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HYPERFINE MAGNETIC FIELDS OF NANOCRYSTALLINE MATERIALS BY MÖSSBAUER SPECTROSCOPY[1]

J. Sitek, M. Miglierini, I. Tóth
Department of Nuclear Physics and Technology, Slovak Technical Univestity,
Ilkovičova 3, 812 19 Bratislava, Slovakia

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Nanocrystallization of some amorphous of FeCuNbSiB and FeZrB(Cu) alloys has been compared. We present effects of sample composition, temperature and annealing time on magnetic structure followed by changes in probability of the field values, average values and standard deviation of the hyperfine magnetic field and relative amount of amorphous rest.

1. Introduction

In the last years new crystalline iron-based alloys were developed with an ultrafine grain structure revealing excellent soft magnetic properties [1, 2]. These materials were cast initially as amorphous ribbons, and subsequent annealing above the crystallization temperature of the amorphous state created an ultrafine grain structure. The most prominent example is nanocrystalline FeCuNbSiB alloy which reveal a homogeneous ultrafine grain structure of bcc FeSi with grain size of 10-20 nm embedded in the amorphous rest [3, 4]. Good examples of such a materials are FeZrB and FeZrBCu nanocrystalline alloys formed also by annealing of amorphous alloys [5, 6]. These materials reveal superior properties (higher magnetization and permeability) than to those of FeCuNbSiB alloys developed initially.

The magnetic properties of these materials seem to be very sensitive to the structure of nanocrystalline component. It is reasonable to presume that the magnetic properties will react very sensitively to the changes in the crystalline and amorphous components.

In this work, we present a Mössbauer study of FeCuNbSiB and FeZrB(Cu) alloys, both in the amorphous and nanocrystalline state. Our main objective has been the magnetic structure characterization derived from the hyperfine magnetic field distribution and other parameters determined from Mössbauer spectra.

2. Method

Mössbauer measurements have been performed on amorphous and nanocrystalline ribbons of nominal compositions $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, $Fe_{70.5}Cu_1Nb_{4.5}Si_{16}B_8$,

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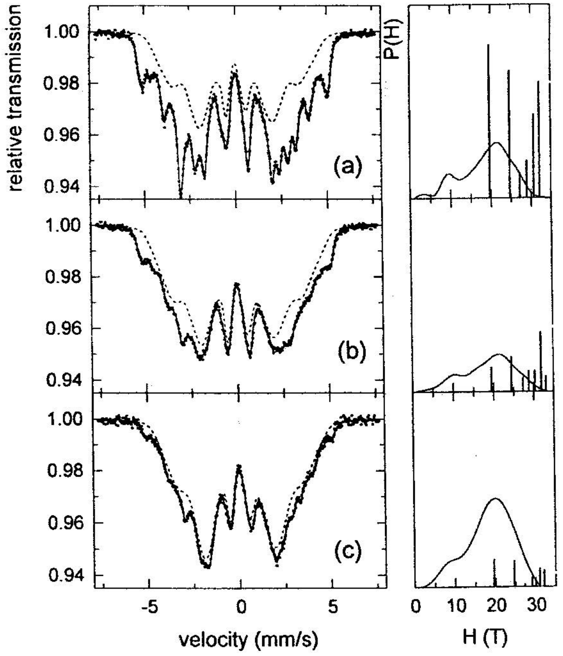

Fig. 1. Mössbauer spectra of nanocrystalline samples after annealing at 550°C for 1 hour: a) $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, b) $Fe_{70.5}Cu_1Nb_{4.5}Si_{16}B_8$, c) $Fe_{72.0}Cu_1Nb_{4.5}Si_{13.5}B_9$

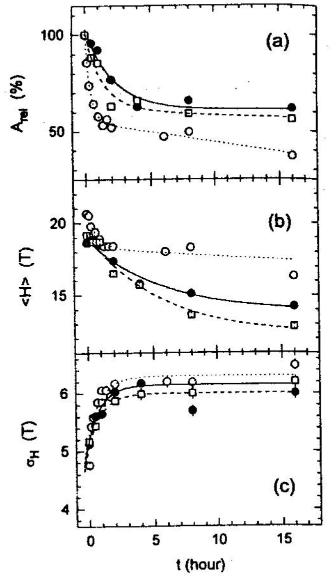

Fig. 2. Time dependence of a) relative area A_{rel}, b) average hyperfine field $\langle H \rangle$, c) standard deviation σ_H circles: $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, squares: $Fe_{70.5}Cu_1Nb_{4.5}Si_{16}B_8$, dots: $Fe_{72.0}Cu_1Nb_{4.5}Si_{13.5}B_9$

$Fe_{72.0}Cu_1Nb_{4.5}Si_{13.5}B_9$, $Fe_{87.5}Zr_{6.5}B_6$ and $Fe_{86.5}Zr_{6.5}B_6Cu_1$. The nanocrystalline samples were obtained by annealing the as-quenched samples in vacuum at the temperature 550°C for 1 up to 16 hours. Mössbauer spectra of the as-quenched amorphous and nanocrystalline samples were recorded at the room temperature. The spectra have been obtained in the transmission geometry using a conventional constant acceleration spectrometer with $^{57}Co(Rh)$ source. Spectra were fitted by NORMOS DIST program.

3. Results and discussion

Fe-Cu-Nb-Si-B alloys

Mössbauer spectra of the as-quenched amorphous Fe-Cu-Nb-Si-B alloys exhibit the known characteristics of an amorphous material. Mössbauer spectra of nanocrystalline samples consist of sharp isolated lines which are superimposed on broad-line components. The sharp lines belong to different crystalline phases. The latter are formed during thermal treatment of the original amorphous precursor. Variety of non-equivalent atomic sites in amorphous structure give rise to broad and unresolved spectral lines

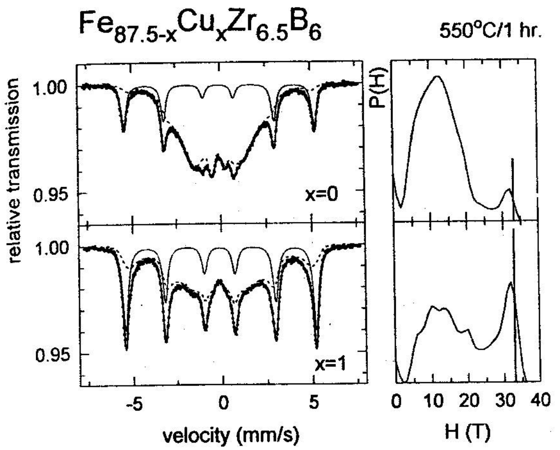

Fig. 3. Mössbauer spectra of $Fe_{87.5}Zr_{6.5}B_6$ and $Fe_{86.5}Zr_{6.5}B_6Cu_1$.

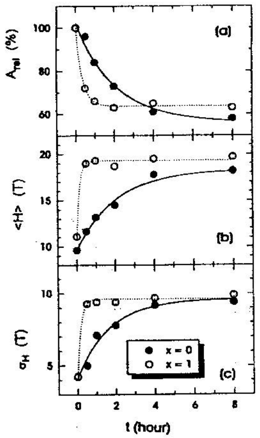

Fig. 4. Time dependence of a) relative area A_{rel}, b) average hyperfine field $\langle H \rangle$, c) standard deviation σ_H of $Fe_{87.5}Zr_{6.5}B_6$ and $Fe_{86.5}Zr_{6.5}B_6Cu_1$.

characterized by $P(H)$ distribution instead of discret hyperfine field values of crystalline components. The analysis of the Mössbauer spectrum of nanocrystalline sample (Fig. 1) yields the typical crystalline iron-silicon phase with Fe_3Si structure corresponding to six subspectra and an amorphous phase with reduced hyperfine field compared to the as-quenched state. Values of hyperfine fields of the crystalline phase are shown by vertical lines in the right side of Fig. 1 together with the $P(H)$ distribution of the residual amorphous phase. By increasing the annealing time the amount of crystalline phase increases at the expense of residual amorphous phase as is shown in Fig. 2a. Relative area A_{rel} of the broad sextet in the Mössbauer spectrum (dotted line) is proportional to the amount of the residual amorphous phase in the specimen. Time dependences of relative areas show rapid decrease of residual amorphous phase during the first 3 hours. Role of particular elements in the crystallization process can be studied through $P(H)$ distribution of the master FeNbCuSiB- type alloy with different compositions. The higher content of Nb or Si causes a moderate decrease in the amount of amorphous rest. The relation between the average hyperfine field $\langle H \rangle$ of the residual amorphous phase and the annealing time is shown in Fig. 2b. Fall of the average field can be associated mainly with the increase in the Nb content. This implies also changes in the short range order which are reflected via standard deviation σ_H of hyperfine magnetic field (Fig. 2c). Deviation in the magnetic structure are also documented by bimodal nature of the $P(H)$ distributions corresponding to two magnetically inequivalent sites of iron atoms in the amorphous phase. The low field component is ascribed to the Fe atoms surrounded by Nb, Cu and B. The high field component represents those Fe atom sites which are occupied mostly by Si and also B atoms, and these are the elements from which the crystalline phases have been formed. Consequently, both the average hyperfine field of the amorphous rest and its relative content are reduced with annealing time.

Fe-Zr-B-(Cu) alloys

Amorphous materials containing zirconium attract a lot of interest due to their complex magnetic structure. Their nanocrystalline counterparts have been developed by utilising the first step of crystallization [7]. Annealing the amorphous $Fe_{87.5-x}Cu_xZr_{6.5}B_6$ alloys ($x = 0, 1$) at the temperature 550°C induces partial crystallization as revealed by the appearence of spectral components with sharp lines as seen in Fig. 3. According to the hyperfine parameters they can be identified as α-Fe. The presence of Cu in the amorphous alloy decreases the crystallization temperature and makes transformation to the nanocrystalline state more efficient than in the case of FeZrB. The relative contribution of α-Fe after annealing at 550°C for 1 hour is about 30% for FeZrBCu as compared with 18% for FeZrB.

Annealing time dependences of relative areas show rapid decrease of amorphous rest up to 4 hours (Fig. 4a). After this the amounts of amorphous phases of both samples are almost stable. Fast crystallization causes a rapid increase of average hyperfine field $\langle H \rangle$ (Fig. 4b) and follows a time dependence of relative area. New chemically and topologically distinct sites of the resonant Fe atoms due to crystallization enhance the structural disorder which is reflected through the increase in σ_H (Fig. 4c).

4. Conclusion

Nanocrystals featuring soft magnetic properties are strong candidates for many technical applications. Utilisation of Mössbauer spectroscopy in the study of these materials has proved to be useful especially when inspecting the particalar physical properties on a nuclear and/or atomic level. Through scanning the nearest surroundings by means of Mössbauer probe atoms it is possible to reveal where, when and what ordering is formed in the sample studied. Moreover, Mössbauer spectroscopy provides an unique opportunity to derive the distributions of hyperfine fields.

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