Structure and magnetic properties of Fe-based amorphous alloys

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ABSTRACT

Purpose: This paper presents studies relating to the structure, magnetic properties and thermal stability of the following bulk amorphous alloys: Fe_{61}Co_{10}Ti_{3+x}Y_{6+x}B_{20} (where x = 0 or 1)

Design/methodology/approach: The investigated samples were prepared in the form of rods by using the suction-casting method. The material structures were investigated using X-ray diffractometry and Mössbauer spectroscopy. The thermal stability was determined on the basis of Differential Scanning Calorimetry (DSC) plots. The magnetic properties were studied using a completely automated set-up for measuring susceptibility and its disaccommodation.

Findings: It was found that both alloys were amorphous in the as-cast state. The DSC curve obtained for Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloy exhibited one exothermic peak, while for the Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} sample, two peaks were distinguishable, corresponding to the crystallization of the sample. The bifurcation of the maximum on the DSC curve for the Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} sample may also testify to the presence of the primary crystallizing phase (FeCo)_{23}B_{6}. Data obtained from the magnetic susceptibility disaccommodation curves clearly show that in the Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloy there is less free volumes than in the second of the investigated alloys, this results in a lesser range of relaxation time. Moreover, Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloy exhibits the better time and thermal stability of magnetic properties. In both of the studied alloys, at low frequencies, the total losses were comparable with those observed in classical silicon-iron alloys.

Practical implications: A Ferrometer was used for the determination of core losses.

Originality/value: The paper presents some researches of the Fe-based bulk amorphous alloys obtained by the suction-casting method.

Keywords: The bulk alloy; Microstructure; Disaccommodation; Permeability; Core losses

Reference to this paper should be given in the following way:

1. Introduction

The amorphous alloys are usually prepared in the form of thick ribbons, wires or rods and tubes [3-6]. These materials are interesting not only from a scientific point of view but also because of potential application [7]. Fe-based amorphous alloys exhibit outstanding magnetic properties and maybe used as magnetic cores in electrical equipments. The bulk amorphous alloys are a new group of materials and are usually multicomponent systems. In order to obtain the bulk amorphous alloys three empirical rules should be fulfilled [8,9]. The alloy...
should contain at least three or more components. Moreover, the atomic radii of main components should differ of about 12% and characterize large negative heat of mixing. These alloys are prepared at relatively low quenching rates which depend on their chemical composition. The low quenching rate enables occurring the relaxation processes during the sample preparation. Due to these process the structure of the as-quenched bulk amorphous alloys seems to be at least partially relaxed. Due to structure relaxations the atom packing density in these materials is higher than in the ordinary amorphous alloys which in turn involves their good thermal stability. Additionally, in [1,2] was shown that in the Fe-Co-B bulk amorphous alloys during prolonged solidification time may occur to formation of primary crystallizing phase (FeCo)23B6.

In this paper we present the results of the structure, thermal stability and magnetic properties studies for the bulk amorphous Fe61Co10Ti2Y7B20, Fe61Co10Ti3Y6B20 alloys.

2. Materials and methodology

Ingots of the alloys were prepared by arc melting of high purity elements in an argon atmosphere. The bulk amorphous Fe61Co10Ti2Y7B20, Fe61Co10Ti3Y6B20 alloys were obtained in the form of rods 1 mm in diameter and 2 cm long by the suction casting method [10]. The structure of the samples was studied by X-ray diffractometry and Mössbauer spectroscopy. Mössbauer spectra in a transmission geometry were recorded by conventional spectrometer working at constant acceleration with 57Co(Rh) radioactive source of 50mCi activity.

The thermal stability was investigated using differential scanning calorimeter. DSC curves were recorded at the heating rate of 10 K/min.

The magnetic properties i.e. permeability, its disaccommodation, susceptibility and core losses were measured by a transformer method using a completely automated set-up.

![X-ray diffraction patterns](image)

Fig. 1. X-ray diffraction patterns for Fe61Co10Ti2Y7B20 (a), Fe61Co10Ti3Y6B20 (b) alloys after solidification

![Mössbauer spectra](image)

Fig. 2. Mössbauer spectra (a, b) and corresponding hyperfine field induction distributions (c,d) for Fe61Co10Ti2Y7B20 (a,c), Fe61Co10Ti3Y6B20 (b,d) alloys after solidification
3. Results and discussion

In Fig. 1 X-ray diffraction patterns for Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20}, Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloys after solidification are shown. The presented patterns are typical for amorphous materials with one broad maximum in the vicinity of 20 = 50°. No sharp peaks, characteristic for crystalline phases have been observed. X-ray diffraction studies cannot unambiguously testify about amorphous structure of the sample. In order to prove amorphous structure additionally were done Mössbauer effect studies. The transmission Mössbauer spectra and corresponding hyperfine field induction distributions for investigated alloys are presented in Fig. 2.

The spectra are typical for the amorphous ferromagnets and have a form of asymmetric sextets with broad and overlapped lines. The hyperfine magnetic field distributions P(B_{hf}) for Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} and Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloys are wide. In amorphous Fe-Co-B type alloys the distribution of hyperfine field induction on ⁵⁷Fe sites is in the range up to 32 T [11,12]. In the case of Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloy the distribution of hyperfine field induction ranges to 35 T, what is connected with presence of primary crystallizing phase (FeCo)_2B [1,2]. At least two components can be distinguished, that suggest the presence of regions in the sample with different iron concentrations. In Fig. 3. are shown DSC curves recorded at the heating rate of 10 K/min.

![DSC curves](image)

The curve obtained for the amorphous Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloy exhibits one exothermic peak. Whereas, as for the amorphous Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} sample, in the DSC curve, it can be distinguished near situated two peaks corresponding to the crystallization of the sample. The shape of the DSC curve for Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} samples may indicate the presence of primary crystallization phase (FeCo)_2B [1,2], which is consistent with the results of Mössbauer spectroscopy.

In Figs. 4-5 low field magnetic susceptibility versus temperature for Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloy after solidification are shown.

![Magnetic susceptibility](image)

The magnetic susceptibility (\chi) increases with temperature and reaches the maximum near the Curie temperature (T_c). For higher temperatures (> T_c) \chi drastically decreases. It can be seen that the magnetic susceptibility for the Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloy slightly increases with temperature confirming its good thermal stability. In the case of Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloy conspicuous increase of magnetic susceptibility versus temperature is observed. Such behaviour can be elucidated taking into account two competitive processes: the decrease of the magnetic anisotropy and magnetization with temperature.

![Magnetic permeability](image)
higher temperatures (>T_c) slightly increases with temperature confirming its good thermal stability. In the case of Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} samples may indicate the presence of primary crystallization phase (FeCo)_{23}B_{6} [1, 2], which is consistent with near situated two peaks corresponding to the crystallization of the sample. The shape of the DSC curve for Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} samples may indicate the presence of primary crystallizing phase (FeCo)_{23}B_{6} [1, 2], which is consistent with the results of Mössbauer spectroscopy.

In the range up to 32 T [11, 12]. In the case of Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloy conspicuous broad maximum in the vicinity of 2θ=30-40° for Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloys after solidification are shown. Such behaviour can be elucidated taking into account the distribution of hyperfine field induction ranges to 35 T, what is connected with presence of primary crystallizing phase (FeCo)_{23}B_{6} [1, 2]. At least two components can be distinguished, that suggest the presence of regions in the sample with different iron concentrations. Mössbauer effect studies. The transmission diffraction studies cannot unambiguously testify about amorphous characteristic for crystalline phases have been observed. X-ray ordering of atom pairs near the free volumes. The maximum magnetic permeability depends on chemical compositions. For the Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} and Fe_{60}Co_{10}Ti_{1}Y_{8}B_{20} alloys these maxima, at the frequency of 50Hz, are equal 3300 and 2900, respectively.

The maximum magnetic permeability depends on chemical compositions of materials. For the Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} and Fe_{60}Co_{10}Ti_{1}Y_{8}B_{20} alloys the distribution of hyperfine field induction for different frequencies are wide. In amorphous Fe-Co-B type alloys the distribution of hyperfine field induction on 57Fe sites is connected with presence of primary crystallizing phase (FeCo)_{23}B_{6} [1, 2]. One form of asymmetric sextets with broad and overlapped lines. The distributions for investigated alloys are presented in Fig. 2. The presented patterns are typical for amorphous materials with anisotropy and magnetization with temperature.

The presented patterns are typical for amorphous materials with anisotropy and magnetization with temperature. For both investigated alloys, at low temperatures, almost temperature independent background, with very low intensity can be seen. At higher temperatures a broad maxima typical for amorphous materials are observed. The values of maxima in isochronal disaccommodation curves of investigated alloys depends on their chemical compositions. The disaccommodation curves are decomposed into three elementary processes, each of them is described by Gaussian distribution of relaxation times [13]. The experimental points and fitted theoretical disaccommodation curve for the amorphous Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloy, as an example, are shown in Fig. 10. Fig. 11 shows the distributions of deviations between the experimental points and the theoretical curve.

From fit of theoretical curve to the experimental points the parameters T_p, I_n, E, \beta and \tau_0 for each relaxation processes are determined and listed in Table 1. The obtained values of the pre-exponential factor of the Arrhenius law (of the order of 10^{-15}) [14] and average activation energies (1.31-1.63 eV) indicate that the disaccommodation phenomenon in these samples is related with directional ordering of atom pairs near the free volumes.

Total core losses (P), versus the amplitude of the magnetizing field induction for different frequencies are presented in Fig. 12.

The isochronal magnetic susceptibility disaccommodation curves \(\Delta(1/\chi)=f(T)\) for Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloy after solidification.

The isochronal magnetic susceptibility disaccommodation curves \(\Delta(1/\chi)=f(T)\) for Fe_{61}Co_{10}Ti_{3}Y_{6}B_{20} alloy after solidification.

Figs. 6-7 show the magnetic permeability versus the amplitude of magnetizing field, measured at different frequencies for the investigated alloys.

Structure and magnetic properties of Fe-based amorphous alloys
Table 1. Peak temperature (T_p); intensity (In) at peak temperature, average activation energies (E), parameter distribution (β) and pre-exponential factor (τ₀) calculated according to Ref. [7] for Fe₆₁Co₁₀Ti₃Y₆B₂₀ and Fe₆₁Co₁₀Ti₂Y₇B₂₀ alloys

<table>
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<tr>
<th>PARAMETER</th>
<th>process</th>
<th>T_p [K]</th>
<th>In 10⁶</th>
<th>E [EV]</th>
<th>β</th>
<th>τ₀ .10¹⁵S</th>
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<tr>
<td>Fe₆₁Co₁₀Ti₃Y₆B₂₀</td>
<td>I</td>
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<td>24.7</td>
<td>1.31</td>
<td>6.23</td>
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<td></td>
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<td>1.44</td>
<td>2.37</td>
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<td></td>
<td>III</td>
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<td>22.1</td>
<td>1.63</td>
<td>0.73</td>
<td>4.88</td>
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<tr>
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<td>427.2</td>
<td>9.92</td>
<td>1.39</td>
<td>4.78</td>
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<tr>
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<tr>
<td></td>
<td>III</td>
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<td>14.1</td>
<td>1.62</td>
<td>0.98</td>
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</tbody>
</table>

On the basis of the core losses changes one can state that the investigated alloys are magnetically soft and at low frequencies the total losses are comparable with those observed in classical silicon-iron alloys [15].

In Fig. 13 total core losses (P) versus square of the magnetizing field frequency for Fe₆₁Co₁₀Ti₃Y₆B₂₀, Fe₆₁Co₁₀Ti₂Y₇B₂₀ samples are presented.

Fig. 13. Total core losses (P) versus square of the magnetizing field frequency for Fe₆₁Co₁₀Ti₃Y₆B₂₀ (a), Fe₆₁Co₁₀Ti₂Y₇B₂₀ (b), measured at the maximum induction B_max = 0.3 T

No linear dependence P(²) is observed, that indicates the significant contribution of hysteresis and eddy current losses. Additionally, some of them are connected also with magnetic viscosity.
4. Conclusions

All obtained by the suction casting method rods were amorphous, what was confirmed by structural studies. Basing on the DSC curves it can be stated that the Fe\textsubscript{61}Co\textsubscript{10}Ti\textsubscript{3}Y\textsubscript{6}B\textsubscript{20} alloy was composed from two amorphous matrices with similar, but not same, chemical compositions. The crystallization front separation means that in a volume of produced alloy in the solidification process comes to segregation of the individual components of the alloy and formation of two amorphous phases, almost equilibrium in terms of energy. Most likely, replacement of 1 at.% of Ti (132 pm) by Y (162 pm), which has a higher atomic radius, resulted in a reduction of energy needed to initiate the crystallization. This means that the amorphous phase characterized by lower crystallization temperature, which corresponds to the first maximum on the DSC curve, has a greater packing density of atoms per volume unit. Atoms in the solidification process, due to a short-range diffusion, should migrate through the transition phase separating between themselves two amorphous matrices, what finally leads to the situation as presented in Fig. 3b. These consideration can be indirectly confirmed by Mösßauer studies, which admittedly only apply to environments of \textsuperscript{57}Fe atoms, and are linked with this component. For the Fe\textsubscript{61}Co\textsubscript{10}Ti\textsubscript{3}Y\textsubscript{6}B\textsubscript{20} alloy in the Mösßauer spectrum (Fig. 2c) it was possible to match additional Zeeman sextet characterized by broad and overlapping lines, which would indicate, with a high probability that in the volume of the alloy may exist second amorphous phase. Within the second amorphous phase may already be present the crystalline embryos or after delivering of high energy comes to their subsequent creation. As was indicated in [1,16], in metal-metalloid amorphous materials on the basis of Co-B and Fe-B, there are trigonal atomic bonds between atoms of Co or Fe, and B, which are mutually and through the wall surface interspersed with elements such as Ln, Zr, Hf, Nb, Y, and Ta, which in turn are designed to combine specified atoms. Systems, where the arrangement of atoms is close to the SRO (short range order), usually affect migration of atoms in the alloy as a result of diffusion processes. These processes are leading to the temporary stabilization (SL), that is the formation of metastable layout. The existence of the described arrangement in the entire family of solid amorphous alloys based on Co and Fe, in which are transition metals and metalloids makes, that in their volume appears primarily crystallizing phase of the face-centered cubic fcc (Fe, Co)\textsubscript{2}B\textsubscript{6} structure, of lattice constant 1.2 nm and unit cell consisting of 96 atoms per unit volume. Unfortunately, as was mentioned above, on the basis of Mössbauer measurements wasn’t possible to confirm the presence of such crystalline phase in the studied samples. Comparing obtained results with the data published in [1], for the alloy of a very similar basis, one can assume, that in one amorphous matrix, present in Fe\textsubscript{61}Co\textsubscript{10}Ti\textsubscript{3}Y\textsubscript{6}B\textsubscript{20} sample, may exist specific clusters or even crystalline nuclei, which are defined as an SRO [16], and can be described by the first arm on the DSC curve (Fig. 3a). In quoted works [1], the exponent in Avrami equation was determined. This exponent had a value close to 1.5 (exactly 1.43), what in accordance with [17] is met in BMGs with SRO-type of arrangement. This type of arrangement plays a major role in the crystallization process. The peak broadening in the DSC curve, that is, marking of second amorphous phase in the Fe\textsubscript{61}Co\textsubscript{10}Ti\textsubscript{3}Y\textsubscript{6}B\textsubscript{20} alloy affected the disaccommodation of magnetic susceptibility. Data obtained from the analysis of the magnetic susceptibility disaccommodation curves clearly show that in the Fe\textsubscript{61}Co\textsubscript{10}Ti\textsubscript{3}Y\textsubscript{6}B\textsubscript{20} alloy there is less free volumes than in the second of the investigated alloys, this results in a lesser range of relaxation time.

In both of studied alloys activation energies of elementary processes was in the range of 1.3-1.7 eV, what according to the Kronmüller’s theory, means that there was a reduction in the amount of free volumes, what resulted in changes in the SRO. This result was also confirmed by Mößbauer studies what was manifested by increase of dispersion of the distribution of hyperfine field induction at \textsuperscript{57}Fe nuclei.

The increase of average hyperfine field value of the amorphous matrix, in Fe\textsubscript{61}Co\textsubscript{10}Ti\textsubscript{2}Y\textsubscript{7}B\textsubscript{20} alloy, may be associated with a decrease in the concentration of free volumes, by increasing the amount of Y at the expense of Ti. The appearance of high-field component in the distributions of hyperfine field induction in Fe\textsubscript{61}Co\textsubscript{10}Ti\textsubscript{2}Y\textsubscript{7}B\textsubscript{20} sample, may be associated with the presence of mentioned (Fe, Co)\textsubscript{2}B\textsubscript{6} phase. The presence of high-field component, resulted in a substantial reduction in the intensity of the disaccommodation of magnetic susceptibility (Fig. 8). Moreover, Fe\textsubscript{61}Co\textsubscript{10}Ti\textsubscript{2}Y\textsubscript{7}B\textsubscript{20} alloy exhibits the better time and thermal stability of magnetic properties. Taking into account the values of the core losses one can state that at low frequencies the total losses are comparable with those observed in classical Fe-Si alloys.

Concluding, the paper is a study of the microstructure and magnetic properties of the Fe\textsubscript{61}Co\textsubscript{10}Ti\textsubscript{2}Y\textsubscript{7}B\textsubscript{20} and Fe\textsubscript{61}Co\textsubscript{10}Ti\textsubscript{3}Y\textsubscript{6}B\textsubscript{20} alloys. During the course of studies was shown that the placement of 1 at.% of Y instead Ti splits the crystallization maximum. This may be related with the presence of two amorphous phases having similar chemical compositions, of which one phase is primarily crystallizing phase of the face-centered cubic fcc (Fe,Co)\textsubscript{2}B\textsubscript{6} structure, of lattice constant 1.2 nm and unit cell consisting of 96 atoms per volume unit.

References


