A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 60 2015 Issue 3
DOI: 10.1515/amm-2015-0337

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AN INVESTIGATION INTO THE EFFECT OF ISOTHERMAL ANNEALING ON MAGNETIC PROPERTIES IN THE ALLOY: $Fe_{64}Co_{10}Y_6B_{20}$

WPŁYW IZOTERMICZNEGO WYGRZEWANIA NA DEFEKTY STRUKTURY W STOPIE $Fe_{64}Co_{10}Y_6B_{20}$

This work presents the results of investigations into the structural and magnetic properties of the bulk amorphous alloy: $Fe_{64}Co_{10}Y_6B_{20}$. The structure, thermal stability and magnetic properties of the alloy were studied using: X-ray diffractometry, differential scanning calorimetry (DSC), and a vibrating sample magnetometer (VSM), respectively. The investigations were performed on samples of the alloy in both the 'as-cast' state, and the state resulting from a process of isothermal annealing at a temperature of 750 K for 30 minutes.

The aim of the conducted studies was to relax the structure and improve the soft magnetic properties of the investigated alloy. The results show that annealing the alloy at a temperature well below its crystallisation temperature leads to an increase in the value of the saturation magnetisation and a decrease in the value of the coercivity. Utilising the 'approach to the ferromagnetic saturation' theorem, the nature of structural defects within the investigated material has been established. For both 'as-cast' and isothermally-annealed samples, the magnetisation process has been found to be connected with the existence of linear structural defects.

W pracy przedstawiono wyniki badań struktury oraz właściwości magnetycznych masywnego stopu amorficznego $Fe_{64}Co_{10}Y_6B_{20}$. Strukturę stopu badano wykorzystując dyfrakcję promieni rentgenowskich, stabilność termiczną z wykorzystaniem różnicowej kalorymetrii skaningowej DSC, a właściwości magnetyczne przy użyciu magnetometru wibracyjnego VSM. Badania przeprowadzono dla próbek stopu w stanie po zestaleniu oraz po procesie izotermicznego wygrzewania w temperaturze 750 K w czasie 30 min. Celem prowadzonych badań było zrelaksowanie struktury i poprawa właściwości magnetycznie miękkich badanego stopu. Na podstawie uzyskanych wyników stwierdzono, ze wygrzewanie stopu w temperaturze znacznie niższej od temperatury krystalizacji prowadzi do zwiększenia magnetyzacji nasycenia oraz zmniejszenia wartości pola koercji. Wykorzystując teorię podejścia do ferromagnetycznego nasycenia określono rodzaj defektów struktury badanego materiału. Zarówno dla próbki w stanie po zestaleniu jak i po izotermicznym wygrzewaniu proces magnesowania związany jest z obecnością liniowych defektów struktury.

1. Introduction

Due to their unique properties, bulk metallic materials featuring amorphous structures are being studied intensively in many research centres around the world. Materials exhibiting so-called 'soft ferromagnetic properties' (i.e. a low value of coercivity and a high value of saturation magnetisation) are part of this group, [1-4]. From the thermodynamic point of view, the structure of the amorphous materials is metastable, and this stability depends largely on the production process and thermal treatment of the materials, [5-6].

In the last 20 years, a new group of amorphous alloys has been intensively studied; this group is called the 'bulk amorphous alloys' (also known as 'bulk metallic glasses' - BMG). The minimum attainable thickness of this material is limited by its production process: the process is 'melt-spinning' and the concomitant lower limit of sample thickness is approximately 100mm, [7-10]. It is also possible to manufacture the iron-based bulk amorphous materials with both very good soft-magnetic and mechanical properties, [11-12]. Improvement of these properties can be obtained by the application of an appropriate annealing process, [13-14]. During the process of annealing amorphous alloys, using temperatures below the crystallisation temperature, positional changes occur at an atomic level within the volume of the material. The mobility of the atoms is a function of the time and temperature of the annealing process itself. The atomic movement results in the release of so-called 'free volumes', created during the production process, to the surface of the material. This displacement of the 'free volumes', facilitated by the atomic movement, causes an increase in the atomic packing density in addition

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to an improvement in the thermal stability of the material. In the ferromagnetic materials, the effect is an increase in the number of magnetic atoms per unit volume, limiting the number of pinning centres; this has a positive influence, giving increases in the values of saturation magnetisation and spin-wave stiffness parameter and a decrease in the coercivity value, [15-16].

This work presents the results of investigations into the structure and magnetic properties of the bulk amorphous alloy: $Fe_{64}Co_{10}Y_6B_{20}$. The samples used in the investigations were produced in the form of rods with the following approximate dimensions: diameter 1 mm and length 20 mm. Samples were prepared in two states: firstly, the 'as-cast' state and secondly, the state following a process of isothermal annealing at a temperature of 750 K for 30 minutes. The aim of this work was to investigate both the effect of the isothermal annealing process on the soft magnetic properties and the type of structural defect influencing the magnetisation process in this alloy.

2. Materials and methods

The samples, used in the investigations, were produced by a combined injection-suction-casting method. The obtained samples of FeCoYB alloys were produced in the form of rods with the following approximate dimensions: length 20 mm and diameter 1 mm.

The structure of the 'as-quenched' ('as-cast') and 'isothermally-annealed' samples was investigated by means of a Bruker 'D8 Advance' X-ray diffractometer, the latter being equipped with a CuKα lamp. The investigations were performed over the 2Θ range from 30° to 120°, using a measurement step-size of 0.02° and an exposure time of 5s per step.

The crystallisation temperature of the 'as–quenched' alloys was determined from DSC curves, recorded at a heating rate of 10 K/min. The DSC measurements for the tested alloy samples were made using the following commercial apparatus: Nietzsche Simultaneous Thermal Analyser, type: STA409C with a 32-bit controller/regulator.

Investigations into the magnetic properties were performed using a LakeShore '7301' vibrating sample magnetometer (VSM). The obtained results were used to study the 'approach to ferromagnetic saturation'.

3. Results of the investigations

Figure 1 shows the X-ray diffraction patterns, obtained for the investigated alloy, both in the state following solidification and after the isothermal annealing process.

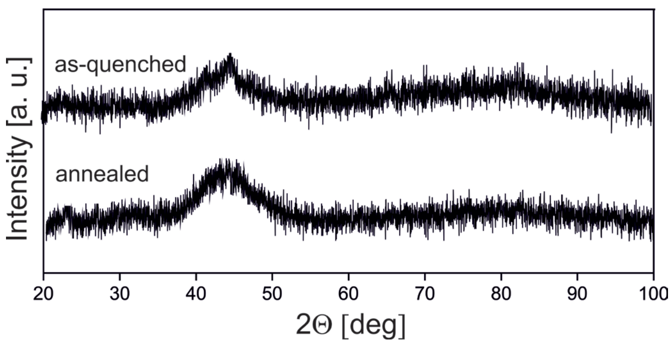

Fig. 1. X–ray diffraction patterns for $Fe_{64}Co_{10}Y_6B_{20}$ in the as-quenched state (a) and after annealing (b)

As can be seen, each diffraction pattern exhibits only a broad single maximum, which is a characteristic of amorphous materials. No peaks ascribed to the crystalline phase are observed, so the samples are found to be fully amorphous.

The DSC curve, recorded for the sample in the as-quenched state, can be seen in Fig. 2.

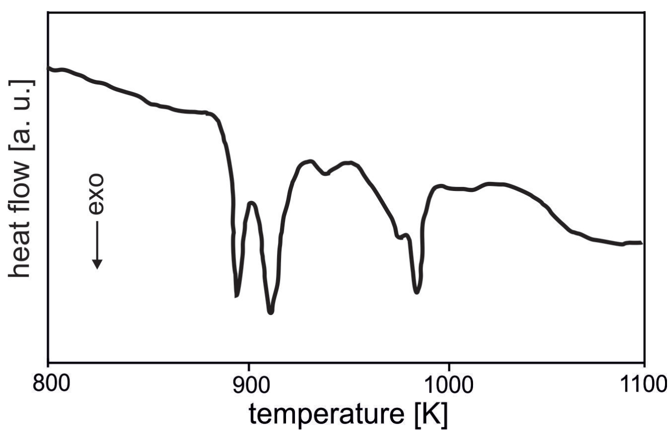

Fig. 2. DSC curve recorded at the heating rate of 10K/min for $Fe_{64}Co_{10}Y_6B_{20}$ bulk amorphous alloy in the as-quenched state

On the basis of the DSC studies, the crystallisation temperature (Tx) of the investigated alloy was established. The aim of the study was to determine the influence of the thermal treatment on the structural changes occurring in the amorphous state. The single aim of annealing the material (at a temperature of 750 K) was to relax the structure. The results of previous research confirmed that structural relaxations in the amorphous state improve the magnetic properties, [17-18].

The magnetisation curves for the as-quenched and isothermally-annealed samples are shown in Fig. 3.

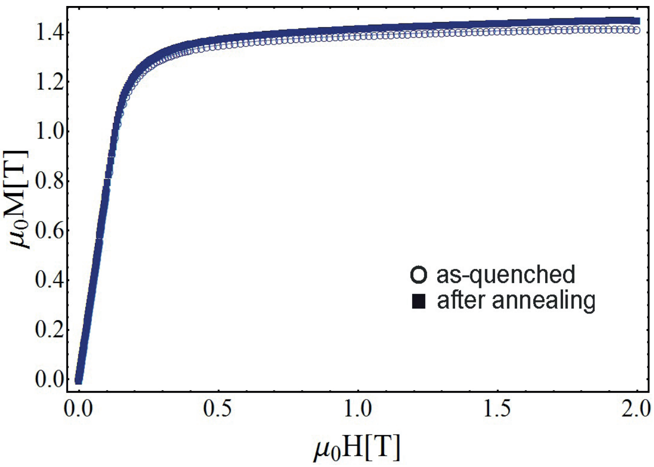

Fig. 3. Initial magnetisation curves for $Fe_{64}Co_{10}Y_6B_{20}$ in the as-quenched state and after annealing

The thermal treatment of the studied alloy resulted in an increase in the value of the saturation magnetisation: from 1.43 T for the sample in the as-quenched state to 1.46 T for the sample subjected to the isothermal annealing process.

Isothermal annealing of the investigated alloy, at the temperature of 750 K for 30 minutes, also resulted in a significant decrease in the value of coercivity HC.

The static magnetic hysteresis loops, measured for the samples of the investigated alloy in the as-quenched state and after isothermal annealing, are presented in Fig. 4.

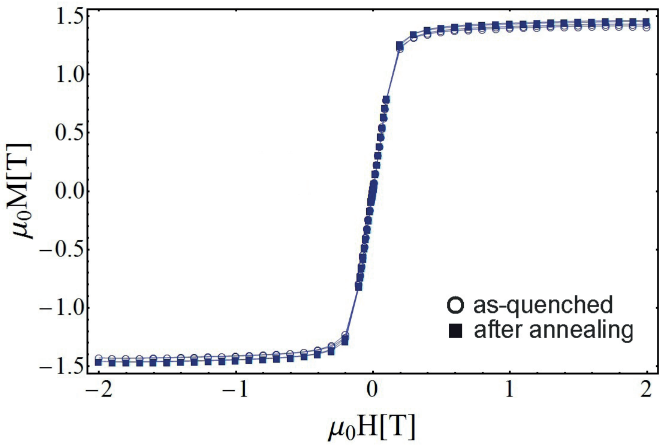

Fig. 4. Static magnetic hysteresis loops for $Fe_{64}Co_{10}Y_6B_{20}$ in the as-quenched state and after annealing

In the case of the amorphous materials, the main mechanism causing hysteresis is the limiting of the domain walls at the local stress-centres. During the annealing process, structural relaxations occur in the material. As a result, more atoms will take locally-ordered positions. This leads to greater stability of the alloy structure and improvements in the magnetic properties (i.e. increase in MS and decrease of HC).

With an increasing magnetising field, the rotations of the magnetisation vectors start to play a major role in the magnetisation process. As a result of the presence of structural defects, which are the source of short-range internal stresses, the sample cannot reach the state of saturation.

The Kronmüller theorem, [19-22], was utilised to determine the type of defect playing the leading role in the magnetisation process within strong magnetic fields.

Fig. 5 shows the high-field magnetisation curve, as a function of magnetic field induction.

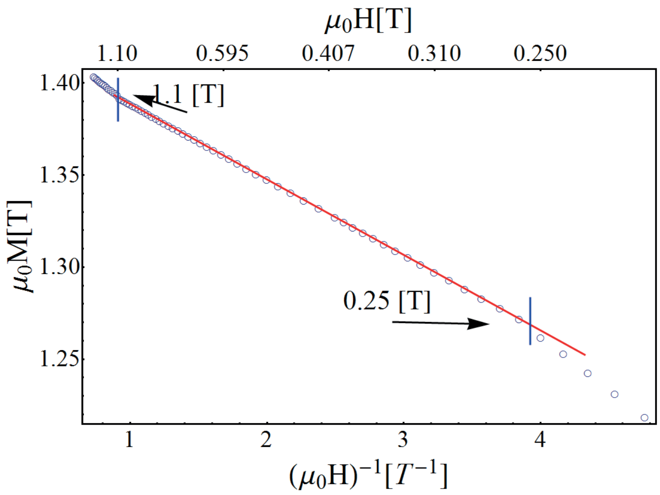

Fig. 5. The curves of high-field magnetisation, as a function of (m0 H)-1, for $Fe_{64}Co_{10}Y_6B_{20}$ in the as-quenched state

Within the magnetic field range of: 0.25 T to 1.1 T, the linear relation $M/M_S\left((\mu_0 H)^{-1}\right)$ is observed, which suggests that over this magnetic field range, the magnetisation process occurs by microscopic rotations of magnetic moments in the vicinity of so-called quasidislocational dipoles.

In Fig. 6, the magnetisation is presented as a function of (m0 H)1/2.

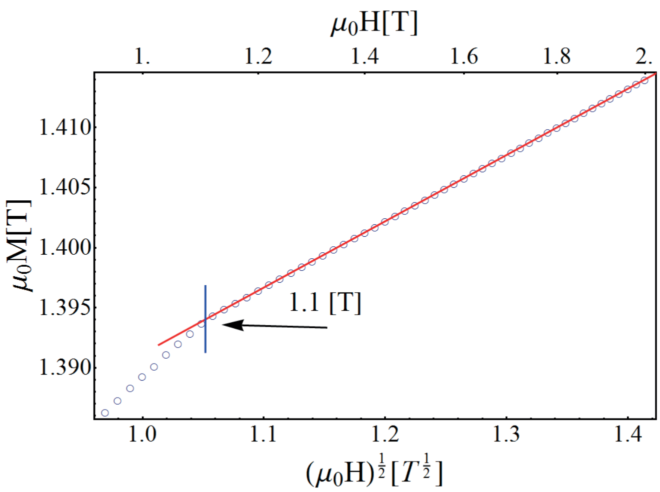

Fig. 6. The curves of high-field magnetisation, as a function of (m0 H)1/2, for $Fe_{64}Co_{10}Y_6B_{20}$ in the as-quenched state

The linear relationship of the magnetisation as a function of (m0 H)1/2 for magnetic fields of greater than 1.1 T, suggests that a further increase in the magnetisation occurs as a result of the Holstein-Primakoff paraprocess, [23-24].

Similar relationships were observed for the $Fe_{64}Co_{10}Y_6B_{20}$ alloy after the isothermal annealing process; this may be seen in Figs. 7 and 8.

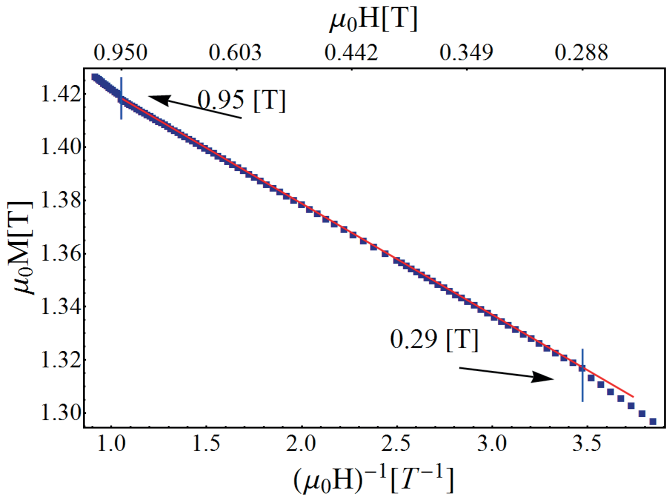

Fig. 7. The curves of high-field magnetisation, as a function of (m0 H)-1, for $Fe_{64}Co_{10}Y_6B_{20}$ after annealing

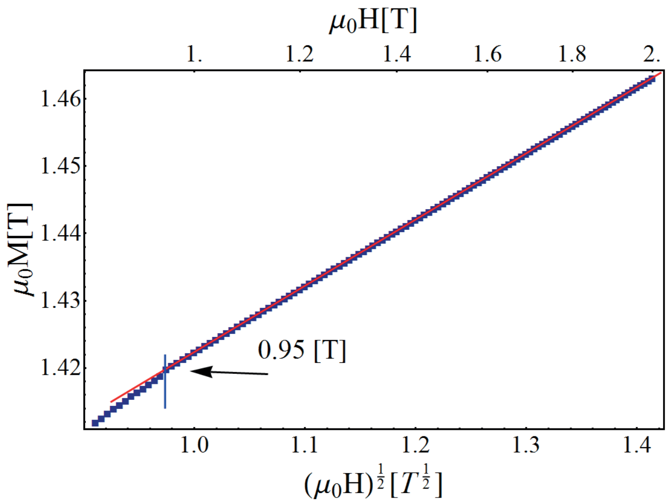

Fig. 8. The curves of high-field magnetisation, as a function of (m0 H)1/2, for $Fe_{64}Co_{10}Y_6B_{20}$ after annealing

For the sample subjected to isothermal annealing, the magnetisation process is related with the presence of linear defects; this is confirmed by the linear relationship of $\mu 0M((\mu 0H)^{1/2})$ in the magnetic field range of 0.29 T to 0.95 T.

In higher magnetic fields, i.e. $\mu 0H>0.95$ T, the Holstein-Primakoff paraprocess was observed; this is connected with the dumping of spin-waves by the magnetic field.

The surface density of defects, Ndip, present in the investigated material, was calculated.

According to the data gathered in Table 1, in the cases of both the as-quenched and isothermally-annealed samples, quasidislocational dipoles play the predominant role in the magnetisation process within strong magnetic fields. However, in the case of the annealed sample their density is significantly higher.

Using the equation [25]:

$$b = 3,54 g \mu_0 \mu_B \left(\frac{1}{4\pi D_{sp}} \right)^{3/2} kT \left(g \mu_B \right)^{1/2} \qquad (1)$$

where: g - Lande splitting factor, μ_B - Bohr magneton, the spin-wave stiffness parameter Dspf, described by [26]:

$$D_{spf} = \sum S_i J \left(\vec{r}_i \right) \vec{r}_i^{\,2} \cos^2 \left(\vec{k}, \vec{r}_i \right) \qquad (2)$$

where: S_i - represents spin in the position r_i in relation to the central atom, $J(r_i)$- exchange integral between the central atom and the atom in the position $\vec{r}_i$, $\vec{k}$ - wave vector.

For the amorphous alloys, $\vec{r}_i$ denotes the position of the atoms in the neighbourhood of the magnetic atom, in relation to the central atom. On the basis of the results presented in the Table, it can be stated that, during the thermal treatment of the alloy, the re-grouping of the atoms leads to the change in parameters in relationship (2); in turn, this leads to a decrease in the value of the spin-wave stiffness parameter Dspf. The lower value of this parameter indicates a decrease in the number of magnetic atoms in the nearest neighbourhood, and smaller distances between them.

Results of the analysis of the magnetisation curves are presented in Table 1.

4. Conclusions

The amorphous materials are unstable systems, from the energy point of view. These alloys are characterized by a lack of long-range atomic order. However, short-range atomic order is observed, in which changes can occur during an annealing process at temperatures well-below the crystallisation temperature. The magnetic properties of the amorphous alloys depend largely on their production process and their thermal history. This means that increased migration of atoms takes place within the alloy volume as

TABLE 1

The results of analysis of the magnetisation curves, as functions of the magnetic field to the powers of -1 and ½, spin-wave stiffness parameter Dspf, and Ndip – density of quasidislocational dipoles.

$Fe_{64}Co_{10}Y_6B_{20}$	$M_S[T]$	$H_C[T]$	$a_1[T^{-1}]$	$b[T^{-1/2}]$	D_{spf} $[meVnm^2]$	N_{dip} $[10^{16}m^{-2}]$
as-quenched	1.43	0.000315	0.041	0.055	45	26
after annealing	1.46	0.000247	0.042	0.098	31	39

a result of the input of sufficient energy to the system. The atomic manoeuvres are observed as a result of the potential barrier being overcome and a decrease in the free energy of the whole system. The atomic movement leads to changes in the topological and chemical distribution of the atoms.

In the investigated alloy, after the annealing process at the temperature of 750 K for 30 minutes, the following effects were observed: increases in the saturation magnetisation and surface density of linear defects, and a decrease in the value of the spin-wave stiffness parameter. The increases in the values of Ms and N were expected, but the decrease in the value of the parameter Dspf requires some explanation. In the case of the alloy in the as-quenched state, it is possible that, during the rapid solidification, the magnetic atoms are being "frozen" in unfavourable positions for ferromagnetic interactions. In this case, the magnetic atoms are positioned in groups, where the distances between them are small enough to favour antiferromagnetic interactions. During annealing of the alloy, structural relaxations occur, resulting in increases in the distances between atoms, and ferromagnetic interactions become favourable. Therefore an increase in the value of the saturation magnetisation was observed for the sample subjected to the thermal treatment. When the distance between atoms increases, the value of the parameter Dspf decreases. The spin-wave stiffness parameter is sensitive to the number of magnetic atoms without taking the sign of the interaction between them. Therefore in the case of the investigated alloy, despite an increase in MS, a decrease in Dspf was observed. In addition, it was found that, in the volume of the investigated material, structural inhomogeneities exist in the form of linear defects. The annealing process itself did not influence the change of the structural defects present in the sample; this is indicated by the almost identical value of coefficient a1. However, annealing led to an increase in the surface density of defects, compared with that of the as-quenched state; this definitely has an effect, increasing the value of the saturation magnetisation.

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Received: 20 March 2015