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Structure and properties of the powder obtained from the amorphous ribbon

J. Konieczny [a], L.A. Dobrzański [a,*], J.E. Frąckowiak [b]
[a] Division of Materials Processing Technology and Computer Techniques in Materials Science, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
[b] Institute of Material Science, University of Silesia, ul. Bankowa 12, 40-007 Katowice, Poland
* Corresponding author: E-mail address: leszek.dobrzanski@polsl.pl

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Materials

ABSTRACT

Purpose: The aim of the work is to investigate the magnetic properties of the cobalt based $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ amorphous alloy subjected to the isothermal annealing, high-energy milling and to a combination of these two technologies.
Design/methodology/approach: The powder test piece obtained from the input amorphous ribbon in high-energy ball milling. Distributions of the magnetic hyperfine P(H) fields were determined for spectra smoothed in this way, by using the HFQS program, employing the Hesse-Rübartsch method. The diffraction examinations and examinations of thin foils were made on the JEOL JEM 200CX transmission electron microscope. Observations of the structure of powders were made on the Opton DSM-940 scanning electron microscope.
Findings: The analysis of the magnetic properties test results of the of the $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ powders obtained in the high-energy ball of milling process proved that the process causes significant decrease in the magnetic properties. The structure and magnetic properties of this material may be improved by means of a proper choice of parameters of this process as well as the final thermal treatment.
Research limitations/implications: For the powders, further magnetical, structure and composition examinations are planed.
Practical implications: The amorphous and nanocrystalline metal powders obtained by milling of metallic glasses feature an alternative to solid alloys and make it possible to obtain the ferromagnetic nanocomposites, whose shape and dimensions can be freely formed.
Originality/value: The paper presents influence of parameters of the high-energy ball milling process on structure and magnetic properties of soft magnetic powder materials obtained in this technique. The paper compares structure and magnetic properties of the $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ alloy obtained in high-energy ball milling process and melt spinning technique.
Keywords: Nanomaterials; Mössbauer spectrum; Magnetic properties; High energy ball milling

1. Introduction

The single- or multi-phase iron, cobalt, or nickel based alloys obtained with the melt spinning method are characteristic of the soft magnetic properties. The amorphous or nanocrystaline alloys obtained in this way are characteristic of the very low coercion field H_c, high magnetic saturation B_s, high initial magnetic permeability and very low remagnetising losses. These properties may be improved by the heat treatment or by heat treatment in the

magnetic field [1, 2]. The nanocrystaline materials display a very low magnetic anisotropy. This is caused by the fact that the originated grains are significantly smaller from the correlation length for the ferromagnetic exchange interactions [3].

Addition of Fe plays the same role in the CoSiB alloys as the Cu addition in the iron based alloys [4, 5]. Additions of Fe and Nb have the advantageous effect on the CoSiB alloy structure. Addition of Nb improves the thermal stability of the amorphous phase and the Fe and Nb additions make it possible to develop the nanocrystaline structure with one FeCo-A2 crystalline phase in the Co-Si-B amorphous alloy. The commutable Nb or Hf elements used in the 5% concentration have the equally effect on the structure [6, 7].

As the metallic amorphous and nanocrystalline materials obtained by crystallization of the metallic glasses are available in the form of thin strips only, the efforts are on the way to obtain the nanocrystaline powder material with various methods [8, 9].

The amorphous and nanocrystalline metal powders obtained by milling of metallic glasses feature an alternative to solid alloys and make it possible to obtain the ferromagnetic nanocomposites, whose shape and dimensions can be freely formed [10-11].

The goal of the work is to investigate the magnetic properties of the cobalt based $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ amorphous alloy subjected to the isothermal annealing, high-energy milling and to a combination of these two technologies.

2. Experimental

Because of the low iron content in the examined specimens and, in addition, due to the low probability of the resonance absorption of the ^{57}Fe γ isotope radiation for the investigated materials, measurement of each Mössbauer spectrum was carried out for about one week. The resonance effect turned out to be very low in spite of the significant extension of the measurement time period and big measurement statistics. Therefore, each measured Mössbauer spectrum was smoothed, which consisted in the decomposition of the experimental spectra to the convergent Fourier series and in discarding those harmonic components that have very small input to the total dispersion, by using the Parseval relationship [12, 13]. Distributions of the magnetic hyperfine P(H) fields were determined for spectra smoothed in this way, by using the HFQS [14] program, employing the Hesse-Rübartsch method [15]. The P(H) distributions obtained are characterised by the following set of parameters:

- <H> - average value of the magnetic hyperfine field,
- <IS> - average value of the isomeric shift,
- D_H - dispersion of the P(H) hyperfine fields distribution.

The D_H parameter characterizes the hyperfine P(H) magnetic fields' distribution breadth and changes of its value are connected with fading or growth of the particular configurations of the vicinity of the 57-Fe isotope that occur in the thermal or mechanical treatment of the amorphous phase. The average values of the isomeric shift <IS> (in a smaller range) and the average values of the hyperfine magnetic field <H> are sensitive to the closest atomic neighbourhood of the 57-Fe isotope and depend on the kind of atoms surrounding the Mössbauer isotope. Analysing changes of the D_H and <H> parameters gives grounds to draw conclusions pertaining to changes occurring in the closest neighbourhood of the Mössbauer isotope, featured by ^{57}Fe.

The diffraction examinations and examinations of thin foils were made on the JEOL JEM 200CX transmission electron microscope at the accelerating voltage of 200 kV equipped with the Oxford EDS LINK ISIS X-ray energy dispersive spectrometer. Thin foils were made from strips and powder material by cutting out disks with 3.2 mm O.D.

Observations of the structure of powders were made on the Opton DSM-940 scanning electron microscope with the Oxford EDS LINK ISIS X-ray energy dispersive spectrometer at the accelerating voltage of 20 kV.

3. Results and discussion

3.1. $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ as quenched alloy

The Mössbauer spectrum of the $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ amorphous ribbon obtained in the melt spinning process is shown in Fig. 1a, whereas the hyperfine fields distribution P(H) calculated for this test piece is shown in Fig. 1b.

The evaluated Mössbauer spectrum is characteristic for the amorphous alloys and has a typical form of the Zeeman spectrum, consisting of 6 broadened asymmetric absorption lines. The average value of the magnetic field <H> = 21.3 T, much lower than the relevant value of the metallic iron (33.0 T), suggests that the iron atoms have atoms like Si and B in their closest neighbourhood, strongly lowering the internal magnetic field.

As it turns out from the research [22], the presence of Co atoms increases the value of the internal magnetic field for the Fe atoms. Therefore, the small, characteristic peak occurring in the zone of the magnetic fields of about 35.0 T may be attributed to the Fe-Co type precipitations. The big value of the proportion of lines' No (2 and 4) intensities to the (3 and 4) ones' intensities, equal to 3.65 indicates that the magnetization vector M is parallel to the test piece plane.

The investigated $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ alloy was delivered in the as quenched state and had the amorphous structure. In the electron diffraction patterns (Fig.6a) the broad blurred rings are visible coming from the amorphous phase. No spot reflexes in the diffraction pattern for a test piece in the as quenched state attests to the absence of the crystalline phase in the structure.

3.2. The $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ alloy annealed at temperature of 500°C

It was found out in the observations carried out on the transmission electron microscope that after annealing the amorphous strip at temperature of 500°C, the Co-α grains increase their size and shape from spherical into the dendritic ones, dendritic grains with bigger size were also found, distributed in a rather inhomogeneous way.

It was found out basing on the electron diffraction that after annealing at temperature of 500°C precipitations of the crystalline phases appeared that were identified as cobalt boride (002) Co_3B and cobalt reflexes from planes (010), (002), (011) i (110) Co-β of the hexagonal with the dense arrangement of atoms.

The Mössbauer spectrum annealed at the temperature of 500°C is very similar to the initial test piece's spectrum in the as quenched state. The values of the <H> and <IS> parameters, increased compared to the initial test piece indicate to increase (netto) of a number of Co atoms in the closest neighbourhood of Fe atoms in the amorphous matrix.

A significant reduction of the Fe-Co type precipitations, occurring in the initial test piece, is also visible. The changes observed are undoubtedly the result of the structural relaxation and holding of the redundant voids at an elevated temperature.

Fig. 2a shows the Mössbauer spectrum of the initial test piece annealed at 500°C and also distribution of the magnetic hyperfine P(H) fields (Fig. 2b).

3.3. Powder obtained from the ribbon after 15 hours of milling

Fig. 3a presents the Mössbauer spectrum evaluated for the powder test piece obtained from the input amorphous strip after 15 hours of milling; whereas Fig. 3b shows the relevant distribution of the P(H) hyperfine fields.

The Mössbauer spectrum of this test piece has the worst quality, which may result from its iron depletion due to the milling process. Anyway, analysis of the smoothed spectrum indicates that a clear separation of magnetic properties occurs in the test piece, connected perhaps with the specific distribution of the nanocrystalline grains with the diametrically different diameters. Two peaks are visible on the P(H) curve, one of which refers to the field value of H1=13.0 T, whereas the second one to the field value of H2=22.0 T. The H_2 field value is close to the average field value for the amorphous test piece annealed at the temperature of 500°C. However, the small value of the field value H_1, may be connected with grains of very small diameters, for which portion of the low-iron configurations of neighbourhoods connected with grain surfaces may be significant. It cannot also be ruled out that the abovementioned grains have superparamagnetic properties.

3.4. Powder obtained from the ribbon after 25 hours of milling

Observations on the transmission electron microscope revealed that the high energy milling carried out even for a relatively short time of 25 hours results in development of the nanocrystalline structure (Fig. 6b). This structure differs from the nanostructure obtained by the isothermal annealing of amorphous strips, it is more irregular, inhomogeneous, and grains present in it are very diversified as regards their shape and size. Basing on analysis of the diffraction patterns from the transmission electron microscope (Fig. 6b) phases of Co-β, Co_2B cobalt boron, Co_2Si and $CoSi_2$ cobalt silicides, as well as the Fe_2B phase were revealed in structure of powder obtained after 25 hours of milling.

Fig. 4a presents the evaluated Mössbauer spectrum of a powder test piece obtained from the input strip after 25 hours of milling; whereas, Figure 4b presents the relevant distribution of the magnetic hyperfine fields P(H).

The Mössbauer spectrum of this test piece is characteristic also for the amorphous material. The field distribution P(H) is shifted towards the lower values of the magnetic fields, compared to the previous test piece. This effect is surely connected with extending the milling time and the resulting decrease of the grains diameter. One should note small peaks appearing in the P(H) distribution for the magnetic fields range bigger than 30.0 T, connected with grains enriched with Fe and Co.

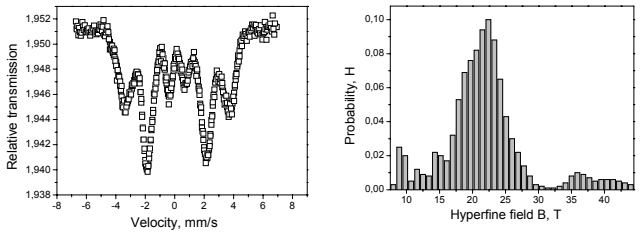

Fig.1a The Mössbauer spectrum of the as quenched $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ amorphous ribbon 1b) Distribution of the hyperfine fields P(H)

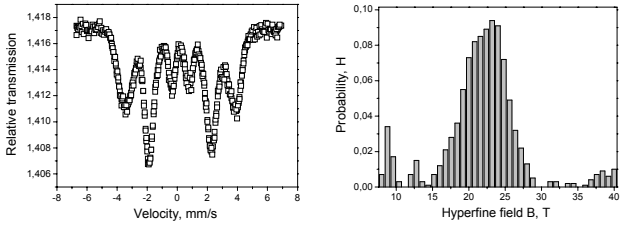

Fig. 2a. The Mössbauer spectrum of the $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ amorphous strip annealed at the temperature of 500°C, b) Distribution of the hyperfine fields P(H)

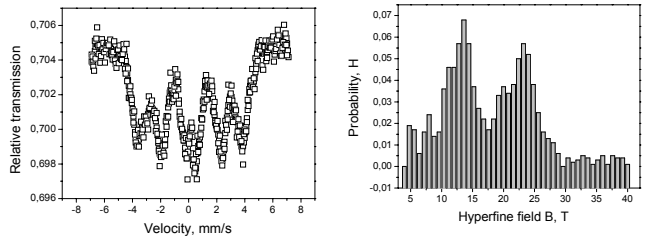

Fig. 3a. The Mössbauer spectrum of the powder obtained from the $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ amorphous strip after 15 hours of milling, b) Distribution of the hyperfine fields P(H)

3.5. Powder obtained from the ribbon annealed at the 500oC after 2 hours of milling

The nanocrystaline structure was revealed in the powder material obtained by grinding the $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ strip annealed before for 1 hour at the temperature of 500°C. The following phases were identified in the analysis of diffraction patterns obtained on the transmission microscope: Co-α, Co-β, $CoSi_2$, and Fe_2B.

Fig. 5a presents the Mössbauer spectrum evaluated for the powder test piece obtained from the input strip annealed at the temperature of 500°C and milled for 2 hours; whereas Fig. 5b shows the relevant distribution of the P(H) hyperfine fields.

The Mössbauer spectrum of this test piece has the evident discrete constituent lines, connected with the phase of the low magnetic field. Admittedly, the separation of peaks is not that clearly visible on the P(H) distribution, as it is in case for the test piece milled for 15 hours; however, this reasoning seems to be correct also in this case.

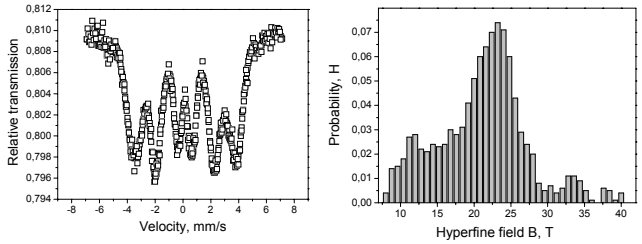

Fig. 4a. The Mössbauer spectrum of the powder obtained from the $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ amorphous strip after 25 hours of milling, b) Distribution of the hyperfine fields P(H)

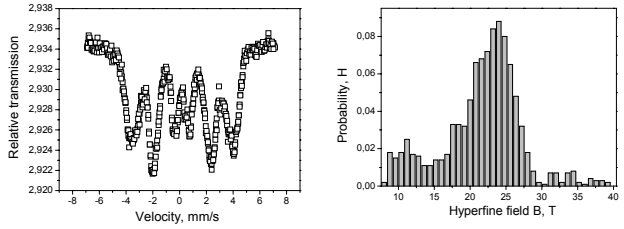

Fig. 5a. The Mössbauer spectrum of the powder obtained from the $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ amorphous strip annealed at the temperature of 500˚C after 2 hours of milling, B) Distribution of the hyperfine fields P(H)

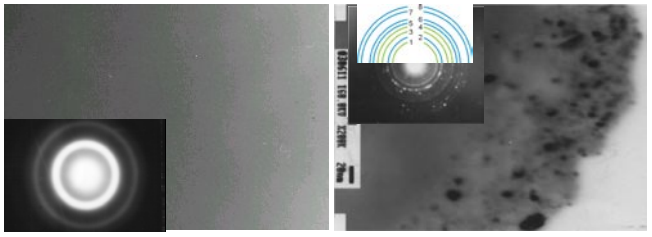

Fig. 6a) Amorphous structure of the $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ alloy, TEM magnification 60000x, b) Diffraction pattern from the grain of powder obtained after 25 hours of the high energy milling of the $Co_{68}Fe_4Mo_1Si_{13,5}B_{13,5}$ amorphous ribbon, TEM; 1 – Co_3B (120), 2 – Co-β (011), 3 - Co_3B (222), 4 - Co_3B (040), 5 - Co-β (110), Co_3B (103), 6 - Co-β (013), 7 - Co-β (022), 8 – Co-β (014)

4. Conclusions

The analysis of the magnetic properties test results of the of the $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ powders obtained in the high-energy ball of milling process proved that the process causes significant decrease in the magnetic properties.

On the basis of the research done, it was stated that the process of the high-energy ball milling combined with thermal crystallisation of the $Co_{68}Fe_4Mo_1Si_{13.5}B_{13.5}$ alloy, results in the production of the nanocrystalline powder material. The structure and magnetic properties of this material may be improved by means of a proper choice of parameters of this process as well as the final thermal treatment.

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