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Magnetic softening of bulk amorphous FeCrMoGaPCB rods by current annealing technique

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Abstract

Glassy rods of the $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ alloy were prepared by copper-mold casting technique under argon atmosphere with diameters of 1.5 and 1.8 mm. As-quenched and dc current annealed (CA) samples were examined by thermal analysis (DSC), X-ray diffraction (XRD), thermomagnetic and magnetic measurements. The appearance of a wide supercooled liquid region $\Delta T_x \cong 60$ K and high reduced glass transition temperature $T_{rg} \cong 0.57$ indicated enhanced thermal stability against crystallization. Electrical resistivity ($\rho \cong 210$–$220\ \mu\Omega$ cm), coercive field ($H_C \cong 3$–10 A/m), saturation polarization ($J_S \cong 83$ emu/g) and Curie temperature ($T_C \cong 448$–460 K) were determined in the as-cast "XRD-amorphous" state. Maximum improvement in coercivity of about 30% was observed after applying a heating power per square area of $P_S \cong 4.4$ and 3.7 W/cm^2 for 1.5 and 1.8 mm rods diameters, respectively. Coercivity behavior after CA treatments indicates the presence of a very small volume fraction of nanoscale crystalline inclusions that apparently hinder stress relief.

Keywords: Transition metal alloys; Amorphous materials; Casting; Current Annealing; X-ray diffraction; Thermal analysis; Magnetic measurements

1. Introduction

Iron-based soft magnetic alloys with high glass forming ability (GFA) have attracted attention due to the novel fundamentals in science of metastable alloys and high technological potential [1,2]. Inoue's empirical rules: (a) multicomponent alloy system with significant atomic size ratio of main constituent elements and (b) negative heat of mixing between most of constituent elements (Table 1) enable extremely difficult long-range diffusion and successfully frustrate process of crystallization.

Impressive progress has been made over the last few years in science and engineering of bulk metallic glasses (BMG) such as understanding their GFA [5,6]. Iron based Fe–Cr–Mo–Ga–P–C–B amorphous alloys exhibit large scale of bulk samples (glassy rods with a diameter of 4 mm by flux-melting/water quenching method [7] and discs with 10 mm outer diameter and thickness of 1 mm by copper mold casting [8]), as well as good soft magnetic properties [9]. In this system the nominal alloy composition $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ has the best thermal stability [10].

However, to our best knowledge, up to now there is no experimental evidence on improvement of BMG rods functional properties by appropriate current annealing (CA) treatments. Besides the benefits of energy and time saving due to relative short time treatment, Joule heating brings specific structural transformations that could not be attained by conventional (furnace) annealing [11,12]. CA is a thermo-magnetic treatment due to the simultaneously effects of self resistively heating and appearance of a magnetic field induced by the current flow [13,14]. These features of CA treatment make it attractive for the optimization of soft magnetic alloys microstructure. In this paper we report the influence of CA on structural and magnetic properties of $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ rods.

2. Experimental

Master alloys of multicomponent $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ were prepared by induction melting of Fe–B, Fe–C, Fe–Ga, Fe–P prealloys and Mo, Cr, Fe, and crystalline B pure elements. Mechanical alloying of Fe-powder with amorphous red P in vibrating mill followed by cold pressing and subsequent induction melting were used to prepare the Fe–P prealloy. Rods were prepared by copper-mold casting technique under argon atmosphere with diameters of 1.5 and 1.8 mm and length of 70 mm [8].

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Table 1
Mixing enthalpy values ΔH_{AB}^{mix} [kJ/mol] of binary subsystems [3,4*] calculated based on Midema's macroscopic model of (Fe,Cr,Mo)–(Ga)–(P-C-B) multicomponent systems

	Fe	Cr	Mo	Ga	P	C	B
Fe	X	−1	−2	−2	−39.5	0	−26
Cr		X	–	−1	−41*	0	−16*
Mo			X	+7*	−45*	0	−19*
Ga				X	–	–	+6
P					X	0	+0.5
C						X	0
B							X

Values marked with asterisk (*) are from Ref. 4.

Structural characterization was performed by X-ray diffraction (XRD) using Co Kα radiation (λ = 0.1789 nm). In order to achieve good resolution rods were crushed into small pieces and bonded into amorphous resin.

Thermal analysis was carried out using a Netzch DSC 404 under a flow of purified argon up to 1473 K at a heating rate of 20 K/min. Cooling to room temperature with a constant rate of 10 K/min was performed in order to follow thermal behaviour of solidification process.

Samples were CA using heating power per square area (P_S) up to 6 W/cm^2 for 60 s to get various stages of relaxation or crystallization. We use P_S as a CA parameter, which is proportional to the steady state annealing temperature, in order to minimize errors introduced by fluctuations of sample resistance and average sample diameter, for details see [15]. Electrical resistance of the rod samples was measured by a four-probe method using specially designed mechanical contacts.

The magnetic properties of the samples were investigated by: (a) hysteresis loops (using a quasi-static hysteresis loop tracer under a maximum field of 20 kA/m), (b) coercive force H_C (by Foerster Koerzimat with premagnetizing field pulses of 200 kA/m), (c) saturation polarization J_S (by a vibrating sample magnetometer (VSM) under a maximum dc magnetic field of 1500 kA/m) and (d) temperature dependence of polarization (by Faraday magnetometer in a field of 460 kA/m at a heating rate of 10 K/min).

3. Results and discussion

Fig. 1a shows constant-rate DSC traces of the both rods obtained at a heating rate of 20 K/min. The glass transition temperature T_g and the crystallization temperature T_x were determined as the onset temperatures of the supercooled liquid region (endothermic event) and crystallization (exothermic event), respectively. The liquidus temperature T_l was determined as the onset of solidification during cooling. The main characteristics temperatures estimated from the shown scans are $T_g = 754$ K, $T_x = 814$ K, and $T_l = 1330$ K, for the 1.5 mm rod and $T_g = 753$ K, $T_x = 812$ K, and $T_l = 1330$ K, for the 1.8 mm rod. The values of the temperature interval of the supercooled liquid region before crystallization $\Delta T_x = T_x - T_g$ of about 60 K, as well as values of the reduced glass transition temperature $T_{rg} = T_g/T_l$ of about 0.567 are characteristic of good GFA and high thermal stability against crystallization. The crystallization enthalpy of the 1.8 mm rod (98.8 J/g) is slightly higher than that of the 1.5 mm rod (95.8 J/g).

The XRD patterns of as-cast rod samples with 1.8 mm diameter are given on Fig. 2I. The patterns display a broad maximum around $2\theta \approx 51^\circ$ that is characteristic for an amorphous structure. However, for some of samples there are additional weak diffraction peaks superimposed to the amorphous halo. This reflects the formation of metastable crystalline phase coexisting with glassy matrix. Previous to the XRD experiments, the same samples were characterized by coercivity measurements. Completely "XRD-amorphous" samples exhibit a very low coercive force ($H_C \cong 3$–10 A/m). As the coercivity is very sensitive to residual stresses induced during the quenching as well as to crystalline inclusions, increase by one order of magnitude (up to 90 A/m) were noticed in samples with weak diffraction peaks (Fig. 2I). Similar results were obtained for as-cast rod samples with 1.5 mm diameter. This clearly demonstrates the highest importance of optimum technological parameters of the casting process during preparation of bulk form samples.

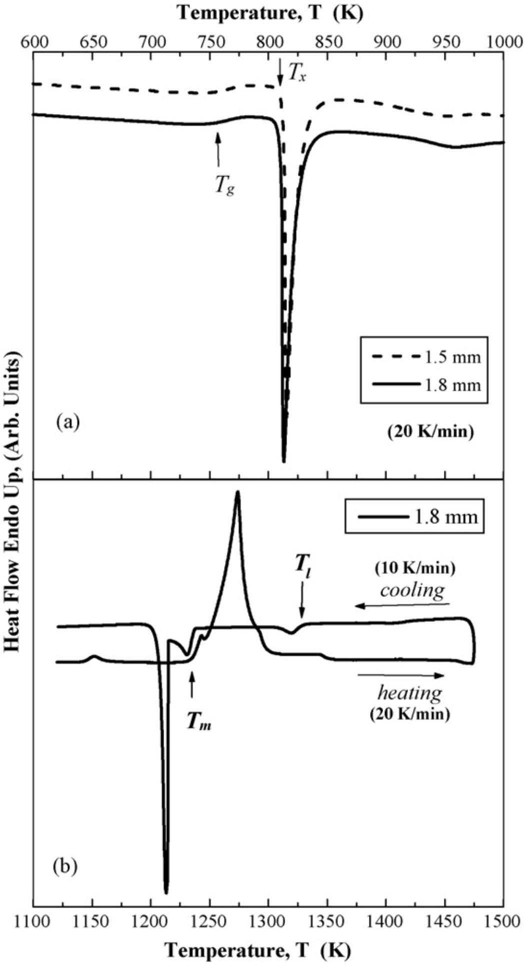

Fig. 1. DSC traces of $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ rods: (a) both rods obtained at a heating rate of 20 K/min, and (b) 1.8 mm diameter rod in the high temperature region showing the melting, overheating and subsequently cooling.

Structural and phase transformations of the rod samples were also examined by measuring the variation of saturation polarization J_S, as a function of temperature. Fig. 3 (curves a and b) shows that there is a peak at 809 K associated with the crystallization process already observed by the DSC as a single-step exothermal process. The determination of Curie temperature T_C was performed by $J_S^{1/\beta}(T)$ curves with the "critical" exponent for metallic ferromagnets $\beta = 0.36$ (for details see [16]). T_C increases from 448 to 460 K with the increase of rod diameter likely due to a more relaxed amorphous structure. However,

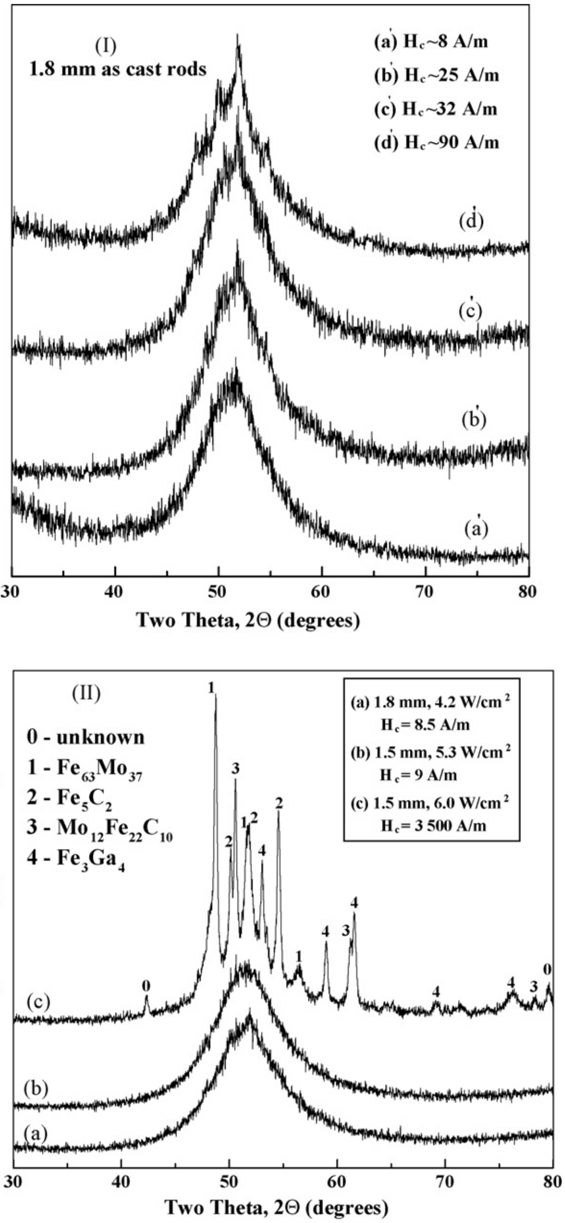

Fig. 2. XRD patterns for $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$: (I) as cast rods 1.8 mm diameter, and (II) after different CA treatments.

after CA T_C does not change much as a result of structural relaxation (curves c and d) as in ribbons of another Fe-based BMG system (Fe, Nb)–(Al,Ga)–(P,C,B) [12]. The structural modifications were detected by the shift and deviation of the $J_S(T)$ curves after crystallization process (as detected by XRD, see pattern c on Fig. 2II) and observed after CA with $P_S = 6\,W/cm^2$ and furnace annealing (FA) up to 973 K (curves e and f on Fig. 3, respectively).

The influence of CA on magnetic softening was followed by coercivity changes shown on Fig. 4. A maximum decrease in coercivity of about 30% was observed for samples after applying a heating power of $P_S \cong 4.4$ and $3.7\,W/cm^2$ for 1.5 mm and 1.8 mm rods diameters respectively due to partial relief of stress-induced anisotropy formed upon casting. Similar extents of coercivity improvement were observed for samples with higher

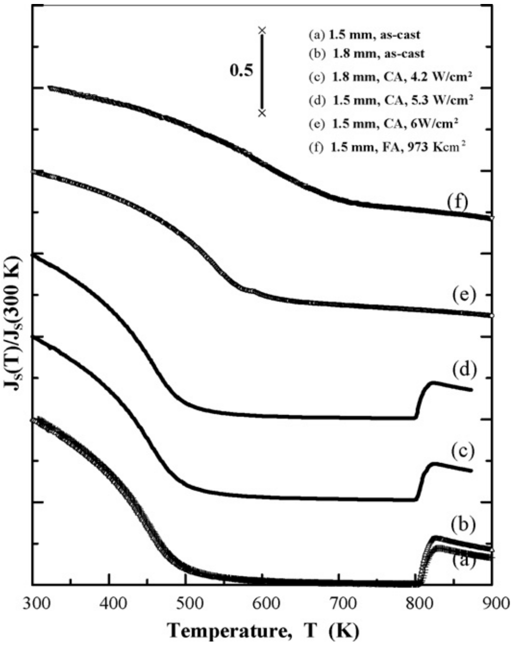

Fig. 3. Temperature dependence of normalized saturation polarization for the $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ rod samples in as cast state: (a) 1.5 mm; (b) 1.8 mm diameter, and after CA: (c) $P_S = 4.2\,W/cm^2$; (d) $P_S = 5.3\,W/cm^2$; (e) $P_S = 6\,W/cm^2$; (f) after FA up to 973 K.

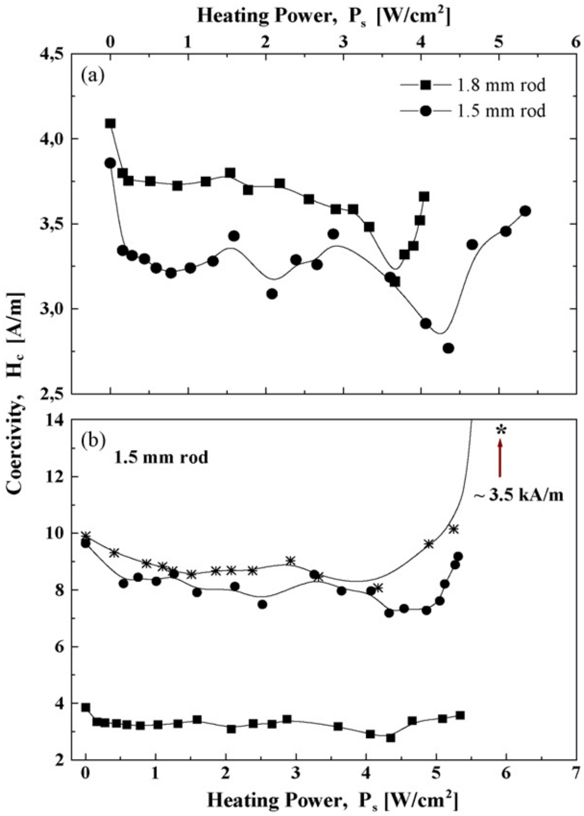

Fig. 4. Coercivity changes of $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ rod samples after CA: (a) comparison of 1.5 mm and 1.8 mm diameter rod samples, and (b) different 1.5 mm rod samples.

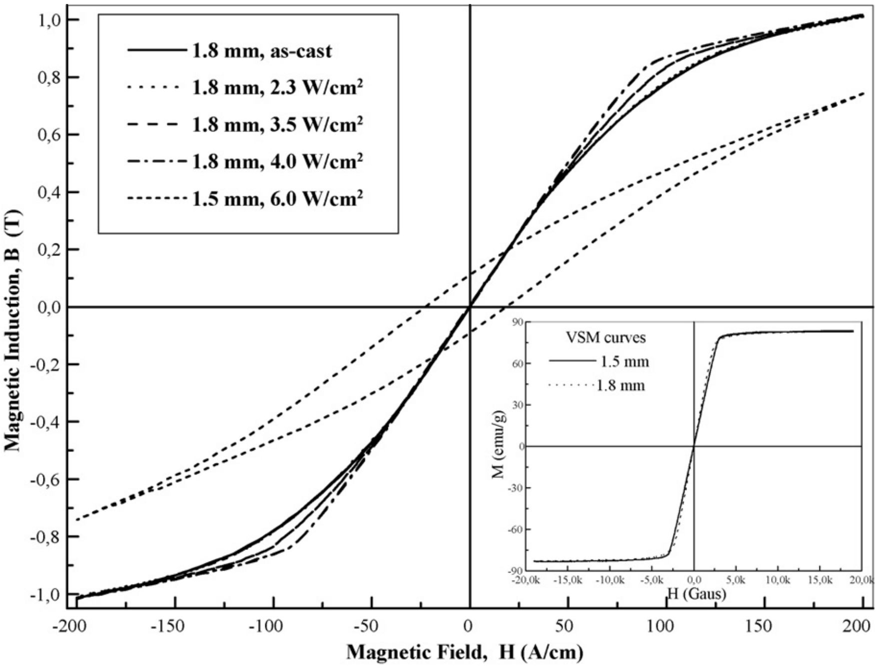

Fig. 5. Hysteresis loops of $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ rod samples: (a) after different CA, and (b) VSM curves—comparison of 1.5 mm and 1.8 mm diameter rod as-cast samples.

values of as-cast coercivity $H_C \approx 10$ A/m. This coercivity behavior after CA treatments indicates presence of a very small volume fraction of nanoscale crystalline inclusions that apparently hinder stress relief. Presence of these inclusions cannot be observed by XRD in reflection configuration performed in this paper but were experimentally evidenced by XRD in transmission configuration [10]. The increase in P_S over the optimum values leads to deterioration of coercivity due to crystallization observed with appearance of very weak diffraction peaks (XRD patterns a and b on Fig. 2II). In our previous study [17], it was shown by Mössbauer spectra analysis of Fe-based BMG that the starting of crystallization randomises the spin texture deteriorating the magnetic properties. After sufficiently high heating power ($P_S \geq 6$ W/cm^2) intensive crystallization takes place (see XRD pattern c on Fig. 2II) through simultaneous precipitation of several (magnetically hard) compounds Fe_5C_2, Fe_3Ga_4, $Fe_{63}Mo_{37}$, $Mo_{12}Fe_{22}C_{10}$ and coercivity significantly increases. As shown on Fig. 5, hysteresis loop of the CA crystallized sample confirms a high increase of coercivity. The electrical resistivity of $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ as-cast rods is relatively high $\rho \cong 210$–$220\ \mu\Omega$ cm. It is attributed to the improved packing structure leading to a reduction of mean free path of electron. This is consistent with the observation that BMG Fe-based alloys attain much higher packing density than that of the conventional amorphous alloys [18]. Therefore, as it is evidenced in studied samples, low coercivity in as-cast state $H_C \leq 3$A/m can be achieved.

4. Conclusions

Our experimental results reveal the good GFA and soft magnetic properties of $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ alloy. Optimized CA treatments enable limited coercivity enhancement of about 30% indicating structure with very small nanoscale crystalline inclusions. The alloy studied may be applied in high frequency devices due to relative high electrical resistivity.

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