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Crystallization Kinetics and Magnetic Properties of $Fe_{80-x}Co_xP_{14}B_6$ Metallic Glasses

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We report about formation mechanism, crystallization kinetics and magnetic properties observed in the series of rapidly solidified $Fe_{80-x}Co_xP_{14}B_6$ metallic glasses with x = 25, 32, 35 and 40 at.%. Magnetic soft $Fe_{80-x}Co_xP_{14}B_6$ metallic glasses have 15–25 µm thick and 2–8 mm wide. The ribbon samples were created to meltspun onto the massive copper wheel from the RF-melted superheated master ingots..

Keywords: meltspun ribbons, eutectic crystallization, phase analysis, magnetosoft properties.
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Introduction

The investigation and application metallic glasses are important and advanced problem for modern science, because metallic glasses have anisotropy as compared to crystal metal. The amorphous structure composition allows improving some the physical property, when a variation of stoichiometry determines limits to applicability of metallic glasses. Today a industry apply metal glass on based $Fe - Ni - P - B$, but replacement Ni to Co [1–3] lead to increased thermostability.

1. Experimental

The metallic glasses on based $Fe - Co - P - B$ were created melt spun on fast-running disk of copper. Initially the preform with known stoichiometry parameters heated to temperatures greater the temperature of melting on 100 degrees (melting temperature is 1313 K), and then the liquid melt was press out on surface of disc by argon pressure through of nozzle ampoule. The growth of crystals was smaller due to the presence of P and B. And thus the metallic ribbons on based $Fe - Co - P - B$ had amorphous state.

The metallic glasses have a glossy surface, width is few millimeters and thickness is 15–25 μm. Except but the surface has grooves (they are distinguishable under a microscope). The grooves were born, because liquid melt interacted with surface of disc.

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The crystallization kinetics was studied the differential scanning calorimetry (DSC) and x-ray diffraction. DSC was conduct on hardware and software system *Hitachi STA* 7300. This complex is carried out thermogravimetric analysis to measure the crystallization temperature and the generated heat. X-ray diffraction was conduct in CuK_α and MoK_α radiations. The investigation of magnetic properties was produced in dynamic regime on difference frequency and maximum magnetic force value.

2. Results and discussion

X-ray diffraction pattern was record in CuK_α reflection and MoK_α transmission radiations. The x-ray pattern of as-cast ribbons was diffusely so it is characteristic for scattering noncrystalline object (red line in Fig. 1). The characteristic size of regions coherently scattering X-rays is small as 1.6 nm.

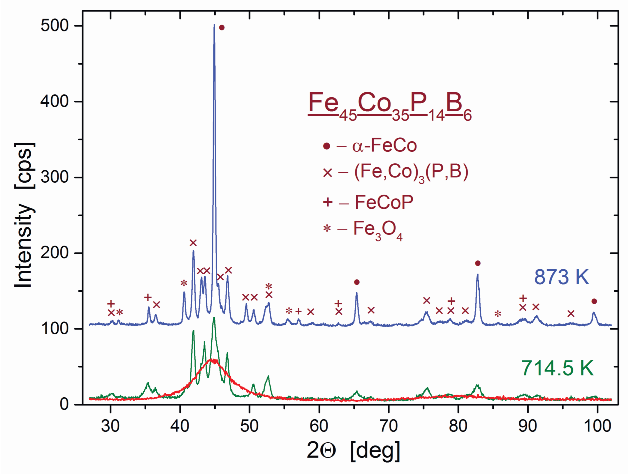

Fig. 1. XRD pattern of Fe45Co35P14B6 ribbon in as-cast (red line) condition and after annealing at 714.5 and 873 K

Finbak-Warren atomic pair distribution function (PDF) phase analysis revealed superposition of two main *bcc* $\alpha - FeCo$ and *bct* $(Fe, Co)_3(P, B)$ phases. Theoretical PDF for $(Fe, Co)_3(P, B)$ phase matches much better a fine structure of the second coordination sphere.

The temperature of crystallization and the generated heat were detected with help **DSC**. The estimation of crystallization temperature allows evaluating the industrial range of application metallic glasses on based $Fe - Co - P - B$ in the form of functional material for magnetic screens and sensors feeble magnetic field.

The Fig. 2 show differential scanning calorimetry thermogram for $Fe_{48}Co_{32}P_{14}B_6$. As you can see by with decreasing the heating rate is decreased the values of crystallization temperature. This connected with different the heating rates of volumes of study samples.

The temperature of crystallization was detected as maximum value on differential scanning calorimetry thermogram (Fig. 2). Whereas crystallization temperature T_x depends on the heating rate α and follows Kissinger law governed by a modified Kolmogorov-Johnson-Mehl-Avrami (KJMA) theory:

$$\ln\left(\frac{T_x^2}{\alpha}\right) = \frac{Q}{T_x} + \ln\left\{\tau_0 Q \left[2f(T_x)F^{-3}(T_x)\right]^{-1/4}\right\}. \quad (1)$$

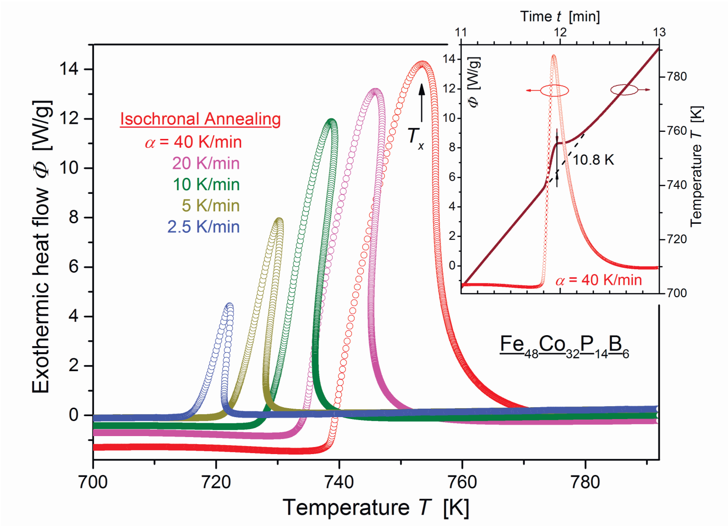

Fig. 2. Differential scanning calorimetry traces for the $Fe_{48}Co_{32}P_{14}B_6$ ribbons heated at five different heating rates α = 2.5, 5, 10, 20 and 40 K/min

Activation energy Q and crystal/glass interfacial energy σ were obtained as fitting parameters (Tab. 1).

Table 1

Specimen	T_x for 40 K/min, K	Q, K	σ, J/m^2
$Fe_{40}Co_{40}P_{14}B_6$	749.6	41021	0.230
$Fe_{45}Co_{35}P_{14}B_6$	754.5	46431	0.239
$Fe_{48}Co_{32}P_{14}B_6$	753.5	46651	0.239
$Fe_{55}Co_{25}P_{14}B_6$	758.9	51846	0.248

The isothermal annealing — a heating under constancy the heat rates to assign temperature, which low of the temperature crystallization and kept there for a long time — allowed detecting living times of amorphous state the metallic glasses on based $Fe - Co - P - B$.

Isothermal annealing made it possible to detect the lifetime of the amorphous state of metallic glasses.

KJMA theory derived exponential temperature dependences of incubation time and the peak value of heat release $t_{inc}(T) = \tau exp\,(Q/T)$, $\Phi_{max}(T) \propto 1/t_{inc}(T)$ nicely accord the experimental data in Fig. 3. There activation energy Q exactly coincides with the one obtained at the process of isochronal annealing.

Comparing XRD spectra recorded for isochronal and isothermal heating regimes we arrived to rather unexpected conclusion. Isothermal annealing always results in the formation of nano-sized nuclei within the amorphous metallic matrix, whereas rapid isochronal heating to high temperatures leads to the formation of crystallites much bigger in size. This conclusion holds even more since isothermally annealed specimens remain in the cooling oven for much longer than incubation time.

For purpose of technology and applications important to conduct calculate by temperature 400 K and 500 K. The relaxation to the crystallization state less than 400 K happens through $\sim 10^{19}$ years, 500 K $\sim 10^9$ years.

The investigation of **magnetic properties** was produced in dynamic regime by change frequency $f = 20 \div 610\ Hz$ and $210 \div 1010\ Hz$ and maximum magnetic force $H_{max} = 100\ A/m$

and 1500 A/m (Fig. 4). The hysteresis $M - H$ loops characterized by a rectangular view, small values the coercive force and relatively small hysteresis loss. This all indicate, that metallic glasses on based $Fe - Co - P - B$ is magnetic soft materials.

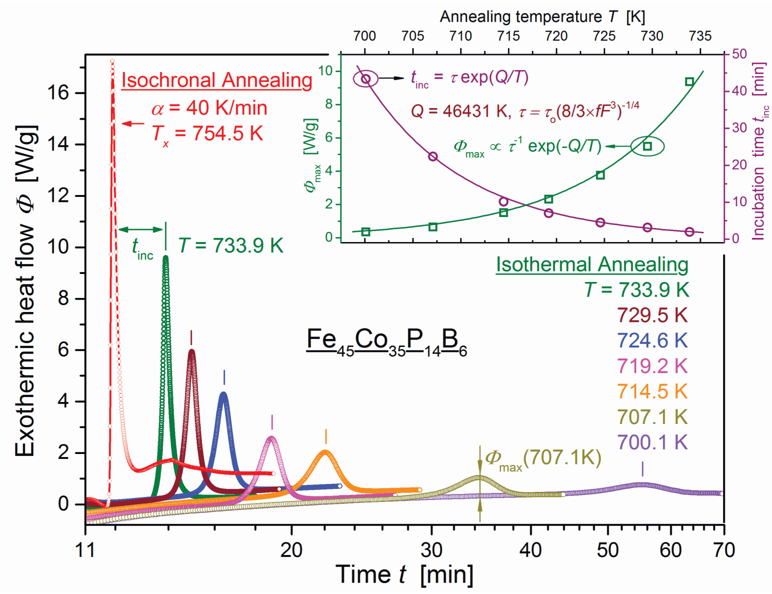

Fig. 3. Differential isothermal calorimetry (DIC) scans of $Fe_{45}Co_{35}P_{14}B_6$ ribbons annealed at seven different temperatures T below the crystallization temperature $T_x = 754.5$ K

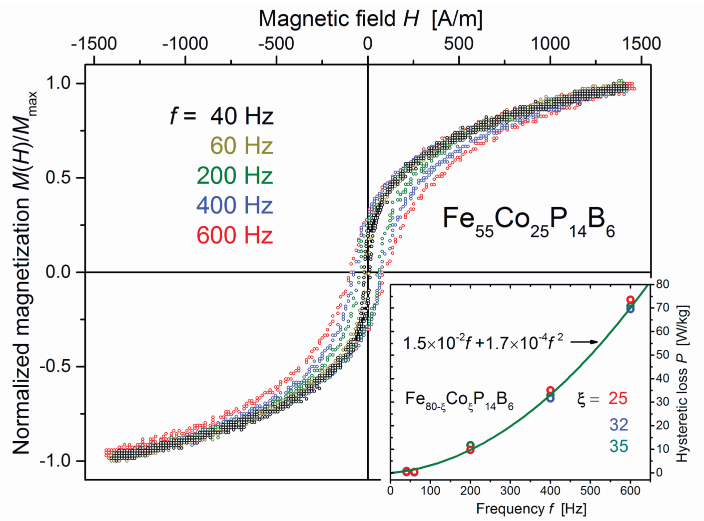

Fig. 4. Hysteresis $M - H$ loops of as-quenched $Fe_{55}Co_{25}P_{14}B_6$ ribbon recorded at different frequencies of sinusoidal exciting field. Inset shows frequency dependence of hysteresis loss

The values of a coercive force was identify from hysteresis $M - H$ loops subject to $M/M_{max} = 0$. For metallic glasses on based $Fe - Co - P - B$ usual with increase the frequency of the external field increases the coercive force. The coercive force growth comes the power function (inclusion of Fig. 4).

Hysteresis $M-H$ loops were recorded to differentiate magnetic hysteresis losses proportional to the first power of the frequency f and eddy-current power loss proportional to f^2. Hysteresis losses in saturated regime $P(f) = (f/d)\oint M(H)dH$ at 60 Hz were estimated to be 0.56 W/kg while the maximum differential permeability was found to be about 110000. Bias magnetic field dependence of incremental magnetic permeability was acquired from the slope of minor loops recorded in superimposed weak ac- and slowly swept dc-magnetic fields.

Also the basic magnetization curves were obtained (Fig. 5). The Fig. 5 shows that basic magnetization curves growing rapidly and view complies curve for ferromagnetic material. The fact characterized by magnetic soft materials.

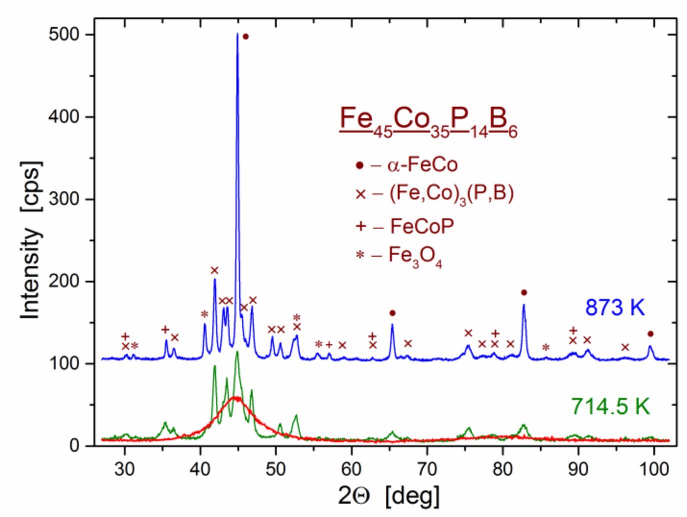

Fig. 5. The basic magnetization curves of melt-spun material on based $Fe-Co-P-B$

The basic magnetization curves can be divided into two areas:

1. The areas have the sharp increase the magnetization of a small change in the magnetic field. This area called site Barkhausen jumps [4]. The sharp increase observable before a value magnetic field 650 A/m.

2. The areas have the stickle increase the magnetization of a small change in the magnetic field. As the case stands magnetization is due to the rotation vectors M_s processes in the direction of the external field [5].

The Fig. 5 show that magnetization curves do not cross in area of saturation, because vector M_s orientation effects are present.

The investigation of **Curie temperature** carried out on *Hitachi STA* 7300, which was fit up constant magnet. We made isochronal annealing in constant magnetic field. During phase transition of the second order was change first weight derivative on 730 K (Fig. 6 red line).

For metallic glasses on based $Fe-Co-P-B$ a difference between the temperature crystallization and Curie temperature is small value. It means than metallic glasses on based $Fe-Co-P-B$ is not impossible annealing in paramagnetic state. Interested that, the magnetic state is changed with the condition structure modification. The phase transition of the first and second order was close together, because we conducted isothermal annealing with a constant magnetic field for better visibility of the metallic glasses condition change (Fig. 7). We observed that crystallization impacted on change a magnetization state, as so as during isothermal annealing the change magnetic and structure state was one by 718 K.

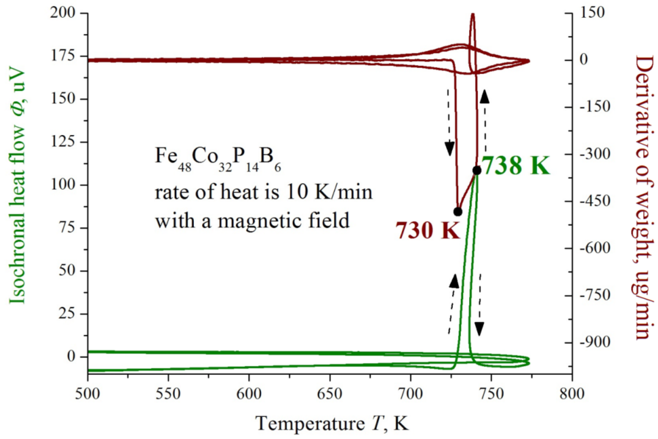

Fig. 6. The curves heat flow (green line) and derivative of weight (red line) *vs.* temperature for as-cast $Fe_{48}Co_{32}P_{14}B_6$, a regime of annealing is isochronal

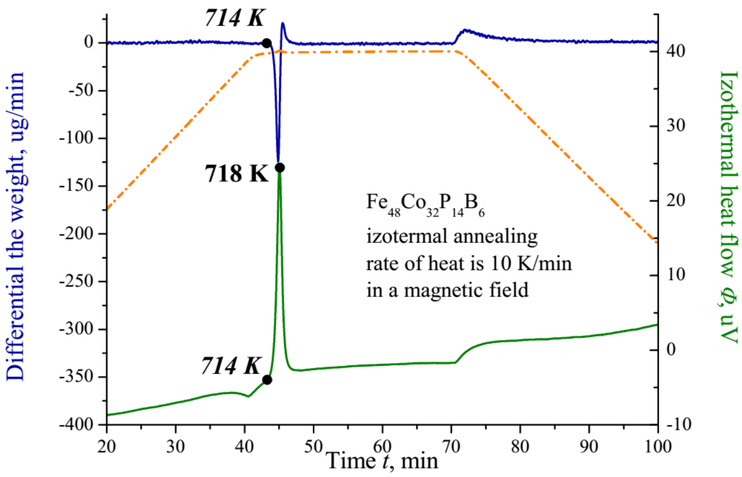

Fig. 7. The curves heat flow (green line) and derivative of weight (blue line) *vs.* time of annealing for as-cast $Fe_{48}Co_{32}P_{14}B_6$, a regime of annealing is isothermal. Yellow line is a temperature *vs.* time of annealing

The Tab. 2 shows values the temperature crystallization and Curie temperature in constancy magnetic field for three different samples of metallic glasses on bases $Fe - Co - P - B$, the rate of heat is 10 K/min.

Table 2

Sample	The temperature of crystallization T_{max}, K	The Curie temperature T_C, K
$Fe_{45}Co_{35}P_{14}B_6$	741	731
$Fe_{48}Co_{32}P_{14}B_6$	738	730
$Fe_{55}Co_{25}P_{14}B_6$	745	703

Conclusions

In summary, we created metallic glasses on based bases $Fe - Co - P - B$ melt-spun. The metallic ribbons have x-ray amorphous condition with the characteristic size of regions coherently scattering is 1.6 nm. The crystal kinetics was defined DSC. The annealing was conducted in two regimes: isothermal and isochronal. The interesting that a isothermal annealing always results in the formation of nano–sized nuclei within the amorphous metallic matrix, whereas rapid isochronal heating to high temperatures leads to the formation of crystallites much bigger in size. The isochronal regime of annealing has allowed to establishing a temperature of crystallization and the industrial range of application metallic glasses on based $Fe - Co - P - B$. The crystallization temperature of metallic glasses on based $Fe - Co - P - B$ has a value over than industrial samples. The investigation of magnetic properties shows that metallic glasses are not impossible annealing in paramagnetic state. The coercive force was detected, and it change with increase a frequency through a power function.

References

[1] M.Hollmark, V.I.Tkatch, A.Grishin, S.I.Khartsev, Processing and properties of soft magnetic $Fe_{40}Co_{40}P_{14}B_6$, amorphous alloys, *IEEE transaction of magnetics,* **37**(2001), 2278–2280.

[2] V.I.Tkatch, A.Grishin, S.I.Khartsev, Delayed nucleation in $Fe_{40}Co_{40}P_{14}B_6$ metallic glass, *Materials science and engineering*, **A337**(2002), 187–193.

[3] V.V.Popov, V.I.Tkatch, S.G.Rassolov, A.S.Aronin, Effect of replacement of Ni by Co on thermal stability of $Fe_{40}Co_{40}P_{14}B_6$ metallic glass, *Journal of Non-Crystalline Solids*, **356**(2010), 1344—1348.

[4] H.Barkhausen, Zwei mit Hilfe der neuen Verstarker entdeckte Erscheinunften, hysische Zeitschrift, 1919.

[5] A.A.Preobrazhensky, E.G.Bishard, Magnetic materials and elements, Moscow, 1986.

Кинетика кристаллизации и магнитные свойства металлических стекол $Fe_{80-x}Co_xP_{14}B_6$

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В настоящей работе показаны основы механизма кинетики кристаллизации быстрозакаленных металлических стекол на основе $Fe_{80-x}Co_xP_{14}B_6$ при x = 25, 32, 35 и 40 at.%. В ходе работы была получены магнитомягкие металлические стекла медотом быстрой закалки на диске из жидкого состояния. Полученные ленты обладают толщиной порядка 15–25 μm и шириной около 2–8 mm.

Ключевые слова: быстрозакаленные ленты, эвтетическая кристаллизация, фазовый анализ, магнитомягкие свойства.