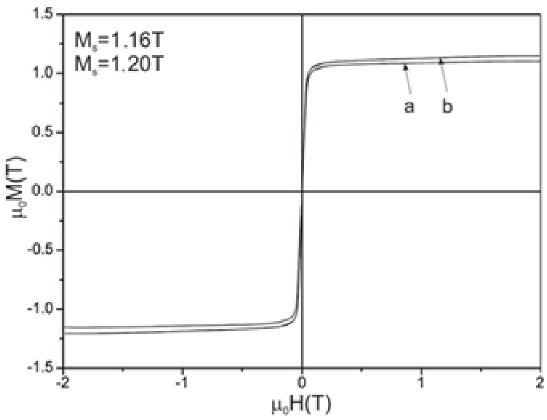

Fig. 3. Static hysteresis loops for the bulk amorphous alloy $Fe_{61}Co_{10}Ti_4Y_5B_{20}$: (a) as-quenched state, and (b) after isothermal annealing at 720 K for 20 min

Table 1

DATA OBTAINED FROM ANALYSIS OF THE STATIC HYSTERESIS LOOPS: μ_0M - MAGNETISATION, H_c – COERCIVITY

Parameter	Ms	Hc
$Fe_{61}Co_{10}Ti_4Y_5B_{20}$	[T]	[A/m]
As-cast	1.16	5.0
After annealing	1.20	3.8

The static hysteresis loops, presented in figure 3, have a shape that is typical for soft magnetic materials. On the basis of these investigations, the saturation magnetisation and the coercive field values were determined (table 1).

The saturation magnetisation for the alloy sample in the as-cast state was found to be equal to 1.16 T, whereas for the sample subjected to the isothermal annealing, the value had been increased to 1.20 T. The annealing process also resulted in a decrease in the coercivity. On the basis of the obtained results, it can be stated that the structure of the alloy after thermal treatment is more relaxed. The dominant mechanism underlying the magnetic hysteresis of the amorphous materials is the blocking of the domain wall movement by local stress centres [11]. During the annealing process, structural relaxations occur; this results in more atoms taking locally ordered positions. In turn, this leads to a higher atomic packing density within the structure and a decrease in the number of free volumes [12].

The magnetisation curves were analysed, concentrating on the so-called *approach to ferromagnetic saturation* region; this facilitated investigation of the influence of the alloy's thermal treatment on the type of structural defects present and their effect on the magnetisation process.

Figure 4 shows high-field magnetisation curves for the bulk amorphous alloy in the as-cast state. Over the

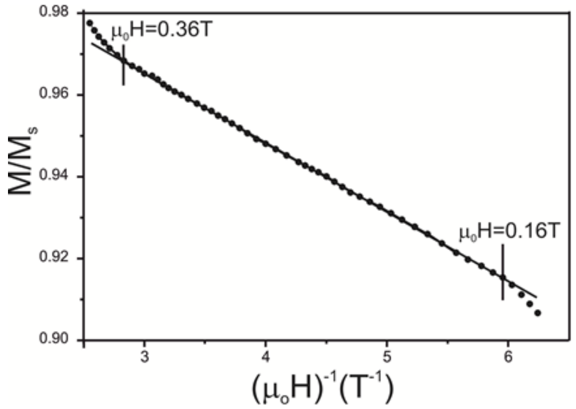

Fig. 4. The high-field magnetisation curve $M/M_s((\mu_0H)^{-1})$ for the bulk amorphous alloy $Fe_{61}Co_{10}Ti_4Y_5B_{20}$ in the as-cast state

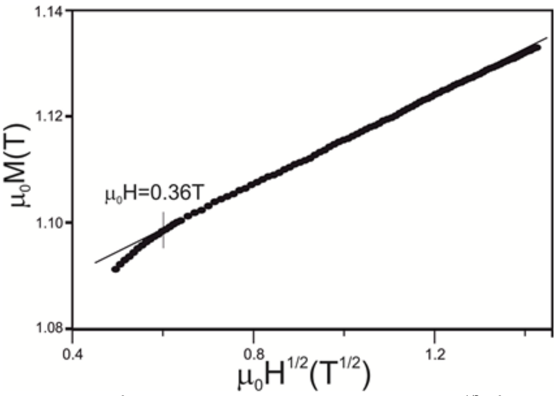

Fig. 5. The high-field magnetisation curve $\mu_oM((\mu_0H)^{1/2})$ for the bulk amorphous alloy $Fe_{61}Co_{10}Ti_4Y_5B_{20}$ in the as-cast state

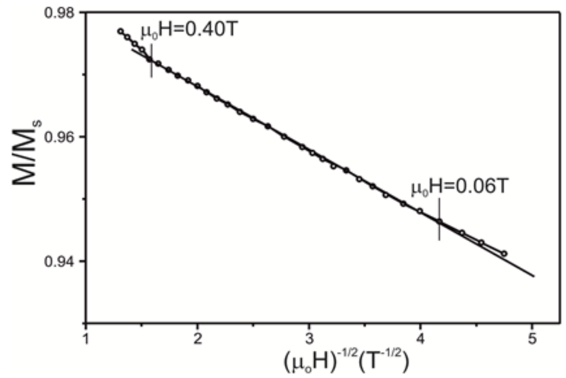

Fig. 6. The high-field magnetisation curve $M/M_s((\mu_0H)^{-1/2})$ for the bulk amorphous alloy $Fe_{61}Co_{10}Ti_4Y_5B_{20}$ after isothermal annealing.

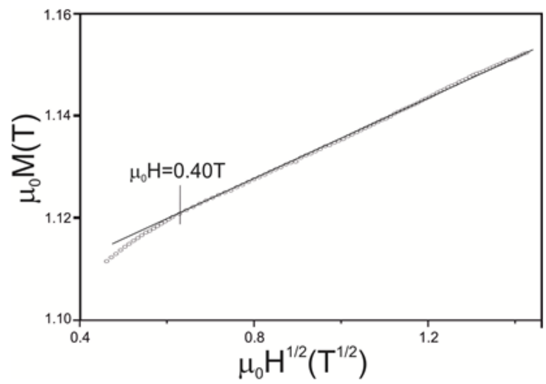

Fig. 7. The high-field magnetisation curve $M/M_s((\mu_0H)^{1/2})$ for the bulk amorphous alloy $Fe_{61}Co_{10}Ti_4Y_5B_{20}$ subjected to isothermal annealing

magnetic field range of 0.16 T to 0.36 T a linear relationship was observed of $M/M_s((\mu_oH)^{-1})$. This means that the magnetisation process within this region of the magnetic field is influenced mostly by quasidislocational dipoles, fulfilling the condition $\chi_H D_{dip} < 1$. Under the influence of stronger magnetic fields, above 0.36 T a linear relationship of M/M_S with $(\mu_oH)^{-1/2}$ was observed (fig. 5). This relationship indicates that the associated magnetisation process is connected with dumping of the thermally-induced spin-waves by the magnetic field and it is called the Holstein-Primakoff paraprocess [13].

The high-field magnetisation curves, obtained for the investigated alloy after the thermal treatment at a temperature of 720 K for 20 min , are presented in figures 6 and 7.

A linear relationship was observed of the reduced magnetisation (M/M_S) versus the magnetic field induction $(\mu_oH)^{-1/2}$ over the magnetic field range from 0.06 T to 0.40 T; this indicates that the magnetisation process within this range is connected with small rotations of the magnetic moments in the vicinity of point defects [14-15]. Within stronger magnetic fields (>0.40 T) a minor increase in the value of the magnetisation occurs, due to the Holstein-Primakoff paraprocess (fig. 7).

Key parameters, obtained from analysis of the magnetisation curves, are presented in table 2.

In the case of the sample in the as-cast state, the second law of the approach to the ferromagnetic saturation is fulfilled. After subjecting the sample to isothermal annealing at a temperature well below its crystallisation temperature, the process of magnetisation in high fields proceeds according to the first law of the approach to the ferromagnetic saturation. This is due to collective re-grouping of mobile atoms within the volume of the alloy and the resulting disintegration of thermodynamically unstable two-dimensional structural defects in the form of quasidislocational dipoles to point defects. The conducted thermal treatment caused homogenisation of the investigated alloy.

Analysis of the initial magnetisation curves, in the region of the Holstein-Primakoff paraprocess, allowed the determination of values of the spin wave stiffness parameter D_{sp}. The sample subjected to isothermal

Table 2

DATA OBTAINED FROM ANALYSIS OF THE MAGNETISATION AS A FUNCTION OF THE MAGNETIC FIELD INDUCTION TO THE POWERS OF -1/2, -1, AND 1/2, AND THE SPIN-WAVE STIFFNESS PARAMETER D_{sp}

PARAMETER $Fe_{61}Co_{10}Ti_4Y_5B_{20}$	$a_{1/2}$ [$T^{1/2}$]	a_1 [$T^{1/2}$]	b [$T^{1/2}$]	D_{sp} [10^{-2}eVnm^2]
As-cast state	------------	**0.0072**	**0.0326**	**65**
After thermal treatment	**0.0324**	-----------	**0.0298**	**69**

annealing was found to yield a larger value for this parameter; this indicates a larger quantity of magnetic atoms, with smaller distances between them, therefore in turn indicating a higher atomic packing density of the magnetic atoms [16, 17]. This is connected with the creation of short-range chemical order. According to Kaul [18] and Corb et. al. [19], each magnetic atom in the fully relaxed material possesses 12 neighbouring atoms, whereas in the unrelaxed state it can have 9-10 of them. On the basis of the conducted studies, it can be stated that the appropriate thermal treatment results in the homogenisation of the structure and its relaxation.

Conclusions

This work has presented the results of investigations into the structure and magnetic properties of the bulk amorphous alloy $Fe_{61}Co_{10}Ti_4Y_5B_{20}$ in the form of a rod.

The amorphicity of the investigated alloy, both in the as-cast state and after thermal treatment, was confirmed by X-ray diffraction studies. In order to determine the optimal temperature for thermal treatment, studies using DSC were performed. It was found that the crystallisation temperature of the alloy is approximately 960 K. Isothermal annealing was carried out at a temperature well below the established crystallisation temperature. The aim of the thermal treatment was solely to relax the structure of the obtained material.

The effect of structural defects on the magnetisation process in the approach to ferromagnetic saturation region were studied. The initial magnetisation curves were analysed according to the H. Kronmuller theorem. For the alloy in the as-cast state, it was found that in higher magnetic fields a dominant role is played by rotations of the magnetic moments in the vicinity of the quasidislocational dipoles (fig. 4). For the isothermally annealed alloy, the magnetisation process is influenced by the presence of point defects (fig. 6). In both cases, in stronger magnetic fields an increase in the value of the magnetisation is due to dumping of the thermally-induced spin-waves (Holstein-Primakoff paraprocess) (figs. 5 and 7). Analysis of the high-field magnetisation curves allowed the determination of values of the spin-wave stiffness parameter D_{sp}, which is sensitive to changes in the chemical and topological atomic arrangement. The sample of $Fe_{61}Co_{10}Ti_4Y_5B_{20}$ alloy which had been isothermally-annealed at the temperature of 720 K for 20 min was found to yield a higher value of this parameter; this indicates a higher value of atomic packing density in this material.

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Manuscript received: 21.08.2016