Mössbauer Study on Local Atomic Structure in $Fe_{80-x}Nb_xB_{20}$ ($x = 4, 6$) Metallic Glasses

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Fe-based amorphous alloys were prepared by the melt-spinning technique and characterized by X-ray diffraction and transmission Mössbauer spectroscopy. The studies were performed on $Fe_{76}Nb_4B_{20}$ and $Fe_{74}Nb_6B_{20}$ metallic glasses in the form of ribbons. The Mössbauer spectroscopy allows to study the local environments of the Fe atoms in the glassy state, showing the changes in the amorphous structure due to the changing of Nb addition. The obtained Mössbauer spectra of ferromagnetic metallic glasses present broad lines resulting from the distribution of non-equivalent iron sites and of interatomic distances. Variation of Nb content in the alloys affects the disorder in as-cast state and also influences on the average radius of the first coordination shell and the number of nearest neighbor Fe atoms.

1. Introduction

In recent years a huge amount of metallic glasses based on Fe and metalloids have been produced extensively. The ferromagnetic Fe-based amorphous materials have been mainly prepared due to the attractive properties for soft magnetic applications. The required magnetic properties are usually large saturation magnetization, low coercive force and high permeability [1].

Nevertheless, still little is known about the atomic structure of Fe-based amorphous alloys. The detailed knowledge about the local structure of these metallic glasses could open new possibilities to better control the properties of these materials. In order to understand their macroscopic properties one should recognize basic phenomena occurring at the microscopic scale level. A combination of X-ray diffraction (XRD) and Mössbauer spectroscopy methods seems to give better structural information of amorphous materials. It is important to note that X-ray diffraction can not differentiate between kinds of atoms and their scattering amplitudes are very similar [2].

The aim of the paper is the local structure analysis of $Fe_{(80-x)}Nb_xB_{20}$ ($x = 4, 6$) metallic glasses in as-cast state using a combination of XRD and Mössbauer spectroscopy methods. The Mössbauer spectroscopy is seen as a very sensitive method to determine the nearest neighbours of the Fe atoms.

2. Experimental

The studies were conducted on $Fe_{76}Nb_4B_{20}$ and $Fe_{74}Nb_6B_{20}$ metallic glasses in the form of ribbons

with the thickness of 0.05 and 0.08 mm and the width of 5 mm. The ingots of studied master alloys were prepared by induction melting the mixtures of pure elements (Fe, Nb, B) together. The amorphous ribbons were prepared by the melt spinning, which is a method of continuous casting of the liquid alloy on the surface of a turning copper wheel [3].

The structure of the ribbons in as-cast state was examined by XRD in reflection mode using diffractometer with Cu K_α radiation. The diffraction patterns were collected by "step-scanning" method in the 2θ range from $30°$ to $90°$. The X-ray broad diffraction halos were also plotted in the scattering vector ($Q = 4\pi \sin\theta/\lambda$) range, where 2θ is the angle between the incident and scattered beam and λ is the wavelength.

Analysis of the position and width of the X-ray amorphous halo may provide some information on the nearest interatomic spacing in the amorphous structure. The position of the X-ray halo maximum is known to be directly related with the average radius ($R = \lambda/2\sin\theta^*$) of the first coordination shell [4], where $2\theta^*$ in this case is the scatter angle at the halo maximum.

The ^{57}Fe Mössbauer spectra were collected at room temperature using a constant acceleration spectrometer with triangular velocity shape, a multichannel analyzer with 1024 channels and linear arrangement of the $^{57}Co(Cr)$ source ($\approx$15 mCi), absorber and detector. The spectrometer velocity was calibrated with a high purity α-Fe foil.

The discrete hyperfine fields analysis was used for fitting the Mössbauer spectra for investigating alloys. According to Gonser et al. approach [5], the measured spectra were decomposed into six discrete components representing average Fe–Fe coordination numbers. The relative absorption areas of the subspectra represented the probabilities for the occurrence of corresponding

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coordination numbers. The relative line intensity ratios of fitted subspectra was 3:*z*:1:1:*z*:3 ($z = 2.5 \div 3.0$), which take into account effect of texture of investigated compounds.

3. Results and discussion

The X-ray diffraction patterns of the samples in the as-cast state are presented in Fig. 1. The diffraction patterns show a broad diffraction halo indicating the formation of an amorphous structure. Moreover, Fig. 2 shows the intensity of the X-ray scattering versus $Q = 4\pi \sin\theta/\lambda$ for the studied alloys. The value of R corresponding to the position of the scatter intensity peak increases from 2.01 ± 0.005 Å for $Fe_{76}Nb_4B_{20}$ to 2.02 ± 0.005 Å for $Fe_{74}Nb_6B_{20}$ when the content of Nb also increases from 4 to 6 at.%. The slight increase in the average nearest inter-atomic spacing is within the error. Nonetheless, it can be explained by a higher radius of the Nb atoms relative to the radii of Fe atoms and the increased fraction of Fe–Nb bonds.

The Mössbauer spectra of ribbons in the as-cast state show broadened sextet patterns typical for the structural disorder of amorphous ferromagnetic materials (Fig. 3). The values of the average hyperfine magnetic field (B_{hf}) as well as the isomer shift (IS) parameters were obtained for the best fitting (Table I). However, a substitution of Fe atoms by Nb lead to an increase of the value of hyperfine magnetic field (B_{hf}). Additionaly, the IS parameter shows a decreasing tendency with higher Nb addition.

The corresponding hyperfine magnetic field distributions could be also decomposed into low and high field components by Gaussian distributions (Fig. 4). The low and high field components of the hyperfine field distribution indicated the coexistence of two different neighborshell surroundings of the Fe atoms. The results could be interpreted in terms of occurrence of two different Fe local environments and the accompanying magnetic exchange frustration in Fe-rich regions.

According to Gonser et al. [5] method, the spectra of alloys were decomposed into 6 subspectra representing average Fe–Fe coordination numbers (N). The coordination numbers for $Fe_{76}Nb_4B_{20}$ alloy are $N = 11, 10, 9, 8,$ and 7.
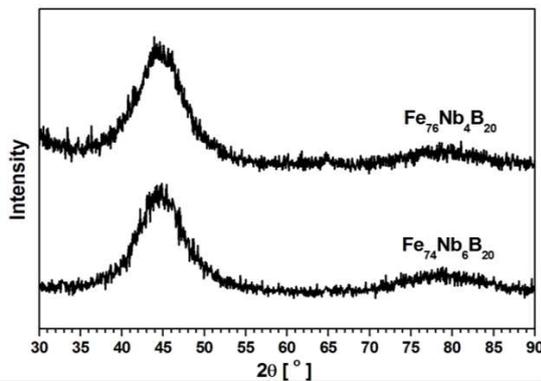

Fig. 1. X-ray diffraction patterns of $Fe_{76}Nb_4B_{20}$ and $Fe_{74}Nb_6B_{20}$ glassy alloys in the form of ribbons.
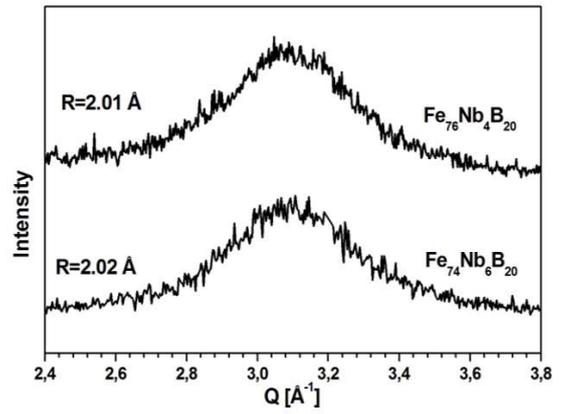
Fig. 2. Average radius of the first coordination shell of $Fe_{76}Nb_4B_{20}$ and $Fe_{74}Nb_6B_{20}$ glassy alloys in the form of ribbons.
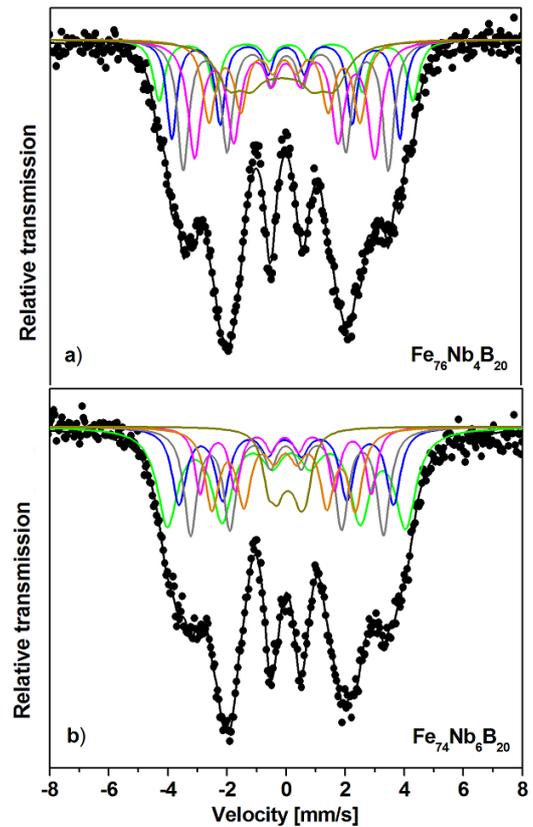
Fig. 3. Transmission Mössbauer spectra and their fits for: (a) $Fe_{76}Nb_4B_{20}$ and (b) $Fe_{74}Nb_6B_{20}$ metallic glasses.

The following coordination numbers $N = 10, 9, 8, 7$ and 6 were calculated for $Fe_{74}Nb_6B_{20}$ alloy. The fit lines observed in Fig. 3 represent the subspectra obtained by the fitting procedure. The relative absorption areas (A) of the subspectra represented the probabilities for the existence of proposed coordination numbers.

The nearest-neighbor coordination numbers for Fe–Fe atoms represent the dominant coordination clusters and
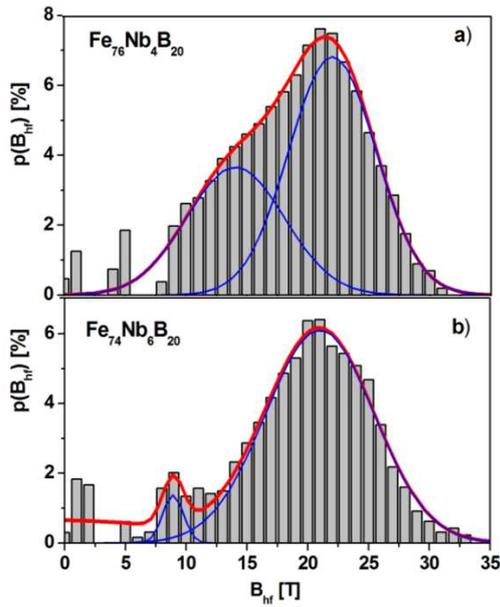
Fig. 4. Hyperfine field distribution of: (a) $Fe_{76}Nb_4B_{20}$ and (b) $Fe_{74}Nb_6B_{20}$ metallic glasses with its deconvolution into low and high field components.

describe the short-range order. Basing on candidates of atomic cluster configurations in metallic glasses proposed by Miracle et al. [6], the cluster with $N = 6$ could be corresponding to octahedron. The $N = 8$ seems to be cuboctohedron cluster of the fcc structure. What is more, clusters with $N = 9$ can be related to the tri-capped trigonal prisms and the $N = 11$ could be an icosahedron with one sphere removed.

TABLE I

Hyperfine parameters of $Fe_{(80-x)}Nb_xB_{20}$ alloys in as-cast state (IS — isomer shift, B_{hf} — hyperfine magnetic field, N — nearestneighbor Fe atoms, A — relative area from the spectra).

Glassy alloy	B_{hf} [T]	IS [mm/s]	N [%]	A [%]
$Fe_{76}Nb_4B_{20}$	26.7	0.119	11	12
	23.8	0.060	10	17
	21.5	0.059	9	20
	19.0	0.030	8	20
	15.7	0.004	7	22
	9.2	0.040	Fe-Nb	9
$Fe_{74}Nb_6B_{20}$	25.1	0.138	10	28
	22.6	0.024	9	20
	20.3	0.056	8	17
	18.0	0.018	7	11
	15.1	-0.010	6	16
	4.0	0.106	Fe-Nb	8

The addition of Nb content from 4 to 6 at.% caused a decrease of the average Fe–Fe coordination numbers due to forming of Fe–Nb atomic pairs. This result is also confirmed by the values of hyperfine magnetic field (B_{hf}), which depend upon the nearest neighbour distribution around Fe atoms.

4. Conclusions

The X-ray diffraction results confirmed the amorphous structure of studied alloys. The XRD results were also used to determine a short-range ordering by calculating an average radius of the first coordination shell for $Fe_{76}Nb_4B_{20}$ and $Fe_{74}Nb_6B_{20}$ glasses. The broad lines of the Mössbauer spectra were caused by the distribution of hyperfine magnetic fields. The bimodal hyperfine field distribution revealed the coexistence of at least two different neighborshell surroundings of the Fe atoms. The spectra of studied glassy alloys were decomposed into subspectra representing average Fe–Fe coordination numbers. The average Fe–Fe coordination numbers can be probably related to the dominant coordination clusters e.g. the trigonal prisms or icosahedrons.

Acknowledgments

References

[1] G. Herzer, *Acta Mater.* **61**, 718 (2013).

[2] S.N. Kane, A. Gupta, Zs. Gercsi, F. Mazaleyrat, L.K. Varga, *J. Magn. Magn. Mater.* **292**, 447 (2005).

[3] R. Babilas, M. Kądziołka-Gaweł, *Acta Phys. Pol. A* **127**, 573 (2015).

[4] H.P. Klug, L.E. Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, Wiley, New York 1962.

[5] U. Gonser, M. Ghafari, H.G. Wagner, *J. Magn. Magn. Mater.* **8**, 175 (1978).

[6] D.B. Miracle, E.A. Lord, S. Ranganathan, *Mater. Trans.* **47**, 1737 (2006).