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**Citation style:** Babilas R., Kądziołka-Gaweł Mariola, Nowosielski R. (2011). Structure studies of Fe-based metallic glasses by Mossbauer spectroscopy method. "Journal of Achievements in Materials and Manufacturing Engineering" (Vol. 45, iss. 1 (2011), s. 7-12).

Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 45
ISSUE 1
March
2011

# Structure studies of Fe-based metallic glasses by Mössbauer spectroscopy method

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Received 10.01.2011; published in revised form 01.03.2011

**Materials**

## ABSTRACT

**Purpose:** The paper presents a structure characterization of selected Fe-based metallic glass in as-cast state.
**Design/methodology/approach:** The studies were performed on $Fe_{72}B_{20}Si_4Nb_4$ metallic glass in form of ribbons. The amorphous structure of tested samples was examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM) methods. Mössbauer spectroscopy method was applied to comparison of structure in studied amorphous samples with different thickness (cooling rates).
**Findings:** The XRD, TEM and Mössbauer spectroscopy investigations revealed that the studied alloy in as-cast state was amorphous. Comparison of diffraction patterns of studied samples with different thickness showed the slightly narrowing of diffraction lines. The TEM observations also revealed a changing of image contrast of glassy ribbons with increase of sample thickness. The Mössbauer spectra presented broadened six line patterns characteristic to the structural disorder of amorphous ferromagnetic materials. The hyperfine magnetic field distributions for studied sample thickness indicated the existence components corresponding to the regions with different iron concentration (an iron-rich and an iron-poor surroundings).
**Practical implications:** The Mössbauer spectroscopy is very useful method in studying the structural environment of Fe atoms on a nearest-neighbor length scale allowing the analysis of iron-containing phases.
**Originality/value:** The obtained examination results confirm the utility of investigation methods in analysis of microstructure in function of sample thickness.
**Keywords:** Amorphous materials; Metallic glasses; Mössbauer spectroscopy; Fe-based alloys

**Reference to this paper should be given in the following way:**
R. Babilas, M. Kądziołka-Gaweł, R. Nowosielski, Structure studies of Fe-based metallic glasses by Mössbauer spectroscopy method, Journal of Achievements in Materials and Manufacturing Engineering 45/1 (2011) 7-12.

## 1. Introduction

Since the first Fe-based metallic glass was obtained in 1967, many scientific investigations have been done to achieve glassy materials with quite good soft magnetic, mechanical and corrosion resistance properties [1, 2].

It is generally known that preparation of glassy materials requires high critical cooling rates of about $10^6$ K/s. This condition limits further application of Fe-based metallic glasses because of the limitation of the sample size in two or one dimension [3].

However, Inoue et al. proposed some alloys which have high glass-forming ability with good soft magnetic properties in the amorphous state. These alloys could be prepared in different forms like ribbons, rods, plates and rings with low critical cooling rates below $10^3$ K/s [4].

Recently, Fe-based bulk metallic glasses were obtained in many systems. Inoue et al. succeeded in fabricating Fe-based bulk metallic glasses by copper mould casting in the following systems: Fe-(Al,Ga)-(P,C,B,Si), Fe-(Zr,Hf,Nb,Ta)-B, Fe-(Cr, Mo)-(C,B), Fe-B-Si-Nb, Fe-Co-Zr-Mo-W-B, Fe-Co-Ln-B and Fe-Nd-Al [5].

The first Fe-based bulk glassy alloys were prepared in 1995, since then, a variety of Fe-based bulk glassy alloys have been formed and their alloy components can be classified into a many groups (Table 1) [6].

Table 1.
Classification of Fe-based metallic glasses [5]

| Alloy group | Examples of Fe-based glassy alloys |
|---|---|
| I. | Fe-(Al,Ga)-(P,C,B,Si) |
| II. | Fe-(Zr,Hf,Nb,Ta)-B |
| III. | Fe-(Cr,Mo)-(C,B) |
| IV. | Fe-B-Si-Nb |
| V. | Fe-Nd-Al |

The paper presents some results of structure characterization of $Fe_{72}B_{20}Si_4Nb_4$ glassy alloy, which is classified for the IV group of Fe-based metallic glasses.

Multicomponent Fe-B-Si-Nb amorphous alloys have attracted a lot of attention because they exhibit good properties combined with high glass-forming ability [6].

The atomic positions in an amorphous solid have non-periodical order. Furthermore, the amorphous structure is postulated to be that of the frozen liquid. Instead amorphous alloys are often described as being nearly topologically close packed [3]. The structure of crystalline materials could be determined by describing of unit cell. However, characterization of amorphous structure is much more difficult to examine because of broadening of diffraction patterns and lack of reflections during X-ray investigations [6].

The X-ray diffraction is not effective when periodically spaced planes of atoms do not exist in amorphous alloys. Therefore, Mössbauer spectroscopy is a very sensitive technique to detect the local atomic surroundings of the resonant Fe atoms. That method is very useful in studying the structural environment of Fe atoms on a nearest-neighbor length scale allowing the analysis of iron-containing phases [7].

The Mössbauer spectroscopy is based on the resonant absorption and emission of γ-rays. The Mössbauer spectrum is described by the number, position, shape and relative intensity of the absorption lines. That lines are described by the hyperfine interactions which induce the nuclear energy levels and form the hyperfine parameters like isomer shift (*IS*) and the magnetic hyperfine field ($B_{hf}$). Mentioned parameters give information about symmetry of the bonding environment and local structure around the Fe atoms [8].

The Mössbauer spectroscopy has advantages over the conventional XRD method because it is more sensitive to identify also amorphous and crystalline phases. Moreover, the Mössbauer spectroscopy can also differentiate some phases which could not be identified by XRD. Therefore, this technique can be used successfully to study the crystallization process in amorphous alloys [7,8].

## 2. Material and research methodology

The aim of the this paper is the local structure analysis of $Fe_{72}B_{20}Si_4Nb_4$ metallic glass samples in as-cast state using XRD, TEM and Mössbauer spectroscopy methods.

The investigated material was cast in form of the ribbons. The ingot of $Fe_{72}B_{20}Si_4Nb_4$ master alloy was prepared by induction melting of a mixture of pure elements of Fe, Nb and ferroalloys Fe-B, Fe-Si under argon protective gas atmosphere.

The previous prepared master alloy was cast as ribbon shaped metallic glasses with thickness ($g$) of 0.03, 0.05, 0.08 and 0.20 mm. The ribbons were manufactured by the "chill-block melt spinning" (CBMS) technique which is a method of continuous casting of the liquid alloy on the turning copper wheel [9-16].

The casting conditions include linear speed of copper wheel of 10-20 m/s and ejection over-pressure of molten alloy under argon atmosphere of 0.02-0.04 MPa.

Structure analysis of the samples was carried out using X-ray diffractometer (XRD) with $Co_{K\alpha}$ radiation. The data of diffraction lines were recorded by "step-scanning" method in $2\theta$ range from 30° to 80° for samples in as-cast state.

Transmission electron microscopy (TEM) was used for the structural characterization of ribbons in as-cast state. Thin foils for TEM observation (from central part of tested samples) were prepared by an electrolytic polishing method after previous mechanical grinding.

Magnetic measurements of studied ribbons, carried at room temperature, included following properties:

(a) relative magnetic permeability ($\mu_r$) − determined with Maxwell-Wien bridge at a frequency of 1030 Hz and magnetic field H = 0.5 A/m;
(b) magnetic permeability relaxation ($\Delta\mu/\mu$) also defined as "magnetic after-effects" − determined by measuring changes of magnetic permeability as a function of time after demagnetization, where $\Delta\mu$ is difference between magnetic permeability determined at $t_1$ = 30 s and $t_2$ = 1800 s after demagnetization [17].

The $Fe^{57}$ Mössbauer spectra were recorded in a room temperature using a constant acceleration spectrometer with Co57:Pd source. Metallic iron powder was used for velocity calibrations of the Mössbauer spectrometer.

All spectra were fitted by means of a hyperfine field distribution using the Hesse-Rübartsch procedure [18] with linear correlation between isomer shift an hyperfine magnetic field and an elementary line width 0.17 mm/s.

## 3. Results and discussion

Samples in as-cast state were examined by XRD and TEM methods to check their amorphous state. The diffraction patterns of tested ribbon samples show the broad diffraction halo characteristic for the amorphous structure (Fig. 1).

Comparison of diffraction patterns of studied samples with different thickness shows the slightly narrowing of diffraction lines. These effects indicate that casting process (time of solidification of molten alloy) caused structural changes of tested amorphous materials.

The TEM examination implied no crystal structure of studied material. Figure 2 shows selected TEM micrographs including selected structure images and electron diffraction patterns with halo rings caused by the amorphous structure. The TEM observations also revealed a changing of image contrast of glassy ribbons with increase of sample thickness.

Figure 3 shows room temperature Mössbauer spectra of $Fe_{72}B_{20}Si_4Nb_4$ metallic glasses for thickness of 0.03, 0.05, 0.08 and 0.20 mm. The spectra show broadened six line patterns characteristic to the structural disorder of amorphous ferromagnetic materials.

In each case, the spectra are composed of six well defined but broadened lines, which is a characteristic feature of amorphous alloys. The broad lines are caused by the distribution of hyperfine magnetic fields due to amorphous disorder. The corresponding hyperfine magnetic fields distributions p($B_{hf}$) for investigated samples are presented in Figure 4. The average hyperfine magnetic field increases, but isomer shift decreases, with increasing of samples thickness above 0.03 mm (Table 2).

Table 2.
Average values of hyperfine magnetic field ($B_{hf}$) and isomer shift ($IS$) of $Fe_{72}B_{20}Si_4Nb_4$ metallic glass in form of ribbons with selected sample thickness

| Sample thickness [mm] | $B_{hf}$ [T] | $IS$ [mm/s] |
|---|---|---|
| 0.03 | 17.1 | 0.143 |
| 0.05 | 16.2 | 0.147 |
| 0.08 | 17.1 | 0.129 |
| 0.20 | 18.5 | 0.124 |

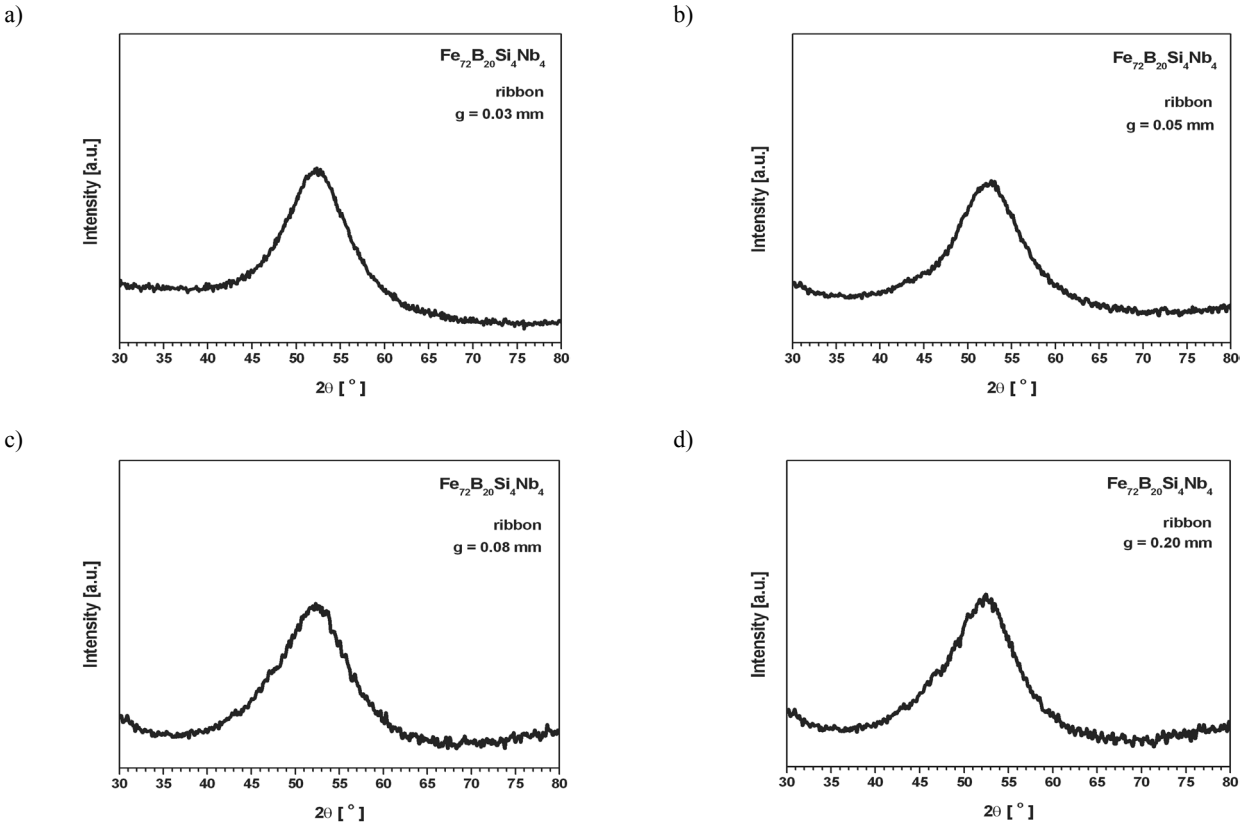
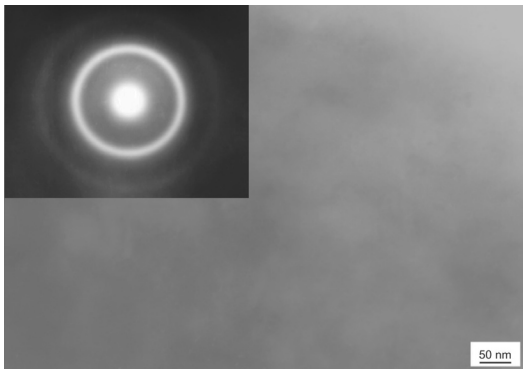



Fig. 1. X-ray diffraction pattern of $Fe_{72}B_{20}Si_4Nb_4$ metallic glass in as-cast state in form of ribbon with thickness of: (a) 0.03 mm, (b) 0.05 mm, (c) 0.08 mm and (d) 0.20 mm

a)

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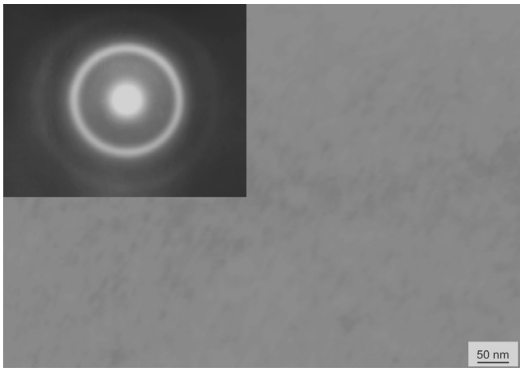


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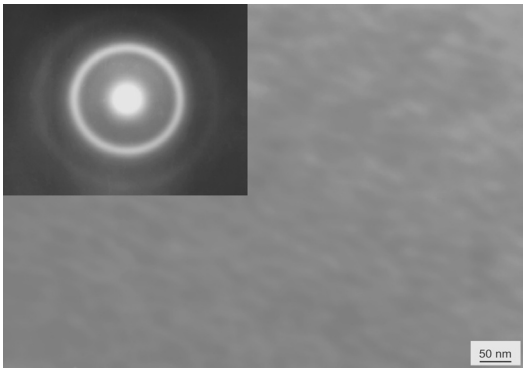



Fig. 2. Transmission electron micrograph and electron diffraction pattern of the as-cast glassy $Fe_{72}B_{20}Si_4Nb_4$ ribbon with a thickness of: (a) 0.03, (b) 0.08 and (c) 0.20 mm

The wide hyperfine magnetic fields distributions indicated the great number of non-equivalents Fe atom 'sites' with different local environment, what is typical for amorphous compounds. However, the distributions of $p(B_{hf})$ shows qualitative changes as a function of the ribbons thickness.

Especially, for thickness higher than 0.05 mm the hyperfine magnetic field distributions indicated the existence at least two components corresponding to the regions with different iron concentration (an iron-rich and an iron-poor surrounding).

Furthermore, it could be also stated that increasing of the average hyperfine magnetic field with sample thickness is connected with structural changing occurred during casting the samples. It could lead the increase of the atom packing density because of reducing free volumes.

Additionally, the initial magnetic permeability ($\mu_r$) and magnetic permeability relaxation ($\Delta\mu/\mu$) of the tested ribbons in relation to sample thickness is shown in Table 3.

Table 3.
The initial magnetic permeability ($\mu_r$) and magnetic permeability relaxation ($\Delta\mu/\mu$) of $Fe_{72}B_{20}Si_4Nb_4$ metallic glass in form of ribbons with selected sample thickness

| Sample thickness [mm] | $\mu_r$ | $\Delta\mu/\mu$ [%] |
|---|---|---|
| 0.03 | 1293 | 9.4 |
| 0.05 | 1786 | 7.6 |
| 0.08 | 1657 | 4.9 |
| 0.20 | 1083 | 3.0 |

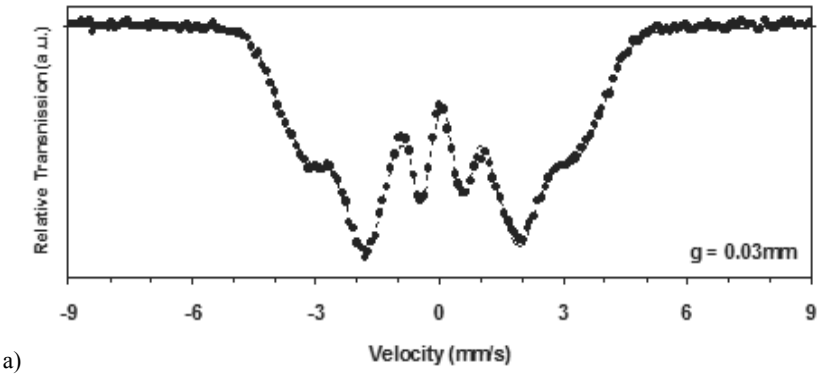
Basing on the literature [17], the intensity of $\Delta\mu/\mu$ is directly proportional to the concentration of the defects in amorphous materials - free volume concentration. The $\Delta\mu/\mu$ decreases with increasing of sample thickness and changes a value from 9.4 to 3.0 % for ribbon with thickness of 0.03 and 0.20 mm, adequately.

These results correspond with the Mössbauer spectroscopy examinations and can probably inform about existence of different amorphous states in samples with various thickness.

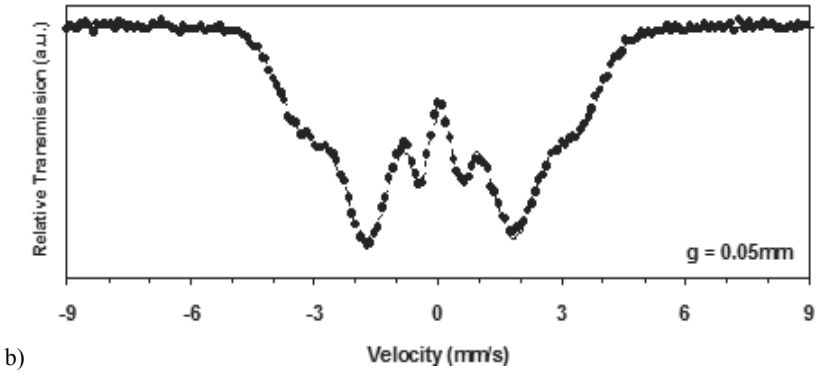
## 4. Conclusions

The investigations performed on the samples of $Fe_{72}B_{20}Si_4Nb_4$ metallic glass allowed to formulate the following statements:

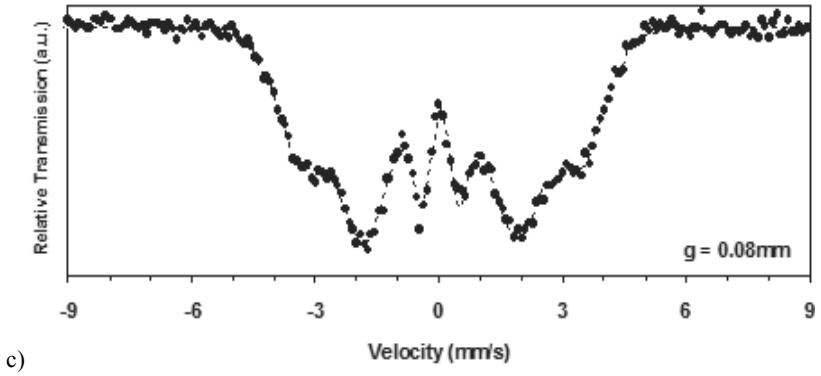
- the X-ray diffraction and transmission electron microscopy investigations revealed that the studied ribbons in as-cast state were amorphous,
- the Mössbauer spectra of as-cast ribbons showed the broadened six line patterns assigned to the typical structural disorder of amorphous state,
- the TEM observations revealed only a changing of image contrast of glassy ribbons with increasing of thickness,
- the measured shapes of the Mössbauer spectra and hyperfine fields distributions showed remarkable changes with increasing of samples thickness,
- increase of thickness leads to existence in sample regions with different Fe concentration,
- the increasing of the average hyperfine magnetic field with sample thickness is connected with structural changing which leads to the increase of the atom packing density (reducing of free volume concentration),
- results of XRD, TEM and the Mössbauer spectroscopy examinations probably inform about existence of different amorphous states in samples with various thickness.



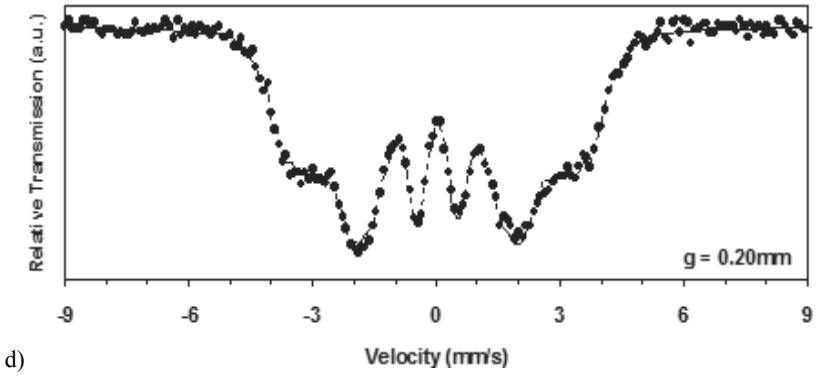

a)




b)




c)




d)

Fig. 3. Mössbauer spectra of $Fe_{72}B_{20}Si_4Nb_4$ metallic glass in form of ribbon with thickness of: (a) 0.03 mm, (b) 0.05 mm, (c) 0.08 mm and (d) 0.20 mm in as-cast state

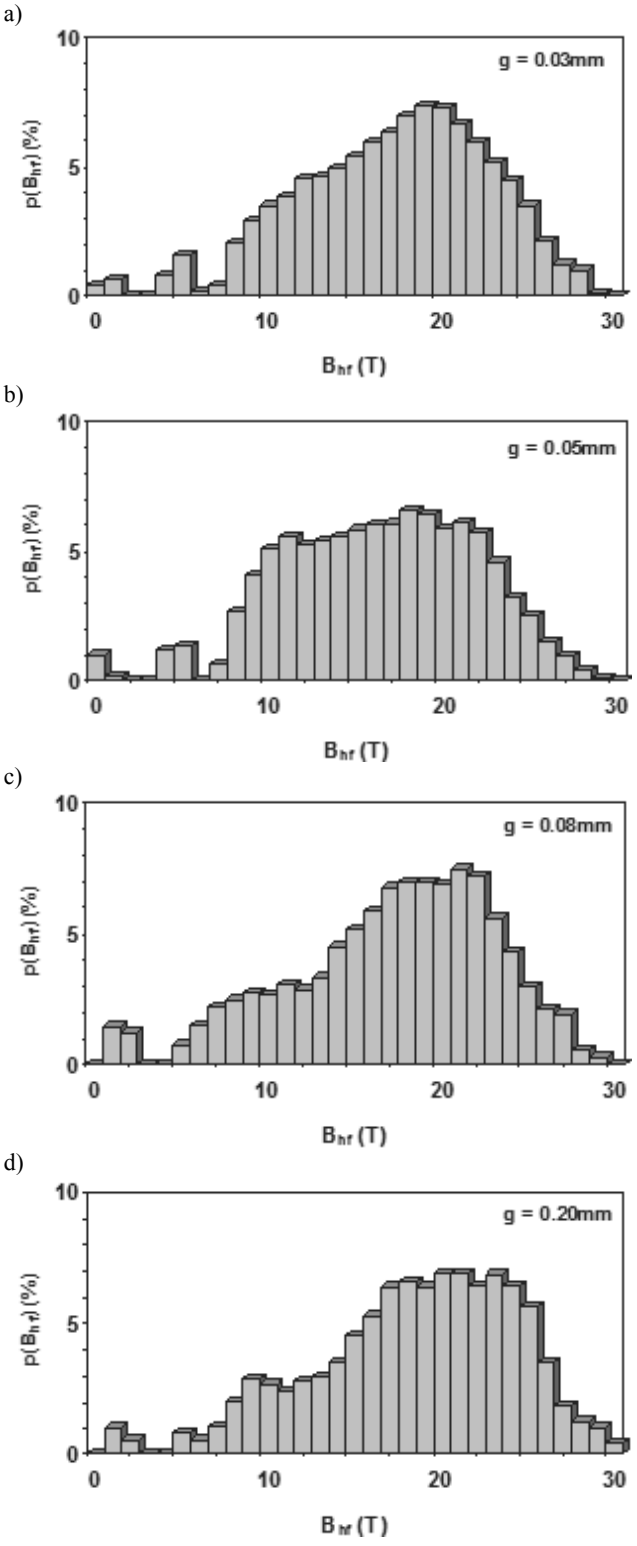



Fig. 4. Hyperfine field distribution for $Fe_{72}B_{20}Si_4Nb_4$ metallic glass in form of ribbon with thickness of: (a) 0.03 mm, (b) 0.05 mm, (c) 0.08 mm and (d) 0.20 mm in as-cast state

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