Mossbauer Studies of Rapid Cooled Amorphous Iron Alloys in as Cast State

MARCIN NABIALEK*

Institute of Physics, Faculty of Production Engineering and Materials Technology, Czestochowa University of Technology, 19 Armii Krajowej Str., 42-200 Czestochowa, Poland

The study investigated the effect of a small alloy addition (1 atomic %) in alloys $Fe_{61}Co_{10}Y_8Nb_1B_{20}$, b - $Fe_{61}Co_{10}Y_8Zr_1B_{20}$, c - $Fe_{61}Co_{10}Y_8W_1B_{20}$, d - $Fe_{61}Co_{10}Y_8Mo_1B_{20}$ on the shape of the Mossbauer spectrum and on the distributions of hyperfine field induction on ^{57}Fe obtained from their numerical analysis. The line factor A <2.5> was also determined in the Zemman's sextet, which is an indirect measure of ordering for the texture of the spins occurring in the volume of alloys. Based on the analysis of the results, it was found that the Mossbauer spectras are typical of amorphous alloys and the hyperfine field distributions are bimodal.

Keywords: Mossbauer spectroscopy, hyperfine field distribution, amorphous materials

The first iron-based amorphous alloys are those which P. Douwez produced in 1967 [1]. The obtained Fe-P-C alloy samples were in the form of tapes, the thickness of which did not allow their broad use. In spite of this large disadvantage, the materials of this shape were later used in the magnetic cores of transformers. Attempts were made to increase the thickness of the produced tapes, but already at a thickness of 120 mm, the tapes began to crystallize and lose their properties. Crystallization of tapes has always been associated with their excessive brittleness.

The main advantage of this kind of materials is their quite high value of saturation magnetization and magnetic permeability and a low value of coercive field and total losses for re-magnetization. In amorphous materials, due to the lack of a crystal structure, a low value of magnetostriction is observed and are often called almost zero magnetostrictive materials [2-6]. For these alloys, a small value of the effective anisotropy energy is recorded, which is the expected effect. All these advantages are presented in the fact that amorphous materials on the iron matrix can be re-magnetized with a small magnetic field and during this process there are no large changes in their dimensions.

In the last few decades, fast-cooled alloys showing an amorphous structure have been intensively studied. To analyse their structure, X-ray diffraction and various types of microscopic techniques are commonly used: transmission and scanning electron microscopy [7-11]. In addition to the analysis of amorphous alloys, these methods can be used to evaluate the quality of metal composites [12-17]. In the case of amorphous alloys formed on the basis of zirconium, palladium, aluminum or magnesium, these are sufficient techniques in assessing their properties ,but for example, iron-based alloys, those techniques are insufficient. Therefore, for transition metal alloys (from 3d group and in particular iron), the Mossbauer transmission or reflection method is used [18]. Using Mössbauer spectroscopy, one can study both the real structure of alloys and their magnetic structure, and estimate the relative distribution of iron atoms and their surroundings.

This work will present the results of research on the structure and magnetic properties of classical (35mm tapes) amorphous alloys: $Fe_{61}Co_{10}Y_8Nb_1B_{20}$, $Fe_{61}Co_{10}Y_8Zr_1B_{20}$, $Fe_{61}Co_{10}Y_8W_1B_{20}$, $Fe_{61}Co_{10}Y_8Mo_1B_{20}$ in the cast state.

* email: nmarcell@wp.pl

Experimental part

All samples were made of high purity components: Fe – 99.99% at, Co – 99.99% at, Y – 99.99% at, Zr – 99.999% at i W – 99.9999% at, Mo – 99.9999%. Boron was added in the form of $Fe_{45.6}B_{54.4}$ alloy. Quickly cooled samples were obtained using the melt spinning method, which, due to the high popularity, need not be discussed further. In the first stage of sample production all melt components were melted. Melting was carried out in an arc furnace under protective gas (Ar). The result of this process are crystal ingots. It should be mentioned that in order to obtain a good mixing of alloy components, ingots were melted several times on each side.

In order to eliminate residual oxygen in the working chamber, pure titanium was melted during the process. Thus obtained ingots were crushed to smaller batch portions, which were used in the production of metallic tapes. Quickly cooled tapes were produced at a linear speed of 30 m/s on a copper cylinder. The hole in the quartz capillary had a diameter of 1.5 mm and was separated from the copper cylinder by 0.3 mm. The pressure of the purging gas was constant. All samples were produced with the same operational parameters.

The real structure of the alloys was analyzed using the POLON Mossbauer spectrometer and the ^{57}Fe source, with 100mCi power, and a half-life of 270 days. Calibration of the system was performed using pure iron foil. All measurements were taken at room temperature.

Mossbauer analysis

It's mainly about the so-called Zeeman effect. The hyperfine influence of the magnetic moment of the Mossbauer nucleus with the electron shell and with the magnetic field present in its vicinity leads to hyperfine magnetic splitting of the nuclear levels. The probability of Mossbauer transitions depends on the forces binding the atom with the solid and the thermal vibrations of atoms. In the case of crystalline materials, it is necessary to know about the energy of bonding atoms in the network and knowledge of the type of network. For amorphous alloys, this is not so easy because there is no symmetry in the arrangement of toms while maintaining angular translations. Therefore, due to the chaotic arrangement of atoms, only the average coordination number is used.

According to literature data [19], this number is similar to that occurring in crystalline materials with the structure of fcc and bcc and ranges from 8 to 12. It results from the assumptions of the amorphous material structure density should be lower than for a crystalline material with the same chemical composition. The description of the structure of the amorphous material itself is difficult and complex. Currently, attempts have been made to define it based on two assumptions: the atomic structure model based on the order similar to the crystalline order and the second one in which the random nature of the atomic arrangement is exposed, with special consideration of the short-range ordering of atoms. In amorphous alloys exhibiting the magnetic properties of ferromagnetic - paramagnetic transition describing the Curie temperature, takes place in a very narrow temperature range and the Curie temperature itself is much lower than in the case of crystalline alloys with the same chemical compositions. The lowering of the Curie temperature in amorphous alloys with respect to crystalline alloys is mainly the cause of chemical disorder. In iron alloys there may be both ferromagnetic and antiferromagnetic ordering. The hyperfine coupling constant for iron (H/m, where H is the mean hyperfine field that the iron core experiences, m is the average magnetic moment per iron ion). The value of the coupling constant is similar for all amorphous alloys on the iron matrix and B and is practically the same as formranges from 100 to 140 kGs /u_B crystalline alloys with the same chemical composition. As a result of the lack of magnetocrystalline anisotropy in amorphous alloys, the main contribution to the effective anisotropy has shape anisotropy and magnetoelastic anisotropy.

In such systems, preferential directions appear, in which magnetic moments in domains are positioned, what is called magnetic texture. In the case of these alloys, one can additionally talk about local anisotropy associated with short-range ordering and local stresses, usually associated with the mere production cycle of amorphous materials. During rapid cooling, there is a rapid freezing of the structure, during which structural defects appear in the form of free volumes and pseudodyslocation dipoles. Based on numerous studies, it should be noted that structural defects in amorphous materials affect mainly the domain structure and magnetization process in the area called the approach to ferromagnetic saturation.

Results and discussions

For iron-based amorphous alloys, a particularly good technique for studying their structure and magnetic properties is the ^{57}Fe based Mossbauer-type spectroscopy. This method makes it possible to determine the distributions of hyperfine parameters and on the basis of their analysis, one can conclude on the subject of atomic and magnetic ordering.

Figure 1 presents transmission Mossbauer spectra recorded for samples of tested melt spinning alloys.

Each of the Mossbauer spectrum shown in figure 1 is similar and consists of six overlapping lines, the so-called Zemman sextet. Their shape indicates that they are in the magnetically ordered phase. Such spectra are adjusted by the least squares method. As one can see, the side lines in all sextets are wider than the middle ones. This means that their width is an increasing function from the center of the spectrum, which implies that the dominant distribution in comparison to others is the distribution of the hyperfine magnetic field. For each of the tested alloys in the form of

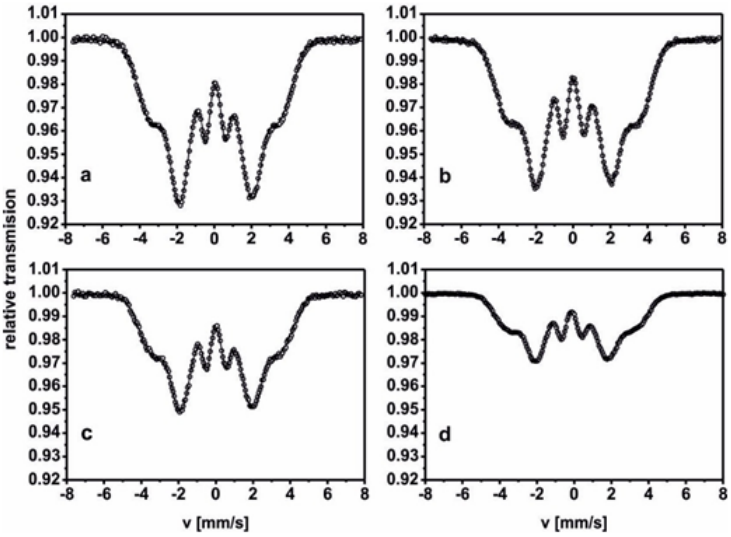

Fig. 1.Transmission Mossbauer spectra for tape Samales with thickness of 35 μm: a - $Fe_{61}Co_{10}Y_8\mathbf{Nb}_1B_{20}$, b - $Fe_{61}Co_{10}Y_8\mathbf{Zr}_1B_{20}$, c - $Fe_{61}Co_{10}Y_8\mathbf{W}_1B_{20}$, d - $Fe_{61}Co_{10}Y_8\mathbf{Mo}_1B_{20}$

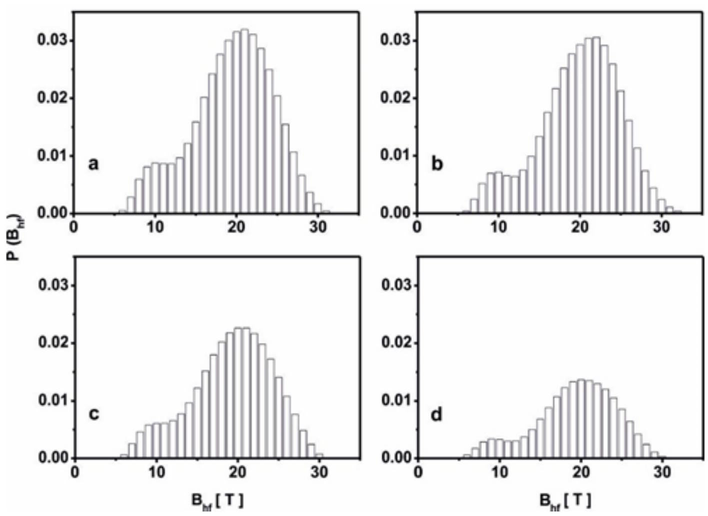

Fig. 2. Hyperfine field induction distributions for: a - $Fe_{61}Co_{10}Y_8\mathbf{Nb}_1B_{20}$, b - $Fe_{61}Co_{10}Y_8\mathbf{Zr}_1B_{20}$, c - $Fe_{61}Co_{10}Y_8\mathbf{W}_1B_{20}$, d - $Fe_{61}Co_{10}Y_8\mathbf{Mo}_1B_{20}$

strips of similar thickness and produced at the same operational parameters, the sextet lines are symmetrically oriented with respect to the center, which is associated with a chemical and topological disorder.

The second picture contains hyperfine spectrum distributions obtained from the transmission analysis of the Mossbauer spectra.

All spectra were fitted with six sextets and subjected to numerical analysis. The hyperfine field distributions determined on its basis consist of low and high-field components. It can be said that they are quite wide and theirs is bimodal. In these distributions, individual bars are visible every 1T clearly showing their probability. For deeper analysis of hyperfine field distributions, Gaussian curves were used (fig. 3).

The designated components are clearly visible. The first of these for each of the tested alloys has the highest value with the induction value of the mean hyperfine field of around 10 T. For each of the tested samples, the initial value of the probability is not greater than zero, which means that there is no order describing the paramagnetism in these samples. The change in the symmetry of the first Gaussian curve is related to the change of one of the components in the alloy. It should be stated here that in the tested samples only one atomic percent of Nb, Zr, W and Mo was changed which affected the shape of the entire hyperfine distribution. The change in the alloy component had a slight effect on the probability of occurrence of certain distributions of ^{57}Fe atoms relative to the central atom.

The second component of the bimodal distribution occurs at higher values of the mean hyperfine field. Its maximum value is around 20 T, and the limit value is around 30 T. Basically, it should be stated that the high-field part is characteristic of areas with lower iron content. This means that the Mossbauer atoms are surrounded by an atomic mixture consisting of magnetic atoms of iron and cobalt and non-magnetic atoms Y, B and for particular alloys Nb, Zr, W and Mo. This environment mainly concerns the first coordination zone. The second low-field component concerns iron-rich areas. In the studied alloys, due to the shape of their Mossbauer spectra and the inductive field distributions obtained on their basis, it should be stated that the distances between magnetic atoms are certainly greater than 0.25 nm. Increased distance between pairs of Fe - Fe pairs as a result of other non - magnetic components influences the increase of the mean hyperfine field.

Data obtained from the numerical analysis of the Mossbauer spectra are given in table 1.

The intensity of the second and fifth lines in relation to the most internal Mössbauer lines is shown as a parameter *b*. This parameter is an indirect measure of the texture of spins in the sample. It is assumed that when there are no stresses in the sample, the spins of atoms are arranged in the direction of induced anisotropy, and the value of parameter b is 4. If in the sample the the texture of spins changes, the value of parameter *b* lies within the limit of $2 \geq b < 4$. It follows from the above that changes in the texture of spins in the sample can be described by changes in the value of parameter *b*. For all samples tested, the value of parameter *b* is close to 3, which means that in the sample the majority of spins are arranged in parallel in the direction of induced anisotropy. As for the value of the mean hyperfine field, for each of the tested alloys it is practically equal. Only for the alloy with the addition of Zr it differs slightly, which means that in this alloy there can be a larger, in terms of topological order in the arrangement of atoms. As indicated by the data in table 1, the samples of the alloys tested have a similar dispersion dispersion value, which means that their structures are similar in terms of ^{57}Fe atom configurations.

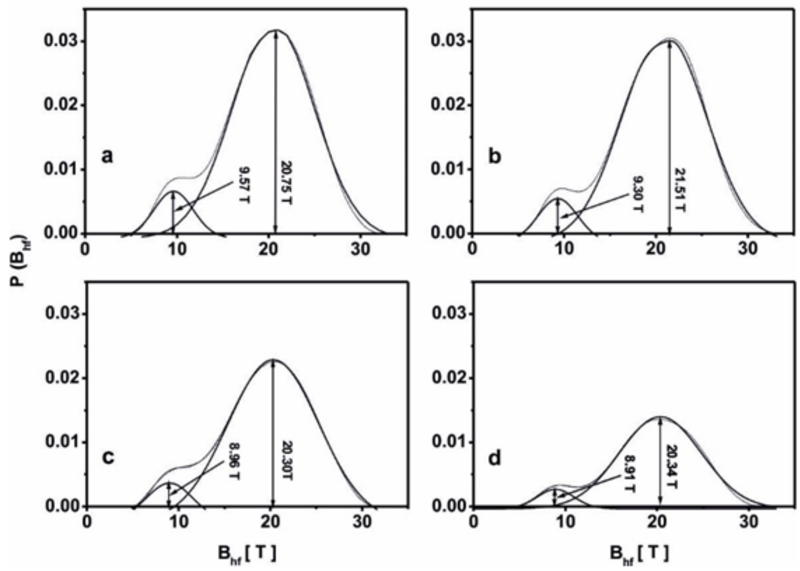

Fig. 3. Hyperfine field induction distributions with Gauss curves: for samples: a - $Fe_{61}Co_{10}Y_8Nb_1B_{20}$, b - $Fe_{61}Co_{10}Y_8Zr_1B_{20}$, c - $Fe_{61}Co_{10}Y_8W_1B_{20}$, d - $Fe_{61}Co_{10}Y_8Mo_1B_{20}$

Table 1
THE VALUE OF THE MEAN HYPERFINE FIELD USING THE ^{57}Fe NUCLEI (B_{ef}) AND DISPERSION OF THE HYPERFINE FIELD DISTRIBUTIONS OF THE AMORPHOUS PHASE (D_{am}), THE RELATIVE INTENSITY OF LINES 2 AND 5 IN THE SEXTET ZEEMAN ($<A_{2,5}>$)

Sample	B_{ef} [T]	D_{am} [T]	$<A_{2,5}>$	Ref.
$Fe_{61}Co_{10}Y_8$**Nb_1**B_{20}	19.39(3)	4.995+-0.022	3.30926+-0.029	[20]
$Fe_{61}Co_{10}Y_8$**Zr_1**B_{20}	19.93+-0.03	5.056+-0.037	2.99134+-0.026	
$Fe_{61}Co_{10}Y_8$**W_1**B_{20}	19.19+-0.03	5.004+-0.025	3.15006+-0.037	[21, 22]
$Fe_{61}Co_{10}Y_8$**Mo_1**B_{20}	19.27+-0.03	4.949+-0.030	3.14140+-0.035	[23, 24]

Conclusions

The paper presents the results of tests performed using Mossbauer spectroscopy. The obtained Mossbauer transmission spectra were subjected to numerical analysis and the hyperfine field distributions on the ^{57}Fe nuclei were obtained. On the basis of this analysis, the following parameters were calculated: the mean value of the hyperfine field, distribution dispersion and the A line factor <2.5> in the Zemman's sextet. The shape of Mossbauer transmission spectra was typical of magnetic amorphous alloys with one magnetic phase - ferromagnetic. The distribution of hyperfine field inductions for the tested alloy samples in the form of tapes with a thickness of about 35 mm was bimodal. It should be deduced from this that in the tapes produced there were areas with different concentrations of iron near the central atom. It is interesting to note that the introduction of 1% atomic elements into alloys did not have much impact on the shape of the obtained spectra and on the hyperfine field distributions obtained on their basis. It can only be mentioned that the Zr addition slightly affected the texture of the spins compared to Nb, W and Mo.

References

1.DUWEZ P., WILLENS R.H., T. Metall. Soc. Aime., **227**, 1963, p.362.

2.INOUE A, GOOK J. S., Mater. Trans. JIM, **36**, 1995, p. 1180.

3.INOUE A., KATSUYA A., Mater. Trans. JIM, **37**, 1996, p. 1332.

4.THOMAS T., GIBBS M. R. J, J. Magn. Magn. Mater., **103**, 1992, p.97.

5.INOUE A., Materials Science and Engineering A, **A226-228**, 1997, p.357.

6.INOUE A., ZHANG T., ITOI T, TAKEUCHI A., Mater. Trans. JIM, **38**, 1997, p. 359.

7.HAN Y., INOUE A., KONG F. L., CHANG C. T., SHU S. L., SHALAAN E., AL-MORZOUKI F., Journal Of Alloys and Compounds, **657**, 2016, p. 237.

8.BIAN Z., HE G., CHEN G. L., Scripta Materialia, **43**, 2000, p. 1003.

9.CHEN J., ZHANG Y., HE J. P., YAO K. F., WEI B. C., CHEN G.L., Scripta Materialia, **54**, 2006, p. 1351.

10.ZHANG J., LIM K. Y., FENG Y. P., LI Y., Scripta Materialia, **56**, 2007, p. 943.

11.MISHRA D., PERUMAL A., SARAVANAN P., ARVINDHA BABU D., SRINIVASAN A., Journal of Magnetism and Magnetic Materials, **321**, 2009, p. 4097.

12.GAWDZINSKA K., CHYBOWSKI L., PRZETAKIEWICZ W., Archives of Civil and Mechanical Engineering, **16,** no. 3, 2016, p. 553.,

13.GAWDZINSKA K., CHYBOWSKI L., PRZETAKIEWICZ W., LASKOWSKI R., Archives of Metallurgy and Materials, **62**, no. 4, 2017, p. 2171

14.GAWDZINSKA K., CHYBOWSKI L., BEJGER A., KRILE S., Metalurgija, **55**, no. 4, 2016, p. 659.

15.GAWDZINSKA K., BRYLL K., NAGOLSKA D., Arch. Metall. Mater., **61,** no. 1, 2016, p. 177.

16.ACHITEI, D.C., VIZUREANU, P., DANA, D., CIMPOESU, N., Metalurgia International, **18**, SI2, 2013, p. 104.

17.BERE, P., BERCE, P., NEMES, O., Composites Part B-Engineering, **43**, no. 5, 2012, p. 2237.

18.GONDRO J., Journal of Magnetism and Magnetic Materials, **432**, 2017, p. 501.

19.BRZOZKA K., Investigation of the structure and properties amorphous and nanocrystalline alloys basis on the Fe using a Mossbauer spectroscopy, Monograph **67**, 2003, p. 48.

20.PIETRUSIEWICZ P., NABIALEK M., DOSPIA£ M., GRUSZKA K., BLOCH K., GONDRO J., BRAGIEL P., SZOTA M., STRADOMSKI M., Journal of Alloys and Compounds, 615, 2014, p. 67

21.NABIALEK M., PIETRUSIEWICZ P., BLOCH K., Journal of Alloys and Compounds, **628**, 2015, p. 424.

22.PIETRUSIEWICZ P., BLOCH K., NABIALEK M., WALTERS S., Acta Physica Polonica A, **127**, 2015, p. 397.

23.PIETRUSIEWICZ P., NABIALEK M., Acta Physica Polonica A, **130**, no. 4, 2016, p. 920

24.GRUSZKA K., Materiali in Tehnologije, **50,** no. 5, 2016, p. 707

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