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Effect of Silicon Substitution for Boron on Structural and Magnetic Properties of Melt-Spun $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_xB_{18-x}$ (x =5–9) Alloys

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The effect of Si substitution for B on the structural and magnetic properties (i.e. magnetic saturation $B_{\max}$, magnetic remanence B_r, coercivity H_c, core power losses P_s) of melt-spun $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_xB_{18-x}$, alloys (where $x = 5$–9) has been investigated. The effect of heat treatment was also examined. The optimal parameters were obtained for the composition $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_5B_{13}$ after heat treatment at 355 °C for 20 min. Hence, they are: $B_{\max} = 1.56$ T, $B_r = 0.46$ T, $H_c = 12.1$ A/m, $P_s = 0.62$ W/kg at $f = 50$ Hz, and magnetic field equals to 1007 A/m. Results from X-ray diffraction showed that each of the studied compositions was partially crystallized on the surface. However, for the compositions with silicon content $x = 8$ and $x = 9$ partial volumetric crystallization was also observed. Presence of the Fe_2B phase in the investigated alloys suppresses soft magnetic properties.

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PACS/topics: soft magnetic materials, metallic glass, magnetic properties

1. Introduction

Soft magnetic materials are widely used in power electronics, which has been developing rapidly in recent years and creates a huge demand for high quality magnetic components. Ferrite materials are limited by the possible operating frequencies low saturation induction ($B_{\max} = 0.4$ T) and low maximum operating temperature (around 120 °C). Therefore, for many years, intensive research on new magnetically soft amorphous and nanocrystalline materials for high frequency, and high induction of saturation applications has been conducted. A significant breakthrough in these studies took place in 1988, when the Japanese company Hitachi Metals developed a new nanocrystalline alloy with $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ composition named as FINEMET, characterized by high $B_{\max}$ reaching 1.2 T, coercive field H_c approximately 1 A/m, high magnetic permeability μ' of ~ 500000, and relatively low power losses in the core $P_s < 0.1$ W/kg [1]. This type of nanocrystalline material is composed of an amorphous matrix in which crystalline α-Fe grains of size from a few to several dozen nanometers are dispersed. Recently, the new generations of high magnetic saturation nanocrystalline alloys were successfully developed. These alloys are sensitive to the primary nucleation and annealing process due to their high Fe content (usually higher than 80%), and the lack of amorphous forming elements, such as Nb and Mo [2]. However, relatively high $B_{\max} = 1.74$ T was also obtained in [3] for Mo containing alloys by the use of ultra-rapid annealing process (heating rate > 100 °C/s).

The effect of Si substitution on the magnetic properties, including the $B(H)$ relationship and P_s of $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_xB_{18-x}$ alloys (where x = 5-9) has been shown in the present work. The conventional heat treatment process (with heating rate 10 °C/min and subsequent isothermal annealing) of alloys system was successfully optimized. For such treated samples the average grain size of the α-Fe phase was estimated by use of X-ray diffraction method, and then was compared with optimal soft magnetic properties.

2. Experimental

In this study, the following chemical composition $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_xB_{18-x}$, where $x = 5$–9, was chosen. Alloys were produced by means of induction melting and then cast in the form of a 10 mm wide ribbon. The casting temperature was 1250 °C, which is 50 °C higher than the liquidus temperature of primary alloys. The structure of casted and heat treated ribbons has been verified by the X-ray diffraction (XRD) method using a diffractometer (Rigaku MiniFlex 600) equipped with CuK_α radiation ($\lambda = 1.5418$ Å) source, K_β Ni filter and the D/teXUltra high-speed silicon strip detector. The thermodynamic approach was applied to determine influence of substitution of boron by silicon on the glass forming ability of $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_xB_{18-x}$ alloys. Three different parameters: configurational entropy (ΔS^{conf}), enthalpy of mixing (ΔH^{mix}) and Gibbs free energy of mixing (ΔG^{mix}) were calculated using [4]:

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$$\Delta H_k^{\mathrm{mix}} = 4\Delta H_{ij}^{\mathrm{mix}} c_i c_j, \qquad (1)$$

$$\Delta H^{\mathrm{mix}} = \sum_{k=1}^{N} \Delta H_k^{\mathrm{mix}}, \qquad (2)$$

$$\Delta S^{\mathrm{conf}} = -R \sum_{i=1}^{n} c_i \ln(c_i), \qquad (3)$$

$$\Delta G^{\mathrm{mix}} = \Delta H^{\mathrm{mix}} - T\Delta S^{\mathrm{conf}}, \qquad (4)$$

where $\Delta H_{ij}^{\mathrm{mix}}$ is the mixing enthalpy between i-th and j-th chemical elements for equiatomic composition in a binary system, c_i and c_j are the concentrations of i-th and j-th elements, k is the atomic pair number, N is the number of different atomic pairs ij ($N = 15$ for $n = 6$), n is the number of chemical elements in alloy (in this study $n = 6$), R is the gas constant, and T is the average casting temperature of alloy from liquid state.

Toroidal cores were wound from the cast ribbon and then heat treated in a vacuum furnace at a given temperature selected from 335 °C to 395 °C range for 20 min. Heat treatment temperature was optimized in order to obtain the best soft magnetic properties. The magnetic properties of heat treated cores ($B_{\max}$, P_s, H_c, B_r) were measured at 50 Hz using the Remacomp C-1200. Moreover, magnetic hysteresis loop measurement was performed for each of the samples.

3. Results and discussion

The structure of as-cast ribbons was analyzed by means of X-ray diffraction. Diffraction patterns of studied samples have been shown in Fig. 1. It can be clearly seen that all the samples are surface crystalline (presence of α-Fe (200) line), and for the content of silicon equal to 8 and 9% the origins of volumetric crystallization can be noticed (presence of α-Fe (110) line).

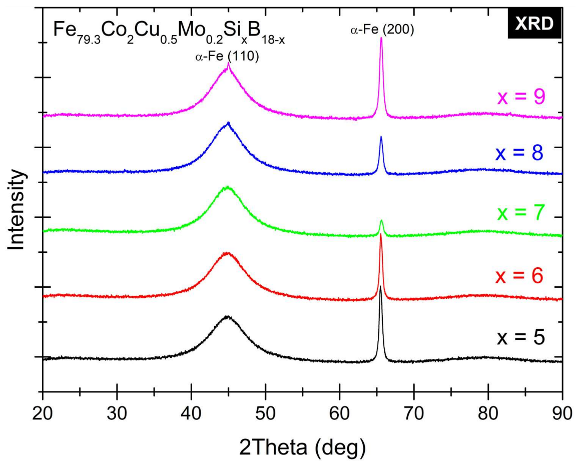

Fig. 1. X-ray diffraction patterns for a sample of $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_xB_{18-x}$ ribbons in the "as cast" state.

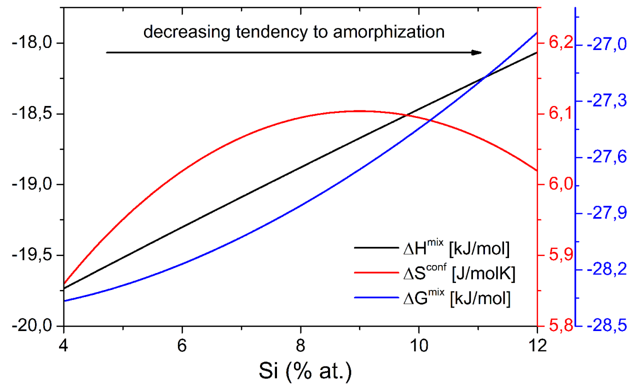

Fig. 2. Thermodynamic parameters: ΔS^{conf}, ΔH^{mix}, and ΔG^{mix} as a function of Si content calculated for $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_xB_{18-x}$ alloys.

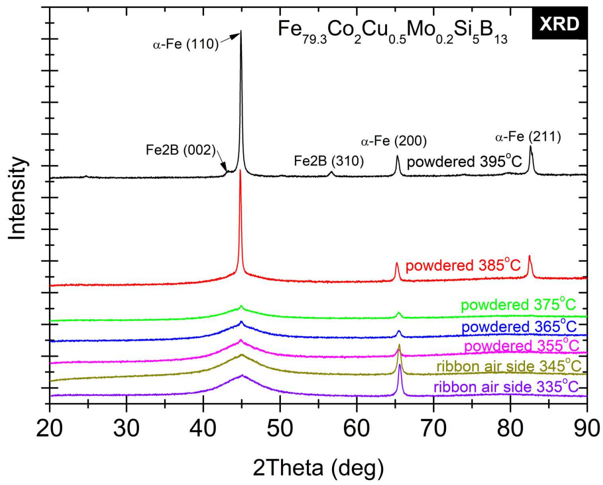

Fig. 3. X-ray diffraction patterns for a sample of $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_5B_{13}$ ribbons measured after heat treatment at temperature range from 335 °C to 395 °C for 20 min.

The thermodynamic analysis results are presented in Fig. 2. It can be noticed, that with increasing Si content the values of both, ΔH^{mix} and ΔG^{mix}, increase. Simultaneously, the value of ΔS^{conf} increases with silicon content up to $x = 9\%$, and then decreases with further increasing Si content. In the optimal conditions, to form an amorphous phase the configurational entropy should be as high as possible, while mixing enthalpy should be the most negative. This manifests itself in a highly negative value of ΔG^{mix}. In this case, substitution of B for Si increases value of ΔG^{mix}. Therefore, the crystallites occur in alloys with Si content above 7%, for which $\Delta G^{\mathrm{mix}} > -28.03$ kJ/mol.

Figure 3 shows the X-ray diffraction patterns for heat treated $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_5B_{13}$ ribbons in the temperature range 335–395 °C. The purpose of this treatment was to determine the temperature where the Fe_2B phase begins to form, which deteriorates the magnetic

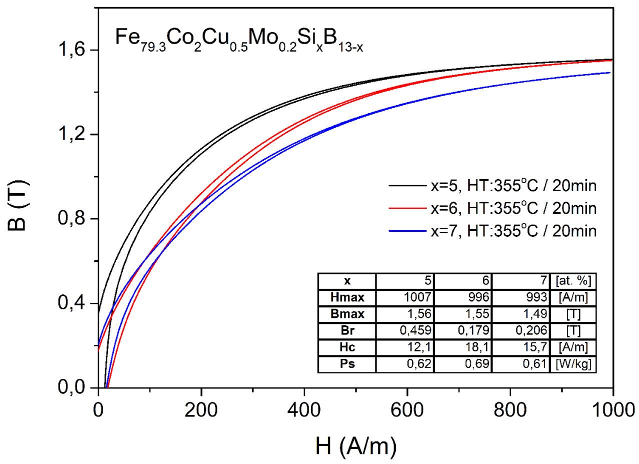

Fig. 4. First quarter of hysteresis loops for $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_xB_{18-x}$ alloys for x =5–7% after heat treatment.

properties. The second goal was to estimate the size of crystallites. For this, the broadening of the diffraction peaks was analyzed for the α-Fe (110) line, according to the Scherrer equation of the form:

$$D = \frac{0.9\lambda}{B\cos(\theta)}, \tag{5}$$

where D is the average grain size, λ is the wavelength of incident X-rays, and B is the full width at half maximum of the diffraction peak [5].

During the heat treatments, which were carried out at too high temperatures, Fe_2B type phase has been formed, which is undesirable in this type of material (Fig. 3). This phase causes deterioration of the soft magnetic properties [6].

In Fig. 4 the first quarter of hysteresis loops of $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_xB_{18-x}$ alloys, where $x = 5$–7%, is presented.

TABLE I

Soft magnetic properties for the heat treated (HT) $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_xB_{18-x}$ alloys measured at $f = 50$ Hz and $H = 1000$ A/m.

HT temp. [°C]	335	345	355	365	375	385	395	405
$Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_5B_{13}$								
$B_{\max}$ [T]	1.49	1.51	1.56	1.56	1.54	1.61	0.159	0.825
B_r [T]	0.521	0.534	0.459	0.352	0.209	1.5	0.056	0.647
H_c [A/m]	13.7	13.3	12.1	12.5	15.3	206	343	567
P_s [W/kg]	0.67	0.63	0.62	0.62	0.69	9.1	0.97	10
D [nm]	–	19.2	20.3	21.5	25	43.9	45.5	–
$Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_6B_{12}$								
$B_{\max}$ [T]	1.45	1.5	1.53	1.55	1.61	0.443	0.394	0.727
B_r [T]	0.508	0.446	0.293	0.179	1.52	0.295	0.227	0.558
H_c [A/m]	14.,1	14.2	13.9	18.1	207	542	462	539
P_s [W/kg]	0.64	0.62	0.62	0.69	8.8	4.9	3.7	8.9
D [nm]	18.8	20.2	21.7	24	40.6	48.5	–	–
$Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_7B_{11}$								
$B_{\max}$ [T]	1.41	1.46	1.48	1.49	1.52	0.415	0.511	0.28
B_r [T]	0.489	0.411	0.294	0.206	0.736	0.256	0.332	0.159
H_c [A/m]	14.2	13.6	14.2	15.7	109	383	552	517
P_s [W/kg]	0.64	0.6	0.6	0.61	3.6	3.8	5.7	2.6
D [nm]	10.2	15.1	19.1	28.1	30.2	40.7	–	–
$Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_8B_{10}$								
$B_{\max}$ [T]	1.06	0.803	1.02	1.57	1.14	0.9	1.02	0.254
B_r [T]	0.188	0.17	0.135	1.2	0.928	0.721	0.819	0.13
H_c [A/m]	38.3	111	70.2	132	602	667	604	436
P_s [W/kg]	0.89	1.1	0.93	5.5	14	13	13	2.1
$Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_9B_9$								
$B_{\max}$ [T]	0.85	1.07	0.835	0.838	1.33	1.08	1.12	0.85
B_r [T]	0.17	0.159	0.172	0.189	0.928	0.882	0.923	0.17
H_c [A/m]	98.2	47.6	111	130	140	641	616	98.2
P_s [W/kg]	1.1	0.91	1.1	1.4	6.8	15	15	1.1

For compositions with Si content $x = 8\%$ and $x = 9\%$, it was unable to achieve satisfactory soft magnetic properties. The measured soft magnetic properties of the studied alloys were collected in Table I, where the influence of composition and heat treatment temperature was shown.

Three (with silicon content equal to 5–7%) of five selected chemical compositions of alloys had satisfactory soft magnetic properties, i.e., saturation induction about 1.5 T with low coercivity and low power losses in the core. These parameters were obtained by optimizing the heat treatment. The best soft magnetic properties were obtained for the composition $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_5B_{13}$ after the heat treatment at $T = 355\,°C$ conducted for $t = 20$ min. For such optimized composition, the following magnetic parameters were obtained: $B_{\max} = 1.56$ T, $B_r = 0.459$ T, $H_c = 12.1$ A/m, $P_s = 0.62$ W/kg at $f = 50$ Hz, and magnetic field strength $H = 1007$ A/m.

4. Conclusion

When one takes as a criterion the high induced saturation induction field, three studied alloys with silicon content $x = 5$, $x = 6$, and $x = 7$ will be able to achieve satisfactory soft magnetic properties through the proper heat treatment. It was found that for the $Fe_{79.3}Co_2Cu_{0.5}Mo_{0.2}Si_5B_{13}$ ribbon, optimal heat treatment conditions should be set to $T = 355\,°C$ and $t = 20$ min. The size of crystallites after this heat treatments were around 21 nm. Despite the fact that all the initial ribbons were surface crystallized, it was possible to obtain final cores with satisfactory soft magnetic properties by performing proper heat treatment process [7].

Acknowledgments

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