The Influence of Heat Treatment on the Shape of ^{57}Fe Hyperfine Field Induction Distribution in Massive Amorphous $Fe_{61}Co_{10}Y_8X_1B_{20}$ (where X = Mo, W)

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The paper presents the results of Mossbauer research for massive amorphous alloys $Fe_{61}Co_{10}Y_8Mo_1B_{20}$ and $Fe_{61}Co_{10}Y_8W_1B_{20}$ manufactured using the method of suction of a liquid alloy into a copper water-cooled mold and subjected to thermal treatment at a temperature of 700K / 60 min and 770K / 210 min. The treatment was carried out below the crystallization temperature and it did not lead to the creation in the volume of alloys of crystalline systems showing long-range order of atoms. Mössbauer research was performed for low energy milled plates in transmission geometry. Then, numerical analysis of these spectra was performed and the corresponding hyperfine field distributions were obtained ^{57}Fe. It has been shown that isothermal annealing has a big influence on the shape of the hyperfine field distribution. As a result of thermal processing, diffusion of the components took place, which caused the occurrence of diverse environments of iron atoms around the central atom. In the volume of all specimens, there was a lack of topological order in the arrangement of atoms.

Keywords: bulkamorphous materials, Mössbauer effect, hyperfine field induction ^{57}Fe

In recent decades, intensive research has been conducted on new materials for use in energetic [1]. Commonly used FeSi crystal sheets having a Goss texture [2-4] or cuboid texture [5] are becoming insufficient because of the Reed to transport of electricity and ecological reasons. Therefore a search for new materials began which will fulfill the requirements. On the basis of many years of studies it was concluded that one of the most significant (beside of chemical composition) parameters of novel material is its structure.

In the 80's of last century an amorphous group of materials were made, which had unique magnetic properties [6, 7]. Initially, these were only powders, thin layers or tapes up to 80μm [8, 9]. Making wires or magnetic cores from such materials was very difficult. With the current development of technology, these materials are slowly being used, but they are rather used in the construction of special execution systems. In 1989, in Japan, A. Inoue from the Tohoku University developed three criteria for producing amorphous alloys with a higher thickness than the 100 μm limit for tapes, which were commonly referred to as massive amorphous alloys [10 – 12]. On the basis of massive amorphous plates, bulky magnetic cores can be created, which can be successfully used in the construction of modern transformers. The main problem in assessing the properties of amorphous alloys is to get to know their structure. In the case of crystalline materials, its description is simple and based on existing already written patterns. On the other hand, as regards amorphous materials, their structure is characterized as disordered in chemical and topological terms without taking into account energy states that influence the changes in the properties of such materials, influencing changes in position of atoms in the volume of material. There are several research techniques that give the opportunity to assess the amorphous structure and its changes. One of them is high-resolution transmission microscopy [13]. Unfortunately, the use of it for the analysis of amorphous materials on the basis of magnetic elements, eg Fe, causes many difficulties and limitations. Another technique that allows the study of such materials is the Mossbauer spectroscopy, in which ^{57}Co is used as a Mössbauer source. Mossbauer spectroscopy gives the possibility to analyze the structure with high accuracy and with the use of appropriate numerical tools it is possible to determine other parameters of the structure and magnetic properties [14-23]. Because the results of Mossbauer research are characterized by high resolving power, using this technique one can easily reproduce changes in the amorphous structure after partial relaxation due to eg thermal treatment below the crystallization temperature [24]. Mössbauer spectra can be obtained in reflection and transmission geometry. However, the reflective technique gives information only from the surface of the sample, while transmission from all its volume.

In this work the results of Mössbauer studies for massive amorphous (0.5 mm thickness plates) $Fe_{61}Co_{10}Y_8W_1B_{20}$ and $Fe_{61}Co_{10}Y_8Mo_1B_{20}$ in condition after solidification and after heat treatment performed at parameters: 700K / 60min and 770K / 210min.

Experimental part

Samples for investigations were made using the method of suction of liquid alloy into a copper water-cooled mold. The components for the production of the research material had a high purity of more than 99.99% at. Boron was added in the form of an alloy with iron of a known chemical composition $Fe_{45.4}B_{54.6}$. The samples were produced in two stages. The first stage was to obtain crystalline ingots. All alloying elements were placed on a copper plate in a hollow and solidified under the influence of an electric arc. Settings during initial melting are: operating current - 280 A, atmosphere in the chamber - 0.3 atm. of Ar. The alloy ingots were melted several times on

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each side, which contributed to its greater homogeneity. Before each melting cycle of the ingots, pure titanium was melted, which served as an absorbent of the oxygen remaining in the chamber. The ingots thus prepared were surface-cleaned using polishing cloth and an ultrasonic cleaner. They were then divided into smaller portions, which were used in the second stage of sample production. The samples in the form of rapid cooled plates were obtained by sucking the liquid alloy into a copper mold with a core of the following dimensions: thickness - 0.5 mm and area 10x10 mm. The samples thus obtained were crushed in a zirconium mortar in a bath of toluene. The crushing was of a low energy nature. The samples were tested in the state after solidification and after heat treatment at the temperature and time of annealing: 700K / 60min and 770K / 210min.

Prepared from plates samples powder of $Fe_{61}Co_{10}Y_8W_1B_{20}$ and $Fe_{61}Co_{10}Y_8Mo_1B_{20}$ alloys was used in Mossbauer research. The preparation was placed in prisms of 10 mm in diameter cut from a thin copper foil. Then a hole in a copper foil was sealed on one side and a crushed sample was poured. The amount of powder should not be too large, what reduces the number of counts, and too small, what reduces the effect of Mössbauer from the sample. Based on previous studies, it was found that the good surface density of the preparation is 0.3 mg/cm^2. Poured on the adhesive tape powder was placed in the heap, then powder is closed with the same tape on the other side. The sample prepared in this way was placed in the POLON 2330 spectrometer, which worked in the transmission geometry in the system of constant acceleration of the source. The source of radiation was ^{57}Co In rhodium matrix. The *Mossbauer* spectrometer was calibrated using a thin film α-Fe (20μm). Numerical analysis of experimental data for Mossbauer spectra was carried out using the NORMOS program [25]. All measurements were taken at room temperature.

Results and discussions

Figure 1 and 2 show the Mossbauer transmission spectra recorded for the investigated alloy samples in the state after solidification and after the isothermal annealing process carried out at temperature and time: 700/60 min and 770K/210 min respectively.

The Mossbauer transmission spectrum shown in figures 1 and 2 are typical for amorphous materials. They consist of wide, asymmetrical overlapping lines well describing Zeeman's sextet. All spectra are similar and their shape indicates that they are magnetic in the magnetically ordered phase. The characteristic tendency is that external lines in the sextet are wider than the internal ones and that their width is an increasing function of the distance from the center of the spectrum [26-28]. For all presented spectra, the symmetry of the line's orientation with respect to the center is observed. This state is related to the disorder in the amorphous materials in the arrangement of atoms in topological and chemical terms. The process of annealing in a fixed time and temperature, which was lower than the temperature of crystallization, did not change the type of structure. In the spectra it was impossible to distinguish narrow components related to the presence of atomic systems describing the crystal structure. On the basis of numerical analysis of Mossbauer transmission spectra, the distribution of hyperfine fields on the ^{57}Fe nuclei was determined (fig. 3 and 4).

Obtained as a result of numerical analysis of Mössbauer transmission spectra (figs. 1, 2), the hyperfine index induction distributions are wide and clearly visible in their bimodal nature. Each hyperfine box induction distribution begins with a value of 5 T at zero probability, which excludes the existence of a paramagnetic component. In the case of $Fe_{61}Co_{10}Y_8W_1B_{20}$ in the condition after solidification, the low-field and high-field components are carefully separated from the Gauss line profile. After heating this sample, the shape of the distribution of hyperfine fields on the testicles ^{57}Fe slightly changed. The separation of components visible in the low hyperfine field (fig. 3 a) has disappeared. For the isothermal heating process of 700K / 60 min and 770K / 210 min the decomposition of the hyperfine transitions is practically the same. The first hump in the hyperfine box distribution (fig. 3 a) ends at about 11 T, and its maximum has shifted by 3 T. The second part of the hypothetical hyperfine distribution for each state that was tested was similar. However, it should be noted that its maximum after heating, regardless of temperature, has moved by two tesla from the state of 21 T in relation to the sample in the state after solidification. In addition, it should be noted that the final part of the second component wing

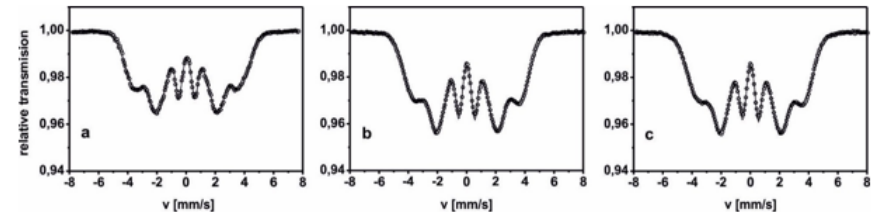

Fig. 1. Mossbauer spectra recorded for alloy samples $Fe_{61}Co_{10}Y_8W_1B_{20}$ in state: a - after solidification, b- 700K/60 min, c - 770K/210 min

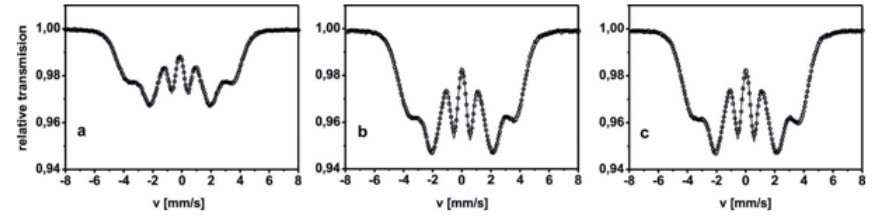

Fig. 2. Mossbauer spectra recorded for alloy samples $Fe_{61}Co_{10}Y_8Mo_1B_{20}$ in state: a -after solidification, b -700K/60 min, c - 770K/210 min

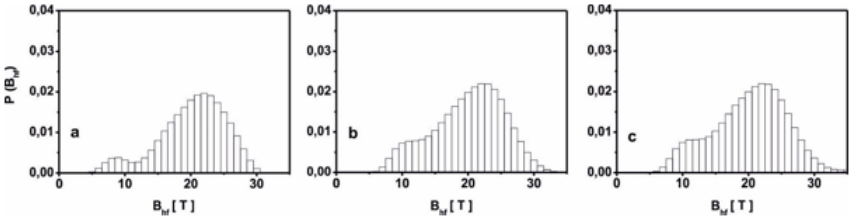

Fig. 3. Distributions of hyperfine fields induction for samples of the alloy $Fe_{61}Co_{10}Y_8W_1B_{20}$ in state: a-after solidification, b - 700K/60 min, c - 770K/210 min

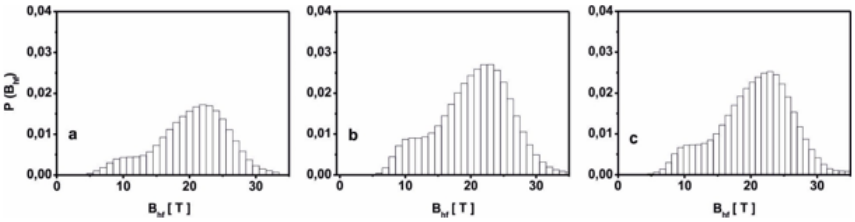

Fig. 4. Distributions of hyperfine fields induction for samples of the alloy $Fe_{61}Co_{10}Y_8Mo_1B_{20}$ in state: a - after solidification, b - 700K/60 min, c - 770K/210 min

Parameter / Sample	State	B_{hf} [T]10^{-1}	D_{am} [T]10^{-1}	Ref.
$Fe_{61}Co_{10}Y_8W_1B_{20}$	ASQ	20.08 [+-0.57]	5.583 [+-0.53]	19, 20, 21
	700K/60 min	20.17 [+-0.43]	5.696 [+-0.43]	
	770K/210 min	20.30 [+-0.41]	5.827 [+-0.47]	19
$Fe_{61}Co_{10}Y_8Mo_1B_{20}$	ASQ	20.21 [+-0.30]	5.446 [+-0.27]	
	700K/60 min	20.46 [+-0.27]	5.730 [+-0.44]	
	770K/210 min	20.55 [+-0.40]	5.664 [+-0.46]	

Table 1
THE INDUCTION VALUES OF THE EFFECTIVE HYPERFINE FIELD B_{hf} ON ^{57}Fe, DISPERSION FIELD DISTRIBUTIONS OF HYPERFINE FIELD D_{am} FOR INVESTIGATED ALLOY SAMPLES $Fe_{61}Co_{10}Y_8X_1B_{20}$ (X = W OR Mo) IN THE STATE AFTER SOLIDIFICATION AND AFTER ISOTHERMAL ANNEALING

as a result of annealing reaches an increasing value (condition after solidification 31 T, 700 K / 60 min 33 T and 770 K / 210 min 35 T). Changes in the shape of the hyperfine index distribution are related to the migration of atoms in the volume of the alloy, which affects the configuration of magnetic atoms and their change around the central atom. For the second of the investigated alloys $Fe_{61}Co_{10}Y_8Mo_1B_{20}$ hyperfine field distributions can be described in the same way as for the first one ($Fe_{61}Co_{10}Y_8W_1B_{20}$). It should only be noted that the change in the chemical composition, the replacement with tungsten by molybdenum, had a major impact on the first wing of the hyperfine field distribution. However, it did not have a significant impact on changing the position of the maxima of the low-level and high-share parts. It was found that after heating in temperature / time 700K / 60 min and 770K / 210 min, these maxima were shifted by 1 T (11 T, 23 T) in relation to the distribution corresponding to the sample in the state after solidification (10 T, 22 T). It should be noted that the high-field part is mainly related to areas in the volume of the sample with a lower iron content. This indicates the presence of a large number of non-equivalent positions of iron atoms. In such areas Mössbauer atoms are surrounded by a mixture of atoms consisting of iron atoms and non-magnetic atoms. These surroundings concern the first coordination zone. Data obtained from numerical analysis of Mossbauer transmission spectra are presented in table 1.

Conclusions

Using the suction casting method, one can create massive amorphous alloys in the form of 0.5 mm thick plates and chemical compositions $Fe_{61}Co_{10}Y_8X_1B_{20}$ (X = Mo or W). The Mössbauer technique gives the opportunity to study the real structure of amorphous alloys. Using the specialized software, on the basis of the transmission analysis of the Mossbauer spectra, it is possible to determine the hyperfine field distributions and determine the characteristic parameters, ie the value of induction of the effective hyperfine field on the nuclei ^{57}Fe and dispersion of hyperfine field distribution. Observations of the hyperfine parameters evolution after the thermal treatment process performed below the crystallization temperature of the tested alloys were observed. As a result of the thermal treatment process, the volume of alloys for the migration of atoms and reduction of local stresses in the sample during the process of their production took place. Diffusion of atoms in the sample leads to a reduction in the amount of so-called free volume, which is associated with an increase in the packing of atoms. Irreversible structural relaxation is the reason for reducing the average distances between atoms, which should increase the induction of an effective hyperfine field on the nuclei ^{57}Fe and dispersion of its distribution. Calculated on the basis of numerical analysis parameters B_{hf} and D_{am} have typical values as for amorphous materials. Their increase after the annealing process is in line with the above considerations and affects the change of the topological and chemical order in the alloy but still within the amorphous state.

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Manuscript received: 21.10.2017