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Influence of Co and Zr Content on Creation of Crystalline Phases in Rapidly-Cooled, Injection-Cast Alloys $Fe_{70}Zr_{8-x}Co_xNb_2B_{20}$ (where $x = 0$, 2, 4, 6 or 8)

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Rapid solidification techniques allow the manufacture of nanocrystalline alloys using a single-stage production process. There is an issue with the reproducibility of this process. However, careful selection of the chemical composition of the alloy allows a degree of control over the process. This paper presents the results of investigations into the structure and magnetic properties of rapidly-quenched alloys based on Fe. For these investigations, alloys with the compositions of $Fe_{70}Zr_{8-x}Co_xNb_2B_{20}$ (where $x = 0$, 2, 4, 6, or 8) were selected. The alloys were made using an injection-casting method. The structure of the obtained alloys was investigated using X-ray diffractometry. Utilising dedicated software, the crystalline phases within the volume of the samples were identified — as the magnetic phases of $Fe_{23}B_6$, αFe, and Fe_2B. The magnetic properties of the produced alloys were determined on the basis of measurements of the magnetic polarisation curves as a function of temperature, and the static hysteresis loops. The thermomagnetic curves confirmed the existence of the $Fe_{23}B_6$ phase within the volume of two samples. The values of the saturation magnetisation and coercive field were determined from the static hysteresis loops. The alloys in which the presence of the $Fe_{23}B_6$ phase was detected (alloy compositions $Fe_{70}Zr_4Co_4Nb_2B_{20}$ and $Fe_{70}Zr_2Co_6Nb_2B_{20}$) were found to exhibit soft magnetic properties. A progressive decline in the presence of the Fe_2B phase within the investigated alloys was observed with increasing Co content (at the expense of Zr content). On the basis of the performed investigations, the major influence of the Co and Zr content on the creation process of the crystalline phases, during the rapid solidification process was confirmed.

topics: rapidly-quenched alloys, X-ray diffractometry, injection-casting method

1. Introduction

Rapidly-quenched alloys based on Fe offer strong potential for applications, due to their good magnetic and mechanical properties [1–3]. This is relevant for alloys with amorphous, as well as nanocrystalline structure. This former class of materials can be characterized by both (i) "soft magnetic" properties, i.e. high values of saturation magnetisation and magnetic susceptibility, and a low value of coercivity [2, 3] and (ii) "hard magnetic" with high coercivity and maximum energy product [4, 5]. During the production process, the structural disorder (typical of liquids) is relatively easy to achieve at a high cooling rate of about 10^5 K/s — as in the method of melt-spinning alloy onto a rotating copper-cylinder [6]. Unfortunately, although this method has been implemented on an industrial scale, it has a major disadvantage. It only allows the production of materials with thicknesses of less than 100 μm, which restricts the applications of materials made by this method. A relatively recent solution is to utilise methods which involve the cooling of the molten alloy in a water-cooled copper die. The suction- and injection-casting methods are examples of this technique [7]. These methods allow cooling rates of up to 10^3 K/s and the production of materials with thicknesses of more than 1 mm. By applying the "three criteria" which were formulated by Inoue (i.e. use of several elements with large difference in the atomic radii and with negative mixing heat), it is possible to obtain an alloy with an amorphous structure for many different chemical compositions and at a lower cooling rate [8, 9]. However, with a high Fe content (i.e. greater than 70%) it is very difficult to achieve an amorphous structure.

In this case, during a single-step production process, there is a possibility of obtaining an alloy with a nanocrystalline structure. The rapid cooling process significantly hinders the crystallisation process. After the solidification process, within the volume of the material the resulting amorphous matrix could contain embedded crystalline grains. The nanocrystalline materials could exhibit better properties in comparison to their amorphous and crystalline counterparts, obtained by traditional production methods.

The aim of this study was to determine the effect of the Co and Zr content on the creation of crystalline phases within the alloy family $Fe_{70}Zr_{8-x}Co_xNb_2B_{20}$, the studied alloy samples being obtained in a single-step production process. In addition, an investigation was undertaken into the effect of the presence of these phases on the magnetic properties of the resulting materials.

2. Materials and methods

Polycrystalline ingots of the investigated alloys, $Fe_{70}Zr_{8-x}Co_xNb_2B_{20}$, were formed using an arc-furnace, with the aid of a protective argon atmosphere. The resulting pre-processed material was then used to produce the required rapidly-quenched alloy samples using an injection-casting method. The alloy was melted using eddy current heating. The molten alloy was injected, under the pressure of the argon, into a water-cooled copper-die. The rapidly solidified samples were made in the form of plates with the following dimensions: 10 mm×10 mm×0.5 mm.

The structure of the resulting materials was studied using X-ray diffractometry. A Bruker D8 Advance X-ray diffractometer was used. The investigations were performed on powdered samples, over the 2θ range of 30°–100°. The magnetic properties of the obtained alloys were measured by means of a Faraday balance. Thermomagnetic curves were recorded over the temperature range from room temperature up to 850 K, at a heating rate of 10 K/s. Static magnetic hysteresis loops were measured, over an external magnetic field range of up to 2 T, using a Lake Shore vibrating sample magnetometer.

3. Results

Reference Fig. 1 presents the X-ray diffraction patterns for the investigated samples. In the presented diffraction patterns, peaks originating from the reflection of the X-rays from the ordered phases are visible as well as the fuzzy, wide maxima within the 2θ range 40–50°.

These maxima could indicate the presence of one or more remaining amorphous phases within the volume of the investigated samples. Using the Match! Software, three magnetic crystalline phases were identified: Fe_2B, $Fe_{23}B_6$ and αFe. In addition, in all cases, there were unidentified peaks. The highest number of unidentified peaks was observed for the sample of the $Fe_{70}Co_8Nb_2B_{20}$ alloy. Quenching the alloys at a high speed of up to 10^3 K/s could lead to the presence of stresses, which in turn could affect the deformation of the phases during the crystallisation process (i.e. yielding a change in the parameter of the crystalline network), and hinder their identification. The intensity of the peaks related with the α-Fe phase was found to decline with increasing Co content; however, in the case of the $Fe_{70}Zr_2Co_6Nb_2B_{20}$ alloy, the presence of this phase was not identified (Fig. 1d). It is interesting that the α-Fe phase appeared again in the sample of the $Fe_{70}Co_8Nb_2B_{20}$ alloy (Fig. 1e). In the case of the Fe_2B phase, the situation was found to be different; this phase was present in all of the investigated samples, except for the $Fe_{70}Co_8Nb_2B_{20}$ alloy (Fig. 1e). Moreover, on the basis of the intensities of the peaks, it could be stated that the volume of the Fe_2B phase within the alloy decreases with increase of Co content (at the expense of the Zr content); this finding agrees with other studies [10].

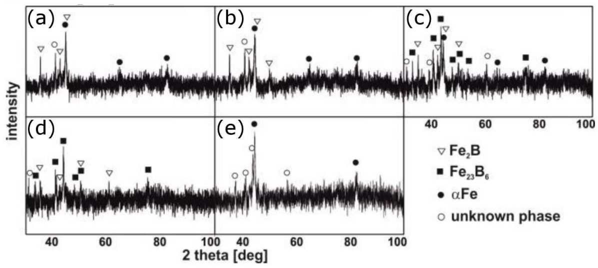

Fig. 1. X-ray diffraction patterns for the samples: (a) $Fe_{70}Zr_8Nb_2B_{20}$, (b) $Fe_{70}Zr_6Co_2Nb_2B_{20}$, (c) $Fe_{70}Zr_4Co_4Nb_2B_{20}$, (d) $Fe_{70}Zr_2Co_6Nb_2B_{20}$, (e) $Fe_{70}Co_8Nb_2B_{20}$.

The presence of the soft-magnetic phase of $Fe_{23}B_6$ was only identified in the $Fe_{70}Zr_4Co_4Nb_2B_{20}$ alloy (Fig. 1c) and the $Fe_{70}Zr_2Co_6Nb_2B_{20}$ alloy (Fig. 1d). It could be suggested that the presence of this phase is promoted through a decrease in the volume of the Fe_2B phase, with an increase in the Co content in the alloy. However, this cannot explain the absence of this phase in the $Fe_{70}Co_8Nb_2B_{20}$ alloy.

The thermomagnetic curves for the alloy samples are presented in Fig. 2.

The recorded curves differ significantly from each other, confirming the major differences in the structure of the materials. In all cases, the curves failed to reach zero magnetisation during the measurements, which indicates the presence of magnetic phases within the volume of the investigated samples at temperatures above 850 K (i.e. above the range of measurement). A single inflection is visible in the shape of the curves in Fig. 3a and b; this is related with the transition of magnetic phase from the ferromagnetic state to the paramagnetic state. It is possible that this inflection is connected with the unidentified crystalline phase. The inflections present on the curves in Fig. 2c and d are related to

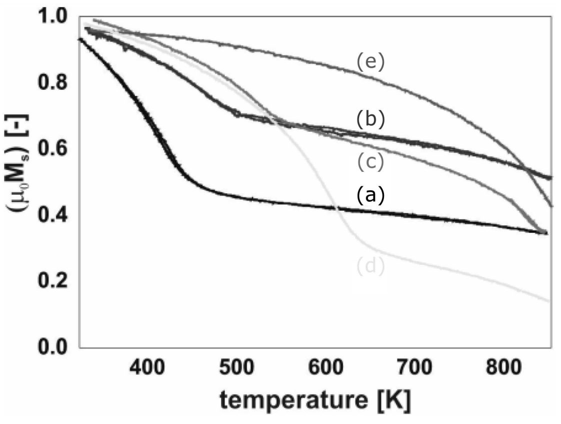

Fig. 2. The thermomagnetic curves for the alloys: (a) $Fe_{70}Zr_8Nb_2B_{20}$, (b) $Fe_{70}Zr_6Co_2Nb_2B_{20}$, (c) $Fe_{70}Zr_4Co_4Nb_2B_{20}$, (d) $Fe_{70}Zr_2Co_6Nb_2B_{20}$, (e) $Fe_{70}Co_8Nb_2B_{20}$.

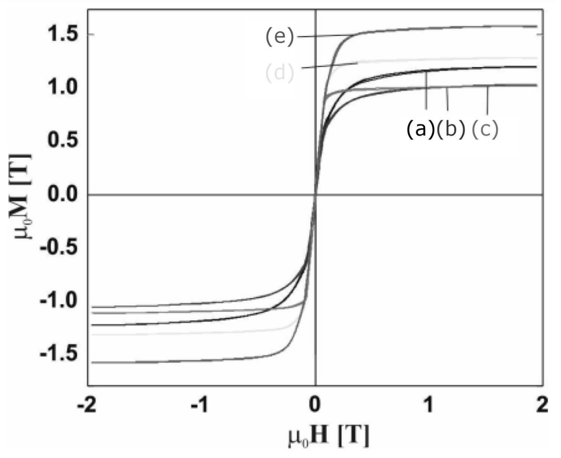

Fig. 3. Static magnetic hysteresis loops for the alloys: (a) $Fe_{70}Zr_8Nb_2B_{20}$, (b) $Fe_{70}Zr_6Co_2Nb_2B_{20}$, (c) $Fe_{70}Zr_4Co_4Nb_2B_{20}$, (d) $Fe_{70}Zr_2Co_6Nb_2B_{20}$, (e) $Fe_{70}Co_8Nb_2B_{20}$.

the presence of the $Fe_{23}B_6$ magnetic phase (identified from the diffraction patterns in Fig. 1c and d), with a Curie temperature of less than 700 K. In the case of the curve for the $Fe_{70}Co_8Nb_2B_{20}$ alloy, due to the measurement range being restricted to 850 K, the transition from the ferromagnetic state to the paramagnetic state was not observed. Figure 3 presents the static magnetic hysteresis loops for the investigated alloys. The investigated materials are characterised by major differences in their magnetic properties. The alloys, in which the $Fe_{23}B_6$ phase was identified, exhibit low values of coercivity, and could be classified as soft-magnetic materials [11].

For the remaining investigated alloys, the value of coercivity is greater than 1000 A/m, which puts them in the class of semi-hard magnetic materials. The alloy without the Zr content exhibits the highest value of saturation magnetisation, which is expected, as this alloy has the highest content of ferromagnetic elements. Table I presents the summary of

TABLE I

Magnetic properties of the $Fe_{70}Zr_{8-x}Co_xNb_2B_{20}$ alloys and the identified crystalline phases.

	M_S [T]	H_C [A/m]	α-Fe	Fe_2B	$Fe_{23}B_6$
$Fe_{70}Zr_8Nb_2B_{20}$	1.23	4766	+	+	–
$Fe_{70}Zr_6Co_2Nb_2B_{20}$	1.04	2611	+	+	–
$Fe_{70}Zr_4Co_4Nb_2B_{20}$	1.08	202	+	+	+
$Fe_{70}Zr_2Co_6Nb_2B_{20}$	1.31	95	–	+	+
$Fe_{70}Co_8Nb_2B_{20}$	1.62	4293	+	–	–

the results. The $Fe_{70}Zr_2Co_6Nb_2B_{20}$ alloy deserves special attention, as it exhibits a relatively low value of coercivity (95 A/m) and a high value of saturation magnetisation (1.31 T).

4. Conclusions

The aim of this work was to determine the effect of the Co and Zr content on the process of creation of crystalline phases within bulk amorphous alloys with the following chemical compositions: $Fe_{70}Zr_{8-x}Co_xNb_2B_{20}$. The obtained samples have a crystalline structure. Analysis of X-ray diffraction patterns revealed the presence of various crystalline phases, depending on the chemical composition of the alloy. As expected, an increase in the Co content restricted the creation of the Fe_2B phase. However, it is more difficult to explain the changes in the volumes of the α-Fe and $Fe_{23}B_6$ phases in the investigated alloys. On the basis of the X-ray diffraction patterns, it was found that, within the volume of the investigated alloys, an unidentified crystalline phase is present. The presence of this phase seems to be most pronounced for the $Fe_{70}Co_8Nb_2B_{20}$ alloy (Fig. 1e). The presence of the identified crystalline phases is reflected in the magnetic properties of the obtained materials. Samples that are rich in the $Fe_{23}B_6$ phase exhibit so-called soft magnetic properties.

The obtained results of the investigations indicate clearly the effect of the Co and Zr proportion on the crystallisation process, during the rapid solidification of the liquid alloy. The presented results indicate the possibility of creating — using a single-stage production process — a nanocrystalline material which exhibits good magnetic properties.

References

[1] M.E. Mchenry, M.A. Willard, D.E. Laughlin, *Progr. Mater. Sci.* **44**, 291 (1999).

[2] P. Rezaei-Shahreza, A. Seifoddini, S. Hasani, *J. Alloys Compd.* **738**, 197 (2018).

[3] S. Hasani, P. Rezaei-Shahreza, A. Seifoddini, *Metall. Mater. Trans. A* **50**, 63 (2019).

[4] K. Pawlik, P. Pawlik, J.J. Wysłocki, W. Kaszuwara, *J. Alloys Compd.* **536S**, S348 (2012).

[5] K. Pawlik, *Acta Phys. Pol. A* **131**, 1264 (2017).

[6] Y. Geng, Y. Wang, Z. Wang, J. Qiang, H. Wang, C. Dong, O. Tegus, *Mater. Des.* **106**, 69 (2016).

[7] M. Nabiałek, *J. Alloys Compd.* **642**, 98 (2015).

[8] M.M. Trexler, N.N. Thadhani, *Progr. Mater. Sci.* **55**, 759 (2010).

[9] A. Inoue, *Mater. Sci. Eng. A* **226-228**, 357 (1997).

[10] H.R. Lashgari, D. Chu, Shishu Xi, Huande Sun, M. Ferry, S. Li, *J. Non-Cryst. Solids* **391**, 61 (2014).

[11] H. Liebermann, *Rapidly Solidified Alloys*, Springer, New Jersey 1993.