Microstructure and low field magnetic properties of bulk Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_2$W$_2$B$_{20}$ amorphous and partially crystallized alloy

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Abstract. The microstructure, initial magnetic susceptibility and its disaccommodation of the amorphous and partially crystallized Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_2$W$_2$B$_{20}$ alloy are investigated. From Mössbauer spectroscopy, X-ray diffraction and electron microscopy studies we have found that the samples in the as-quenched state are fully amorphous. Moreover, we have stated that in the annealed samples the crystalline $\alpha$-FeCo phase shows the long range order of atoms. The amorphous rod exhibits the lower intensity of disaccommodation than the sample in the form of ribbon. It is due to annealing out of some free volumes during preparation.

1. Introduction
The initial magnetic susceptibility disaccommodation (MSD) is one of the after-effect phenomena. In crystalline ferromagnetic alloys this effect is mainly ascribed to the directional ordering of point-like defects and substitutional atom pairs or thermal activated dislocation motions, and observed as a decrease of the initial magnetic susceptibility with time after the demagnetization of a sample [1]. The similar effect is also observed in amorphous and partially crystallized materials [2]. MSD in these materials is more complicated than in crystalline ones because in the same temperature range reversible and irreversible structure relaxations may simultaneously occur [3]. Moreover, MSD in amorphous alloys may not be described by a single relaxation time as in crystalline materials but by a distribution of relaxation times. The commonly accepted model of MSD in amorphous alloys has been proposed by H. Kronmüller [2]. According to it MSD phenomenon in amorphous alloys is connected with the reorientation of atom pair axes in the vicinity of free volumes which play similar role as vacancies in crystalline materials. As mentioned above MSD in amorphous alloys is highly influenced by free volumes, and indirectly by preparing and annealing conditions. The density of free volumes in the as-quenched samples depends on the quenching rate. In this way the distinct difference between disaccommodation intensity for ribbons and bulk amorphous materials is expected.

The goal of this paper is to present the results of the microstructure and low magnetic field properties studies for amorphous and partially crystallized Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_2$W$_2$B$_{20}$ alloy.

2. Experimental
The bulk amorphous Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_2$W$_2$B$_{20}$ alloy was in the form of ribbons and rods. Ribbons, prepared by melt spinning technique in protective argon atmosphere, were 70 µm thick and 3 mm wide. Rods, obtained by a suction-casting method [4], were 2 cm long and 1 mm in diameter. The amorphicity of...
the as – quenched samples and microstructure of the annealed samples were examined by X–ray diffraction, transmission electron microscopy and Mössbauer spectroscopy. X–ray diffraction patterns and Mössbauer spectra were recorded at room temperature for powdered samples.

The initial magnetic susceptibility, $\chi$, was measured by a completely automatic set-up at the magnetizing field with the amplitude of 0.16 A/m and frequency of 2 kHz in the temperature range from 140 K up to 550 K. The MSD was calculated according to the equation:

$$\Delta \left( \frac{1}{\chi} \right) = \frac{1}{\chi_2} - \frac{1}{\chi_1}$$

where $\chi_1$ and $\chi_2$ are the values of magnetic susceptibility at $t_1 = 2$ s and $t_2 = 120$ s after demagnetization of the sample, respectively. MSD results were presented as isochronal curves. All investigations were carried out for specimens in the as-quenched state and after annealing at 850 K for 0.5 h in vacuum of $10^{-5}$ hPa.

3. Results and discussion

All investigated samples are fully amorphous which is confirmed by X-ray diffractometry, Mössbauer spectroscopy and transmission electron microscopy. The diffraction patterns (Fig. 1) obtained for these alloys in the form of ribbons and rods are typical of amorphous state and only single broad maxima are observed indicating the lack of long range order in atom configuration. In Fig. 2 the transmission Mössbauer spectra of the powdered samples after rapid solidification are presented. The spectra of these samples are asymmetric and consist of broad lines which are characteristic of amorphous systems. In the hyperfine field distributions obtained from these spectra one can distinguish a few components which are attributed to different local environments of iron atoms. The microstructure and corresponding electron diffraction pattern for the rod-shaped as-quenched sample of the amorphous Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_{2.5}$W$_{2}$B$_{20}$ alloy are depicted in Fig. 3. The microstructure image does not show crystalline grains and electron diffraction pattern in the form of halo ring indicates that the sample is fully amorphous.

Fig. 1. X-ray diffraction patterns for the bulk amorphous Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_{2.5}$W$_{2}$B$_{20}$ alloy in the as-quenched state in the form of: rod (a) and ribbon (b).

The X-ray diffraction pattern and Mössbauer spectra for the samples annealed at 850 K for 0.5 h are presented in Figs. 4 and 5. In comparison with the as-quenched state, in X-ray diffraction patterns the additional narrow maxima corresponding to the crystalline phase are observed. The formation of the crystalline phase during annealing of the samples is also stated by Mössbauer spectroscopy (Fig. 5). As seen in Fig. 5 the spectra with narrow lines of low intensities are superimposed on broad line feature. In hyperfine field distributions at least four components can be visible. The high field component is ascribed to the crystalline $\alpha$-FeCo phase and the other to the amorphous matrix. From these distributions one can state that the amorphous matrix in partially crystallized samples is very inhomogenous. Taking into account the average hyperfine field, isomer shift and standard deviation of the hyperfine field distributions corresponding to crystalline phase it is found that this phase exhibits the B2 superstructure in atom arrangement [5]. The Bragg-Williams long range order parameter and the iron content in the crystalline phase derived from the
spectra analysis are equal to 0.72 and 64 at. %, respectively. The volume fraction of the crystalline Fe$_{64}$Co$_{36}$ is estimated to be about 0.10.

![Mössbauer spectra and corresponding hyperfine field distributions for the powdered bulk amorphous Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_2$W$_2$B$_{20}$ alloy in the as-quenched state: rod-shaped (a, c) and ribbon-shaped (b, d).](image)

Fig. 2. The transmission Mössbauer spectra and corresponding hyperfine field distributions for the powdered bulk amorphous Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_2$W$_2$B$_{20}$ alloy in the as-quenched state: rod-shaped (a, c) and ribbon-shaped (b, d).

![Transmission electron image (a) and the electron diffraction pattern (b) for the as-quenched amorphous Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_2$W$_2$B$_{20}$ alloy in the form of ribbon.](image)

Fig. 3. Transmission electron image (a) and the electron diffraction pattern (b) for the as-quenched amorphous Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_2$W$_2$B$_{20}$ alloy in the form of ribbon.

![X-ray diffraction patterns of the Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_2$W$_2$B$_{20}$ alloy annealed at 850 K for 0.5 h obtained in the form of rod (a) and ribbon (b).](image)

Fig. 4. X-ray diffraction patterns of the Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_2$W$_2$B$_{20}$ alloy annealed at 850 K for 0.5 h obtained in the form of rod (a) and ribbon (b).
The investigated alloy in the amorphous state is magnetically soft ferromagnet and exhibits high initial magnetic susceptibility, \( \chi \), as compared to the classical crystalline alloys. In Fig. 6 the initial magnetic susceptibility as a function of temperature for the bulk amorphous Fe\(_{61}\)Co\(_{10}\)Hf\(_{2.5}\)Zr\(_{2.5}\)Ti\(_2\)W\(_2\)B\(_{20}\) alloy in the as-quenched state is presented. The initial magnetic susceptibility of the sample in the form of rod slightly depends on temperature in the temperature range from 120 K up to 470K. It indicates that this sample is at least partially stress-relieved during preparation due to low quenching rate. Near the Curie temperature the slight
increase of $\chi$, because of phase transition, followed by the rapid decrease of the initial magnetic susceptibility is observed. The sample in the form of ribbon shows the distinct increase of $\chi$ with temperature.

The shape of $\chi(T)$ curves distinctly changes after annealing the samples at 850 K for 0.5 h (Fig. 7). The curves exhibit very broad and flat maxima and the initial magnetic susceptibility monotonically decreases in the temperature range from 300 up to 550 K. It is connected with the distribution of the Curie temperature in the inhomogeneous amorphous matrix which is confirmed by Mössbauer spectroscopy investigations (Fig. 5).

Fig. 7. The initial magnetic susceptibility, $\chi$, versus temperature for the annealed at 850 K for 0.5 h sample of Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_{2}$W$_{2}$B$_{20}$ alloy in the form of rod (a) and ribbon (b).

In Fig. 8 the isochronal disaccommodation curves for the bulk amorphous Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_{2}$W$_{2}$B$_{20}$ alloy in the as-quenched state are depicted. The as-quenched samples show very broad disaccommodation spectra. It is worth noticing that intensity of disaccommodation for the sample in the form of rod is lower than for the ribbon shaped one.

Fig. 8. Isochronal disaccommodation $\Delta \left( \frac{1}{\chi} \right)(T)$ curves for the bulk amorphous Fe$_{61}$Co$_{10}$Hf$_{2.5}$Zr$_{2.5}$Ti$_{2}$W$_{2}$B$_{20}$ alloy in the as-quenched state in the form of rod (a) and ribbon (b).
The observed effect is connected with the different density of free volumes in the samples. As mentioned above the quenching rate in the case of rod is lower than for ribbon and this elucidates the lower intensity of disaccommodation. Assuming the Gaussian distribution of relaxation times \[6\]:

\[
P(\ln \tau) = \beta^{-1} \pi^{-\frac{1}{2}} \exp \left[-\left(\frac{\ln \tau - \ln \tau_m}{\beta}\right)^2\right]
\]

where: \(\beta\) is the width of the distribution, \(\tau_m\) is the average relaxation time and \(\tau\) the relaxation time the isochronal disaccommodation curve is decomposed into three elementary processes according to the equation:

\[
\Delta \left(\frac{1}{\chi}\right) = \sum_{i=1}^{3} \int_{-\infty}^{\frac{\beta}{\ln \tau_m}} \beta^{-1} \pi^{-\frac{1}{2}} I_{pi} T_{pi} \left(\frac{1}{\tau_m T} \int_{-\infty}^{\frac{\beta}{\ln \tau_m}} e^{-\frac{t_1}{\tau_m}} - e^{-\frac{t_2}{\tau_m}}\right) e^{\left(\frac{z}{\beta}\right)^2} dz
\]

where: 
\[z = \ln \left(\frac{\tau}{\tau_m}\right) I_{pi}\] – the intensity of \(i\)th process at temperature \(T_{pi}\), \(T\) - temperature, \(t_1 = 2s, t_2 = 120s\)

From the analysis of the isochronal disaccommodation curves we have found that the average activation energies of elementary processes range from 0.9 to 1.44 eV and pre-exponential factors in Arrhenius law are about 10^{-15} s. These data indicate \[2\] that disaccommodation phenomenon in this alloy is connected with ordering of atom pairs near the free volumes. After annealing of the samples at 850 K for 0.5 h the drastic decrease of the disaccommodation intensity in the temperature range from 120 K up to 325 K is observed. It is due to the annealing out of the free volumes in the amorphous matrix during heat treatment of the samples. The enhancement of disaccommodation intensity takes place at higher temperature. It is because of the transition of amorphous matrix from ferromagnetic to paramagnetic state. The contribution of the crystalline \(\alpha\)-FeCo phase to the disaccommodation is not evident.

4. Conclusions

- The bulk Fe_{61}Co_{10}Hf_{2.5}Zr_{2.5}Ti_{2}W_{2}B_{20} alloy in the as-quenched state is fully amorphous.
- \(\alpha\)-FeCo phase in partially crystallized samples exhibits long range order of atoms.
- The as-quenched amorphous samples show broad disaccommodation spectra. The intensity of disaccommodation strongly depends on the shape of the sample.
- After annealing the sample at 850 K for 0.5 h in the wide temperature range only almost temperature independent background in disaccommodation curves is observed.

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