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 2
DOI: 10.1515/amm-2015-0261

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MICROSTRUCTURE AND MAGNETIC PROPERTIES OF THE FeZr(Y)NbCuB AMORPHOUS ALLOYS

MIKROSTRUKTURA I WŁAŚCIWOŚCI MAGNETYCZNE STOPÓW AMORFICZNYCH FeZr(Y)NbCuB

In this paper, the results of investigations are presented, into the microstructure and magnetic properties of the following amorphous alloys in the as-quenched state: $Fe_{82}Zr_7Nb_2Cu_1B_8$ and $Fe_{86}Zr_4Y_3Nb_1Cu_1B_5$. The studied material was produced in the form of thin ribbons of 3 mm width and 20 μm thickness. The structure and microstructure of the samples have been investigated by means of Mössbauer spectrometry and X-ray diffractometry. In addition, the magnetic properties of these materials have been determined, i.e. the low-field magnetic susceptibility, and the magnetisation as a function of temperature and magnetising field.

On the basis of the performed investigations, it has been found that a minor change in the quantities of elements favouring amorphisation, such as: Zr and Y, has an influence on the value of the Curie temperature and the magnetic properties of the resulting alloys. It should be noticed that the changes, introduced in the chemical composition of the alloys, don't change the combined volume of these elements, i.e. Zr_7 and Zr_4Y_3.

Keywords: amorphous alloys, Mössbauer spectroscopy, magnetic susceptibility

W pracy przedstawiono wyniki badań struktury i mikrostruktury oraz właściwości magnetycznych stopów amorficznych $Fe_{82}Zr_7Nb_2Cu_1B_8$, $Fe_{86}Zr_4Y_3Nb_1Cu_1B_5$ w stanie po zestaleniu w postaci cienkich taśm o szerokości 3 mm i grubości 20 μm. Strukturę oraz mikrostrukturę próbek badano wykorzystując spektrometrię mössbauerowską i spektroskopię rentgenowską. Dokonano również pomiarów właściwości magnetycznych, takich jak: niskopolowa podatność magnetyczna, magnetyzacja w funkcji temperatury i funkcji pola magnesującego. Na podstawie przeprowadzonych badań stwierdzono, że niewielka zmiana amorfizatorów takich jak: cyrkon i itr znacząco wpływa na wartość temperatury Curie, a także wpływa na właściwości magnetyczne tych stopów. Należy zwrócić szczególną uwagę na fakt, że wprowadzone zmiany składowe nie zmieniają ich ilości tzn. Zr_7 i Zr_4Y_3.

1. Introduction

The amorphous alloys are characterised by their lack of long-range atomic order, and, as a result, their complicated magnetic structure and anomalies of certain physical properties [1-3].

The magnetic properties of the amorphous alloys depend, amongst other influences, on their chemical composition, production conditions and thermal treatment [4, 5].

Controlled thermal treatment of these alloys could lead to the production of a nanocrystalline material featuring crystalline grains of diameter >100 nm [6, 7].

The nanocrystalline alloys make up a very interesting group of materials, both from the fundamental research and applications points of view. Using amorphous alloys and a planned process (involving careful selection of the: chemical composition, production method, cooling rate and thermal treatment), soft magnetic materials can be obtained which feature a Curie temperature (T_C) close to room temperature (293K). Therefore the appropriate chemical composition allows the manufacture of amorphous alloys with relatively low Curie temperature and which exhibit the magnetocaloric effect.

Iron, cobalt, nickel and elements which stabilise the amorphous structure, (i.e.: silicon, boron and phosphorus) [8-10], are amongst main components of the soft magnetic amorphous alloys; these alloys can be produced by rapidly quenching the molten material on the surface of a rotating wheel. This method allows for the manufacture of thin ribbons of approximate thickness 30 μm. The manufacturing process of these amorphous ribbons is performed using a cooling rate of greater than 10^4 K/s.

In this work, the results of investigations are presented revealing the structure, microstructure and magnetic properties of $Fe_{82}Zr_7Nb_2Cu_1B_8$ and $Fe_{86}Zr_4Y_3Nb_1Cu_1B_5$ amorphous alloys in the as-quenched state.

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2. Materials and methods

For these studies, amorphous alloys in the form of ribbons of width 3 mm and approximate thickness 20 μm were used. High- purity alloying elements were melted using an electric arc; this facilitated the production of polycrystalline ingots of the desired alloys, which featured the nominal compositions: $Fe_{82}Zr_7Nb_2Cu_1B_8$ and $Fe_{86}Zr_4Y_3Nb_1Cu_1B_5$.

The amorphous ribbons were prepared using a method involving the rapid-quenching of the molten metal on a single, rotating copper wheel. The process was carried out under a protective atmosphere of argon.

Studies of the microstructure and structure were performed on samples in the as-quenched state, at room temperature. A POLON Mössbauer spectrometer, equipped with a ^{57}Co (Rh) radiation source of activity 50 mCi, was used for observation of the magnetic structure and microstructure of the samples. X-ray investigations were carried out by means of a Brucker Advance D8 diffractometer, over the 2θ range from 30 to 100°, with a 0.02° step-size, and an exposure time of 7 s. X-ray spectra recorded in Bragg-Brentano geometry, using a semi-conductor counter and a CuKα source, facilitated the confirmation of the amorphicity of the studied alloys.

After appropriate preparation of the samples, investigations into the magnetic susceptibility were performed; a fully-automated arrangement was used, implementing the transformer method. The Curie temperatures of the studied ribbons were determined from analysis of the saturation magnetisation curves as a function of temperature, according to the relationship $\sigma^{1/\beta}$(T) (where β − critical exponent, which for so-called "Heisenberg ferromagnets" has a value of 0.36). These measurements were performed using Faraday's magnetic scale. Utilising a method for investigating the so-called "critical" behaviour of magnetisation at temperatures approaching the Curie temperature, the values of this temperature for the investigated alloys were established [11]. According to the Curie temperature, the respective range of magnetic susceptibility measurements was determined. For the $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy (T_c = 335K), the measurements were performed over the temperature range from 210 to 345 K, whereas for the sample of $Fe_{86}Zr_4Y_3Nb_1Cu_1B_5$ alloy (T_c = 298K) the temperature range was from 130 to 310K.

3. Results and discussion

X-ray diffraction patterns for the investigated alloys are presented in Fig. 1.

Within these patterns, narrow maxima corresponding to the crystalline phase are not visible; only wide halos can be observed at the 2Θ of 50°. This is typical of the iron-based amorphous alloys. The amorphicity of the investigated samples was confirmed by the Mössbauer investigations. The transmission Mössbauer spectra for the samples of the $Fe_{82}Zr_7Nb_2Cu_1B_8$ and $Fe_{86}Zr_4Y_3Nb_1Cu_1B_5$ alloys, in the as-quenched state, are shown in Fig. 2

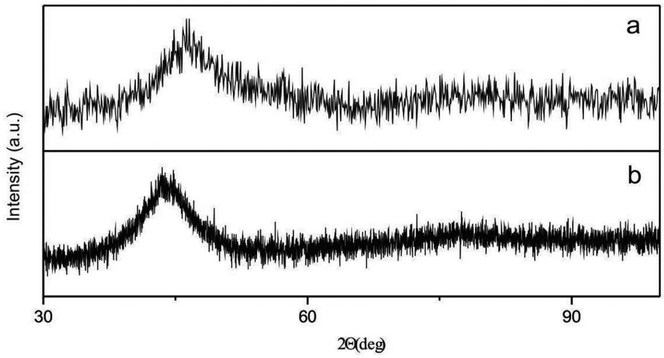

Fig. 1. X-ray diffraction patterns for the investigated alloys: $Fe_{82}Zr_7Nb_2Cu_1B_8$ (a), $Fe_{86}Zr_4Y_3Nb_1Cu_1B_5$ (b)

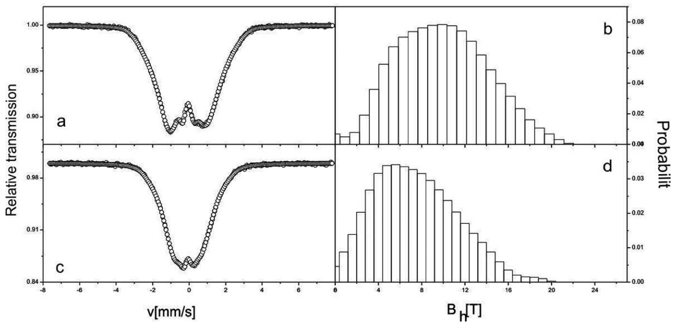

Fig. 2. Transmission Mössbauer spectra (a, c) and corresponding hyperfine field distributions (b, d) for the amorphous alloys: $Fe_{82}Zr_7Nb_2Cu_1B_8$ (a, b) and $Fe_{86}Zr_4Y_3Nb_1Cu_1B_5$ (c, d) in the as-quenched state

The Mössbauer spectra (Fig. 2. a, c) are typical for the amorphous ferromagnetic alloys of FeZrB with high iron content [12, 13]. The hyperfine field distributions are asymmetrical (Fig. 2. b, d) and consist of low- and high-field components. The shape of the Mössbauer spectrum for the $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy (Fig. 2. a) differs from that obtained for the $Fe_{86}Zr_4Y_3Nb_1Cu_1B_5$ alloy (Fig. 2. c), which suggests higher homogeneity.

Results of the analysis of the Mössbauer spectra for the investigated alloys in the as-quenched state are presented in Table 1.

TABLE 1

An average induction of the hyperfine field $(B_{hf})_{ef}$, standard deviation of the hyperfine field induction (ΔD_s), relative intensity of the $A_{2,5}$ lines of the Mössbauer spectra

Alloy composition	$(B_{hf})_{ef}$ [T]	ΔD_s [T]	$A_{2,5}$
$Fe_{82}Zr_7Nb_2Cu_1B_8$	9.86 (2)	4.17 (2)	2.7 (1)
$Fe_{86}Zr_4Y_3Nb_1Cu_1B_5$	7.45 (2)	3.87 (2)	2.00 (2)

In the case of the alloy with the higher boron content, the ferromagnetic interactions are stronger; this is confirmed by the higher value of the average hyperfine field induction (Table 1). The atomic radius of boron (85 pm) is much smaller than that of yttrium (180 pm), and, as a result, the exchange interactions are much stronger in the alloy with higher boron content. As a "larger" element, yttrium is separating the magnetic moments and weakening the interactions; this results in a decrease in the average induction of the hyperfine field, as observed in Table 1. A decrease is also observed in the value of the standard deviation of the hyperfine field induction (ΔD_S), which is a measure of the dissimilar surrounding of the iron atoms. For the $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy, the tendency for magnetisation vector to align with the ribbon plane is observed; this is manifested as a larger value of the $A_{2.5}$ parameter. An increase in the value of the high-field component in the hyperfine field distributions for the $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy is observed (Fig. 2. b); this is connected with the presence of regions in which, in the vicinity of the iron atoms, atoms of other elements (such as boron and zirconium) are located.

In order to estimate the values of the Curie temperature of the investigated alloys, measurements of the magnetisation versus temperature were performed.

Fig. 3 depicts the relevant magnetisation curves (σ) as a function of temperature, at a constant magnetic field of 0.75 T, for the investigated alloys.

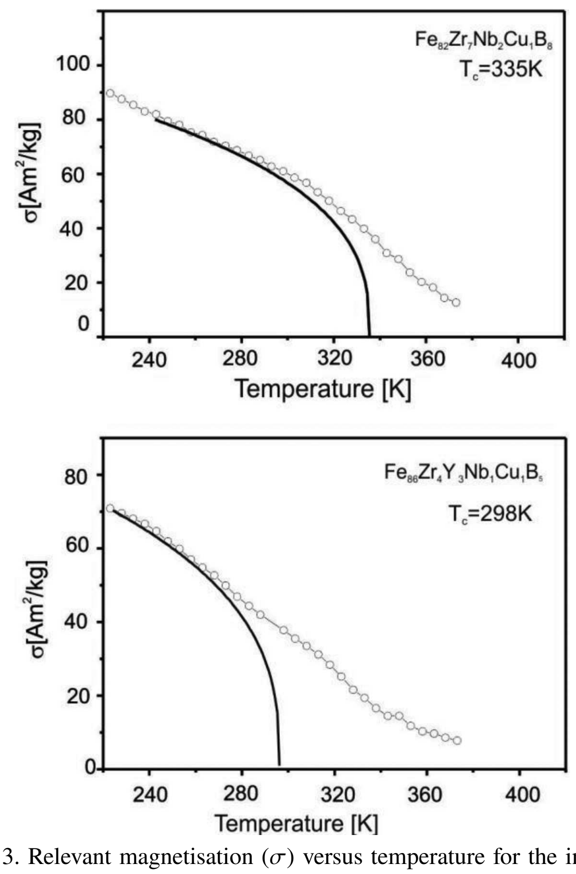

Fig. 3. Relevant magnetisation (σ) versus temperature for the investigated alloys

For both alloys, magnetisation was found to decrease (without reaching zero) with increasing temperature. This is connected with the inhomogeneity of the investigated alloys, in which areas with similar values of the Curie temperature exist.

A significant decrease in the value of the Curie temperature was observed after replacement of zirconium atoms with yttrium, and a subsequent increase in the volume of the iron atoms with loss of boron atoms.

The Curie temperature for the investigated alloys also was confirmed from the magnetic susceptibility curves. Fig. 4 shows the magnetic susceptibility curves for these alloy samples as a function of temperature, in a magnetic field of amplitude 0.26 A/m and at a frequency of 2 kHz.

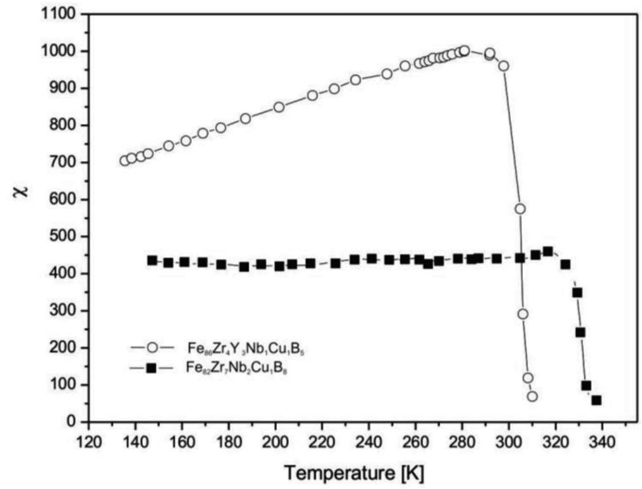

Fig. 4. The magnetic susceptibility curves for the amorphous alloys in the as-quenched state

For the $Fe_{86}Zr_4Y_3Nb_1Cu_1B_5$ alloy, the magnetic susceptibility was found to increase with increasing temperature. In the vicinity of 290 K, a sudden drop in the magnetic susceptibility could be observed.

For the second of the investigated alloys, the magnetic susceptibility was found to be stable with increasing temperature up to about 325 K at which point a sudden decrease was observed.

The sudden drop in the value of the magnetic susceptibility is connected with the ferro-paramagnetic phase transition [14, 15]. Due to fluctuations in the composition of the amorphous alloys, the value of the Curie temperature can be only estimated. It should be observed that the alloy of $Fe_{82}Zr_7Nb_2Cu_1B_8$ has a larger value of the Curie temperature; this is related to the stronger interactions of Fe-Fe magnetic pairs. This is confirmed by the results of the Mössbauer investigations, which indicate a higher value of the average induction of the hyperfine field.

4. Conclusions

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

- Samples of the $Fe_{82}Zr_7Nb_2Cu_1B_8$ and $Fe_{86}Zr_4Y_3Nb_1Cu_1B_5$ alloys, in the form of ribbons in the as-quenched state, were fully amorphous;
- The investigated alloys were found to exhibit good soft magnetic properties over a wide temperature range;
- Increased boron content in the $Fe_{82}Zr_7Nb_2Cu_1B_8$ alloy caused an increase in the value of the average hyperfine field, this being connected with the larger distances between the iron atoms;
- Alloy with the addition of yttrium and lower boron content exhibited a lower value of the Curie temperature;
- In the investigated alloys, areas of differing chemical composition were observed. As a result, in the vicinity of the Curie temperature, instead of the narrow Hopkinson max-

imum, a wide ferro-paramagnetic transition was observed on the χ(T) curves.

Due to their low Curie temperature – close to room temperature – the investigated alloys exhibit potential for application in magnetic refrigeration. The method of 'magnetic cooling' is an alternative to currently-used refrigeration methods, which are not environmentally-friendly due to both the nature of the refrigerant and the excessive energy requirements for operation.

As shown in the research described in this work, given certain chemical compositions of the alloys, even a minor change (Zr_7, Zr_4Y_3) has a major influence on the value of the Curie temperature.

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Received: 20 February 2014.