Melt-spun Fe-Co-P-B metglas: structure, crystallization kinetics, magnetic properties

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Abstract. Crystallization kinetics and magnetic properties were studied in series of rapidly solidified metallic glasses Fe\(_{80-\xi}\)Co\(_\xi\)P\(_{14}\)B\(_6\) with \(\xi = 25, 32, 35\) and 40 at. %. Differential scanning calorimetry (DSC) was employed to determine crystallization temperature and to demonstrate the incubation phenomenon at isothermal annealing. Fitting DSC traces recorded in non-isothermal and isothermal regimes, we obtained the same activation energy \(Q\). It describes atomic transfer across crystal/amorphous interface in Kolmogorov-Johnson-Mehl-Avrami (KJMA) model of the transition of metallic glasses into crystalline state. As-quenched metglas ribbons have amorphous structure and superior soft magnetic properties: coercive field 4 A/m, ac magnetic permeability as high as 110 000 at 60 Hz.

1. Introduction

Unique combination of functional properties as high saturation magnetization, permeability and magnetostriction, low coercive field and high mechanical strength and corrosion resistance makes metallic glasses to be indispensable material for magnetic screens and high frequency transformer cores, magnetic field, tensile and angular position sensors. Although a lot of new filmy and bulk metallic glasses were discovered recently, magnetosoft Fe-, Ni, and Co-based amorphous alloys remain to be the reference materials to engineer preassigned nanocrystalline structure and to explore its relation to magnetic properties. Early it was shown that the replacement of Ni by Co in the well-known Fe\(_{40}\)Ni\(_{40}\)P\(_{14}\)B\(_6\) composition raises significantly a thermal stability of metglas [1, 2]. In this paper we investigate how Fe-to-Co concentration ratio defines properties of as-quenched and crystallized Fe\(_{80-\xi}\)Co\(_\xi\)P\(_{14}\)B\(_6\) alloys.

2. Experimental

Preparation technique of 20-30 \(\mu\)m thick metallic Fe-Co-P-B glass ribbons by a single roller melt spinning process has been described in details elsewhere [1]. They were annealed in protective Ar atmosphere with different heating rates \(\alpha = 2.5, 5, 10, 20\) and 40 K/min using Hitachi STA7300 simultaneous thermal analyzer. Crystalline structure of as-spun and annealed ribbons was examined by X-ray diffraction in Cu\(K_\alpha\) and Mo\(K_\alpha\) radiations. Magnetic hysteresis loops were recorded with \(M-H\) tracer in magnetic field up to 100 A/m in the frequency range from 20 to 600 Hz.

3. Results and discussion

3.1 Thermal Stability. Differential scanning calorimetric study was performed to determine the temperature range of practical use of fabricated metallic glasses. Annealing process was carried out in two regimes: steady (isochronal) heating with a constant rate \(\alpha = 2.5, 5, 10, 20\) and 40 K/min and
isothermally – fast heating with a rate of 40 K/min to a predetermined temperature $T$ and expose specimen at reached temperature for prolonged time.

Sharp exothermic peaks appear at DSC traces for all the samples (see figure 1). As shown in figure 2, at isochronal annealing, peak’s temperature $T_{\text{max}}$ is higher for specimens with a higher Fe content.

![Figure 1. DSC traces for as-spun Fe$_{48}$Co$_{32}$P$_{14}$B$_{6}$ ribbons annealed at different heating rates $\alpha$.](image)

![Figure 2. Dependence of the position of crystallization peak $T_{\text{max}}$ on heating rate $\alpha$ for three different metallic glasses.](image)

The activation energy $Q$ of metglas crystallization process was determined in Kolmogorov-Johnson-Mehl-Avrami (KJMA [3]) model (figure 3). $Q$ was found to be 46430 K, 46650 K, and 51850 K for Fe$_{45}$Co$_{35}$P$_{14}$B$_{6}$, Fe$_{48}$Co$_{32}$P$_{14}$B$_{6}$, and Fe$_{55}$Co$_{25}$P$_{14}$B$_{6}$ alloy, respectively.
Figure 3. Kissinger [4] plots of crystallization peak temperature $T_{\text{max}}$ at different heating rates for three metallic Fe-Co-P-B glasses.

At isothermal annealing DSC traces in figure 4 reveal the incubatory effect. Ribbon with the nominal composition Fe$_{45}$Co$_{35}$P$_{14}$B$_{6}$ was fast heated up with a rate of 40 K/min to the preassigned temperature and kept there for a long time. At isochronal annealing with $\alpha = 40$ K/min, crystallization peak appears at $T_{\text{max}} = 754.7$ K. Isothermal annealing performed at lower temperatures $T$: 700.1, 707.7, 714.5, 719.2, 724.6, 729.5, and 733.9 K leads to the retardation of the appearance of the exothermic peak.

The incubatory effect is a time delay $t_{\text{inc}}$ between the appearance of exothermic peak during isochronal and isothermal annealing processes. As shown in inset to figure 4, experimental temperature dependence of incubation time $t_{\text{inc}}(T)$ strictly follows exponential curve calculated within KJMA model. Fitting parameters $Q$ appear to be the same both in isochronal and isothermal heating regimes of crystallization for all three samples under study.

Figure 4. DSC traces of isothermal annealing of as-spun Fe$_{45}$Co$_{35}$P$_{14}$B$_{6}$ amorphous alloy.

3.2 The structure. Figure 5 (a) shows X-ray diffraction pattern of as-spun Fe$_{55}$Co$_{25}$P$_{14}$B$_{6}$ ribbon recorded in MoK$_\alpha$ radiation. Scattering factors as well as ionic radii of Fe and Co atoms are very close, thus XRD patterns of ribbons with different Fe-to-Co concentration ratio look similar to each other.
As-quenched ribbons are X-ray amorphous. Very broad peaks around $2\Theta = 20^\circ$, $34^\circ$, $52^\circ$ and one shoulder at $41^\circ$ might be relied upon, respectively, to (110), (211), (220), and (222) diffraction reflections of $\alpha$-FeCo bcc phase. To carry out phase analysis we employed C. Finbak - B.E. Warren method of atomic pair distribution function $D(r)$ (PDF). From XRD pattern in figure 5 (a) we calculated experimental $D(r)$ and compared this PDF with theoretical $D(r)$ functions we built for $\alpha$-FeCo and $(\text{Fe, Co})_3(P, B)$ crystalline structures. $D(r)$ for $(\text{Fe, Co})_3(P, B)$ gives much better correspondence to the experiment. Therefore, $(\text{Fe, Co})_3(P, B)$ we consider as nuclei of an extant parent phase in amorphous matrix.

After annealing, a lot of new Bragg reflections appear in CuK$_\alpha$ XRD spectrum in figure 5 (b). This pattern is a superposition of bcc $\alpha$-FeCo (ICSD-56273) and bct (body-centered tetragonal) $(\text{Fe, Co})_3(P, B)$ phases. Percent composition of crystallized phases was determined using Rietveld refinement method [5]. To describe $(\text{Fe, Co})_3(P, B)$ structure we assumed isomorphic Co substitution of Ni atoms in Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$ (ICSD-614312) compound. It was proven that during the isochronal annealing up to 873 K percentage of $(\text{Fe, Co})_3(P, B)$ phase rapidly increases for Fe-rich metallic glasses at the expense of $\alpha$-FeCo phase.

![Figure 5. X-ray diffraction patterns of Fe$_{55}$Co$_{25}$P$_{14}$B$_6$ ribbon in MoK$_\alpha$ and CuK$_\alpha$ radiations. (a) – as-spun specimen, (b) – ribbon isothermally annealed at $\alpha = 40$ K/min. XRD spectrum shows a mixture of $\alpha$-FeCo (marked with circular symbols) and $(\text{Fe, Co})_3(P, B)$ phases.](image-url)

3.3 Magnetic properties. Figure 6 presents an example of hysteresis $M$–$H$ loops recorded at 20 Hz for as-quenched Fe$_{55}$Co$_{25}$P$_{14}$B$_6$ and Fe$_{55}$Co$_{25}$P$_{14}$B$_6$ glassy ribbons. The coercive force $H_c$ was found to be 8-10 A/m. Hysteresis losses grow with a frequency of ac-signal. It is clearly shown in Figure 7 from the frequency dependence of coercive force. Differential permeability calculated as a derivative $dM/dH$ of magnetization curve $M(H)$ at $H = H_c$ appears to be higher than 110 000 at 60 Hz.
Figure 6. Hysteresis $M–H$ loops of the as-quenched Fe$_{45}$Co$_{35}$P$_{14}$B$_6$ and Fe$_{55}$Co$_{25}$P$_{14}$B$_6$ melt-spun glassy ribbons recorded at 20 Hz in magnetic field parallel to ribbons’ surface.

Figure 7. Frequency dependence of coercive force in as-quenched amorphous Fe-Co-P-B metallic glasses.

4. Conclusions

We studied crystallization kinetics during isothermal and non-isothermal heating of rapidly quenched melt-spun Fe-Co-P-B metallic glasses. Kolmogorov-Johnson-Mehl-Avrami model gives adequate description both of these processes. Crystallization temperature is higher in Fe-rich metallic glasses indicating their higher thermal stability. Activation energy $Q$ appeared to have the same value to nicely fit crystallization at fast isochronal annealing and incubation effect at long isothermal heating.

Acknowledgements

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