Microstructure and magnetic behaviour of bulk amorphous 
\((\text{Fe}_{61}\text{Co}_{10}\text{Zr}_{2.5}\text{Hf}_{2.5}\text{W}_{2}\text{Ti}_{2}\text{B}_{20})_{100-x}\text{Y}_{x} ~ (x = 0 \text{ or } 2)\) alloys

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\textbf{Abstract.} Microstructure and some magnetic properties of the bulk amorphous \((\text{Fe}_{61}\text{Co}_{10}\text{Zr}_{2.5}\text{Hf}_{2.5}\text{W}_{2}\text{Ti}_{2}\text{B}_{20})_{100-x}\text{Y}_{x} ~ (x = 0 \text{ or } 2)\) alloys are studied. Addition of 2 at. % of Y to the \text{Fe}_{61}\text{Co}_{10}\text{Zr}_{2.5}\text{Hf}_{2.5}\text{W}_{2}\text{Ti}_{2}\text{B}_{20} alloy leads to the decrease of the Curie temperature from 520 K to 438 K. Investigated alloys are magnetically soft although the Y addition gives rise to the magnetic hardening; the coercive field increases from 71 A/m for \(x=0\) to 87.6 A/m for \(x=2\). Approach to the magnetic saturation is governed by point-like or linear defects in the tube-shaped samples, and by linear defects in the rod-shaped samples.

1. \textbf{Introduction}

Bulk amorphous alloys are a new group of materials exhibiting many interesting properties from both scientific and technological point of view. Bulk amorphous materials are usually multicomponent systems and consist of more than three elements [1]. In these systems the short range interactions between atoms are more energetically favourable than long range and periodic ones characteristic of crystalline systems. Moreover, basic component of these bulk amorphous alloys should have negative heat of mixing which leads to the increase of the viscosity of the molten alloy [2]. The large viscosity hinders the atom rearrangements and crystal nucleation during the sample preparation. Additionally, it has been stated that the difference of the atomic radii of the main chosen components should be more than 12 % [1]. The fulfillment of the above rules enables to obtain amorphous materials at the quenching rate much lower than in the case of classical amorphous thin ribbons. The low quenching rate during fabrication of the bulk amorphous alloys makes the structure be more relaxed. The free volumes have the possibility to migrate and create larger agglomeration of defects. In ferromagnetic materials these defects, due to magnetoelastic coupling, influence the distribution of magnetic moments and can be studied by measurements of the magnetization at high magnetic field [3].

The purpose of this paper is to study the microstructure and approach to ferromagnetic saturation in bulk amorphous \((\text{Fe}_{61}\text{Co}_{10}\text{Zr}_{2.5}\text{Hf}_{2.5}\text{W}_{2}\text{Ti}_{2}\text{B}_{20})_{100-x}\text{Y}_{x} ~ (x = 0 \text{ or } 2)\) alloys.

2. \textbf{Experimental procedure}

The ingots of the \((\text{Fe}_{61}\text{Co}_{10}\text{Zr}_{2.5}\text{Hf}_{2.5}\text{W}_{2}\text{Ti}_{2}\text{B}_{20})_{100-x}\text{Y}_{x} ~ (x = 0 \text{ or } 2)\) alloys were obtained by arc melting in a protective argon atmosphere. Subsequently, the bulk amorphous alloys in the form of rods and tubes were prepared by suction – casting method [4, 5]. The rods were 2 cm long and 1 mm in diameter. Tubes were 2 cm long, 3 and 4 mm in inner and outer diameter, respectively. The structure
of the as–quenched, powdered samples was investigated using X–ray diffraction and Mössbauer spectroscopy. The crystallization temperature of the as – quenched alloys was determined from DSC and thermomagnetic curves recorded at the heating rate of 10 K/min. From the thermomagnetic curves, obtained by a force magnetometer, the Curie temperature was also found. Using vibrating sample magnetometer (VSM) the approach to ferromagnetic saturation was studied.

3. Results and discussion

In Fig.1 the X–ray diffraction patterns for the as–quenched samples of the \((\text{Fe}_{61}\text{Co}_{10}\text{Zr}_{2.5}\text{Hf}_{2.5}\text{W}_{2}\text{Ti}_{2}\text{B}_{20})_{100-x}\text{Y}_{x}\) (x = 0 or 2) alloys in the form of rods are shown. As can be seen, the diffraction patterns exhibit only broad single maxima which are characteristic of amorphous materials. No peaks ascribed to the crystalline phase are observed, so the samples are fully amorphous.

![Fig. 1. X–ray diffraction patterns for the as–quenched bulk amorphous \((\text{Fe}_{61}\text{Co}_{10}\text{Zr}_{2.5}\text{Hf}_{2.5}\text{W}_{2}\text{Ti}_{2}\text{B}_{20})_{100-x}\text{Y}_{x}\) alloys in the form of rods: x = 0 (a), x = 2 (b)](image)

The amorphicity of the samples is also confirmed by Mössbauer spectroscopy. In Fig. 2 the transmission Mössbauer spectra and corresponding hyperfine field distribution are depicted. The Mössbauer spectra with broad and overlapping spectral lines are typical of the amorphous state. The hyperfine magnetic field distribution for the sample not containing yttrium (x = 0) shows at least two maxima at \(B_{hf}\) of 3 T and 18 T (Fig. 2. a and b). These maxima can be attributed to the regions which differ distinctly in iron concentration. Addition of some yttrium atoms to the alloy probably causes much more homogeneous structure because the hyperfine magnetic field distribution does not reveal the maximum at low hyperfine induction (Fig. 2. c, d).

The thermomorphic curves \(\mu_0 M_s(T)\) for the samples in the form of tubes are shown in Fig. 3. As can be seen, the magnetic polarization of saturation, \(\mu_0 M_s\), decreases monotonically with temperature but it does not take the zero value even at high temperature due to inhomogeneity of the material leading to the Curie temperature, \(T_C\), distribution. Further increase of temperature causes the enhancement of \(\mu_0 M_s\) because of the crystallization. In this way the crystallization temperature equal to 870 K is found. The same investigations performed for the rod – shaped sample reveal the crystallization temperature of 850 K. Similar results are observed from DSC curves. The quenching rate during rods preparation is lower than in the case of tubes. In this way more quenched – in nuclei in the rod sample are created and for grain growth lower activation energy is needed and thus the crystallization takes place at lower temperature. In spite of the Curie temperature distribution in amorphous materials its average value can be evaluated from the critical behavior of the magnetization near the transition region [6]:

\[
\mu_0 M_s(T) = \mu_0 M_s(0) \left(1 - \frac{T}{T_C}\right)^\beta
\]  

(1)
where $\mu_0 M_s(0)$ is the magnetic polarization saturation at 0 K and $\beta = 0.36$ is the critical exponent for the Heisenberg ferromagnet.

Fig. 2. The transmission Mössbauer spectra (a, c) and hyperfine magnetic field at $^{57}$Fe nuclei distributions (b, d) for the powdered rods of the bulk amorphous (Fe$_{61}$Co$_{10}$Zr$_{2.5}$Hf$_{2.5}$W$_2$Ti$_2$B$_{20}$)$_{100-x}$Y$_x$ alloys: $x = 0$ (a, b) and $x = 2$ (c, d).

Fig. 3. The thermomagnetic curves for the bulk amorphous (Fe$_{61}$Co$_{10}$Zr$_{2.5}$Hf$_{2.5}$W$_2$Ti$_2$B$_{20}$)$_{100-x}$Y$_x$ alloys in the form of tubes: $x = 0$ (a) and $x = 2$ (b).
In Fig. 4 the linear dependence of $[\mu_0 M_s(T)]^{1/\beta}$ on temperature is depicted for alloys with and without yttrium in tube–shaped samples. The average Curie temperature of the Fe$_{61}$Co$_{10}$Zr$_{2.5}$Hf$_{2.5}$W$_2$Ti$_2$B$_{20}$ alloy is equal to 520 K. Addition of 2 at. % of yttrium to this alloy lowers the Curie temperature to 438 K. The same $T_C$ values are obtained for the samples in the form of rods. It is worth noticing from Figs 3 and 4 that the Curie temperatures are well below the crystallization ones.

The relative magnetization curves versus the induction of the effective magnetizing field for the samples (Fe$_{61}$Co$_{10}$Zr$_{2.5}$Hf$_{2.5}$W$_2$Ti$_2$B$_{20}$)$_{100-x}$Y$_x$ in the form of tubes are presented in Fig.5. One can see that the samples containing Y is a little bit magnetically harder (higher magnetic anisotropy) and exhibits the higher magnetization near the ferromagnetic saturation. Also the coercive field, $H_C$, measurements confirm the magnetic hardening of this material. $H_C$ equals to 71 A/m and 87.6 A/m for the tube-shaped samples of the Fe$_{61}$Co$_{10}$Zr$_{2.5}$Hf$_{2.5}$W$_2$Ti$_2$B$_{20}$ and (Fe$_{61}$Co$_{10}$Zr$_{2.5}$Hf$_{2.5}$W$_2$Ti$_2$B$_{20}$)$_{98}$Y$_2$ alloys, respectively. Despite of the increase of the effective magnetic field the magnetization saturation is not reached because of the distribution of the magnetic moment, resulting from magnetoelastic coupling in the vicinity of structural defects and the excitation of spin waves [7]. Approach to magnetic saturation is a convenient way for the indirect structural defects investigation. The magnetic polarization at high magnetic field can be described by the relation:

$$\mu_0 M(H) = \mu_0 M_s \left(1 - \sum_i \frac{a_i}{(\mu_0 H)^{1/\beta}}\right) + b(\mu_0 H)^{1/\beta} \tag{2}$$

where $\mu_0 M_s$ is the magnetic saturation polarization, terms $\frac{a_i}{(\mu_0 H)^{1/\beta}}$ are connected with different kind of defects; $i = \frac{1}{2}$ for point like defects, $i = 1$ and 2 for linear defects called quasidislocation dipoles, the last term is ascribed to the Holstein–Primakoff paraprocess[8]. In Fig. 6 the magnetization curves for the bulk amorphous (Fe$_{61}$Co$_{10}$Zr$_{2.5}$Hf$_{2.5}$W$_2$Ti$_2$B$_{20}$)$_{98}$Y$_2$ alloy in the form of a tube and rod are depicted. In
The relative magnetization polarization, $M/M_S$, versus the induction of the effective magnetic field of the bulk amorphous (Fe$_{61}$Co$_{10}$Zr$_{2.5}$Hf$_{2.5}$W$_2$Ti$_2$B$_{20}$)$_{100-x}$Y$_x$ alloy: (a) $x = 0$, (b) $x = 2$.

In the magnetizing field range $0.094 – 0.136$ T the relative magnetization scales with $1/\sqrt{\mu_0 H}$ and at higher field up to $0.54$ T the linear relation $\frac{M}{M_S} \left( \frac{1}{\mu_0 H} \right)$ is observed for the sample in the form of tube. Whereas in the case of amorphous rod the relative magnetization depends linearly on $1/(\mu_0 H)$ in the field range from $0.07$ to $0.46$ T. The presence of the linear relation $\frac{M}{M_S} \left( \frac{1}{\sqrt{\mu_0 H}} \right)$ in the field range $0.094 – 0.136$ T (Fig. 6a) indicates that in this range the magnetization process takes place mainly by the rotation of magnetic moments in the vicinity of point–like defects [3,7]. However, at higher magnetic field range (up to $0.54$ T) the rotation near the linear defects seems to be decisive (Fig. 6b). In the case of amorphous rods (Fig. 6c) in the comparable magnetizing field range linear defects play a dominant role. The observed effect can be attributed to the different type of defects created during rapid solidification. In the case of tubes the quenching rate is higher than for rods. During tube preparation of the tube the structure relaxations are hindered. Point–like defects have only limited possibility to agglomerate giving larger linear defects as a result. In rod preparation the migration of point like defects is not suppressed and the creation of large quasi – dislocation dipoles takes place. This explains the dependence of magnetization versus the effective magnetizing field. At higher magnetizing field Holstein–Primakoff paraprocess is observed (Fig. 6d). The similar effect also occurs for the alloy not containing yttrium.

4. Conclusions

- The addition of 2 at. % of yttrium to the bulk amorphous Fe$_{61}$Co$_{10}$Zr$_{2.5}$Hf$_{2.5}$W$_2$Ti$_2$B$_{20}$ alloy enables to obtain more homogeneous structure.
- The investigated alloys are magnetically soft, although yttrium causes magnetic hardening.
- Quenching rate during the preparation of the samples distinctly influences the magnetizing process at high magnetic field.
Fig. 6. The relative magnetization $M/M_S$ versus different range of the magnetizing field at room temperature for the bulk amorphous $(Fe_{61}Co_{10}Zr_{2.5}Hf_{2.5}W_{2}Ti_{2}B_{20})_{98}Y_{2}$ alloy in the form of the tube (a-b) and rod (c), Holstein-Primakoff paraprocess (d)

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