Journal of Magnetism and Magnetic Materials 424 (2017) 233–237

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Effects of surface crystallization and oxidation in nanocrystalline FeNbCuSiB(P) ribbons

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ARTICLE INFO

Keywords:
Domain structure
Magnetic anisotropy
Magnetic measurements
Mechanical loading, Mössbauer spectroscopy
Nanostructured materials

ABSTRACT

Si-poor $Fe_{74}Nb_3Cu_1Si_8B_{14-x}P_x$, ($x$=0, 3) nanocrystalline ribbon-form alloys often form surfaces, which exert in-plane force on underlying ribbon interior when nanocrystallized in even modest presence of oxygen. Mostly unwanted hard-ribbon-axis magnetic anisotropy is standard result. Essential sources of the surface-caused stress have been sought and influence of P instead of B substitution on this effect was studied too. Preferred surface crystallization (PSC) was found to be the major reason. However P substitution suppresses PSC and promotes Fe-oxide formation, which eases the stress, softens the surfaces and provides different annealing evolution of surface properties.

1. Introduction

Nanocrystalline structures with ultra-fine grain size are known in Fe-rich soft magnetic materials prepared by planar flow casting method for a long time [1,2]. Due to the ribbon shape that comes from the technological process, as-prepared material generally shows large surface/volume ratio. The chemical and structural differences between surfaces and interior of the ribbon often bring internal macroscopic mechanical stress that can affect final magnetic properties [3] and attracts researchers' attention even at other ribbon-shape magnetic materials [4].

Impure inert gas (oxygen reduced but not excluded) supercritical (above 500 °C) annealing of Si-poor Finemet Fe–Nb–Cu–B–Si $_{<12}$ alloys creates surfaces, which are richer in oxides and contain more Fe crystalline phase than the ribbon interior [5–7]. Such surfaces often apply in-plane compressive force (squeeze) on the ribbon interior beneath [8]. At present, similar alloys but with higher saturation and lower price are looked for [9,10].

This trend brings about reduction of Si and B percentage, alternatively omitting Nb or Nb substituting Mo too. To ease some problems connected with these composition changes, phosphorus is tried [11]. Squeezing surfaces generate mostly unwanted magnetic anisotropy of the type hard-ribbon-axis (HRA) on these inevitably positively magnetostrictive ribbons by engaging magnetoelastic interaction. However, creep-induced-like anisotropy (CILA) can contribute too –for at% Si < 9 in the same sense as magnetoelastic interaction; in the opposite sense for at% Si > 10 [12]. What makes P to CILA is so far unknown – we looked at this. So we chose the basic reference composition (see Material and methods) labelled as P0 so as not to bring any measurable CILA (tested) to simplify interpretation. A P-containing alloy (P3) is compared to the reference. Unfortunately, P3 could not be tested/compared in all experiments due to its brittleness after annealing.

2. Material and methods

Non-crystalline precursor ribbons of $Fe_{74}Nb_3Cu_1Si_8B_{14-x}P_x$, ($x$=0, 3) were prepared by the planar-flow casting on air; labelled as: P0 for x=0, P3 for x=3. Strips of 10 mm width, 10 cm long were annealed in vacuum or in technical purity Ar ambience at 500, 520, 540 °C for 1 h. Iron-based transmission Mössbauer spectroscopy (TMS) and Conversion electron Mössbauer spectroscopy (CEMS -information depth ~0.2 μm) was used to look for surface-interior differences. Hysteresis loops were recorded using a digitizing hysteresisgraph at 21 Hz in Helmholtz drive coils along the ribbon long axis. Structure, critical temperatures were checked by XRD and DSC. Electron Dispersive Spectroscopy (EDS) was used to look for differences of element abundance between surfaces and bulk. Magnetic domains were observed by Kerr-effect method (MOKE). Mechanical test of the annealed samples P0 and P3 at different atmosphere was performed by mechanical loading in TAQ400E of TA Instruments dilatometer.

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http://dx.doi.org/10.1016/j.jmmm.2016.10.068
Received 19 April 2016; Received in revised form 3 October 2016; Accepted 15 October 2016
Available online 15 October 2016

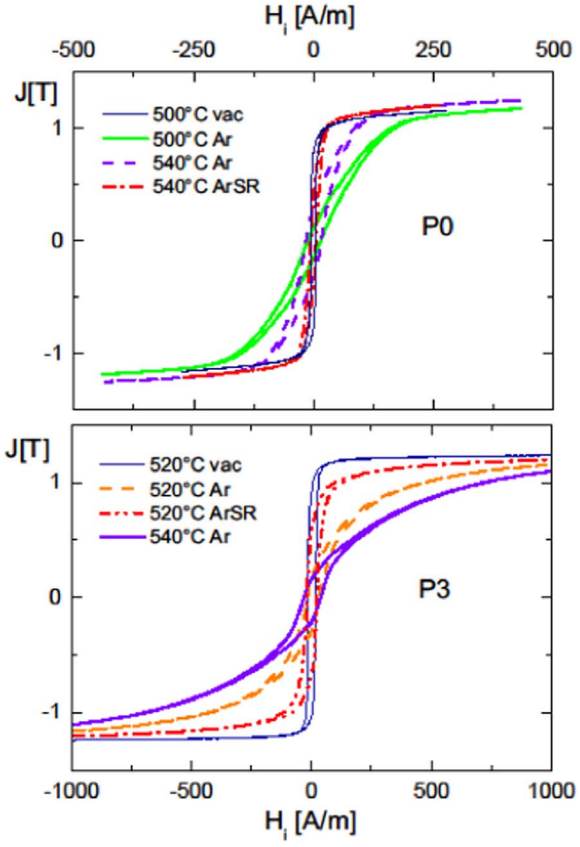

Fig. 1. Hysteresis loops (21 Hz) of P0 and P3 samples annealed at temperatures 500, 520 and 540 °C 1 h in Ar and vacuum atmosphere.

3. Results and discussion

3.1. Magnetic properties

Thermal analysis shows only small differences in Curie temperature of amorphous precursors – P0 and P3 ribbon show TC=300° and 308 °C, respectively. The onset and the peak of first crystallization temperature were determined by DSC measurements: P0 (517 and 540 °C) and P3 (520 and 565 °C). Nanocrystallization process is governed by grain-growth kinetics, which is often observed in Finemet-type alloys [13]. Low-Si Finemets crystallize to the bcc-Fe(Si) phase with grain size ~15 nm, P addition gently reduced the nanograins which were verified by XRD measurements.

Resulting hysteresis loops after annealing at 500, 520 and 540 °C during 1 h in two different atmospheres are shown in Fig. 1. Unlike vacuum annealing, Ar annealing above crystallization temperature results in a slant loop (i.e. HRA anisotropy is generated) as a rule for most of Si-poor (at% Si < 12) compositions [3,8]. We assume two effects could be responsible: magnetoelastic interaction $\lambda\times\sigma$ and/or creep-induced-like magnetic anisotropy if a mechanical stress σ (in-plane squeeze) is exerted by surfaces on ribbon interior after or during nanocrystallization respectively. P0 is just the composition not creating the latter anisotropy. Since the surface removal (SR) (see Fig. 1 in P0, label ArSR) removes loop tilt too, it was indeed the surfaces that generated the stress and ensuing magnetic anisotropy.

3.2. Mössbauer spectroscopy

To better explain source of the mechanical stress coming from surfaces, we performed TMS and CEMS measurements of satisfactory nanocrystallized samples annealed in vacuum and Ar atmosphere at 540 °C. TMS in Table 1 and CEMS in Table 2 show significant differences: whereas sextets related to Fe–Si crystalline phase appear in the spectra of all samples, P0-Ar sample attained higher crystalline share than P3-Ar one. Similarly this character is seen for P0-vac and P3-vac, but with lower overall crystalline share.

Table 1
Transmission Mössbauer Spectroscopy results (after annealing at 540 °C/1 h in Ar/vacuum).

	< Bam >	am%	Fe_3O_4%	Fe_2O_3%	Fe–Si%	doublet%
P0-Ar	17.1	38.06	0.23	0.44	61.15	0.12
P0-ArSR	18	39.66	0.09	0	58.61	1.64
P0-vac	18.9	58.7	0	0.07	41.2	0.03
P3-Ar	16.5	42.7	0.18	0.31	56.8	0.01
P3-vac	19.1	72.52	0.04	0	27.43	0.01

Table 2
Conversion electron Mössbauer spectroscopy results (after annealing at 540 °C/1 h in Ar/vacuum).

	< Bam >	am%	Fe_3O_4%	Fe_2O_3%	Fe–Si%	doublet%
P0-Ar	11.04	15.75	0.01	2.97	79.16	2.11
P0-ArSR	14.88	38.99	0.01	5.45	45.86	9.69
P0-vac	19.91	66.09	0	0	32.73	1.18
P3-Ar	14.97	16.36	5.42	24.29	52.83	1.1
P3-vac	18.31	60.27	0.37	0	39.35	0.01

Regarding CEMS results it can be pointed out that the surface crystallinity of P0-Ar is higher than P3-Ar one and no crystalline share is seen in P3-vac (see Fig. 2 – CEMS P3).

Moreover the sample containing phosphorus shows more of Fe-oxides. The sextet showing magnetic hyperfine field about B_{hf} =51 T is attributed to the hematite – Fe_2O_3 (it is best visible in the CEMS spectra of sample P3-Ar, at both surfaces). Two coupled sextets of the magnetic hyperfine field about 45 T and 49 T, is related to magnetite

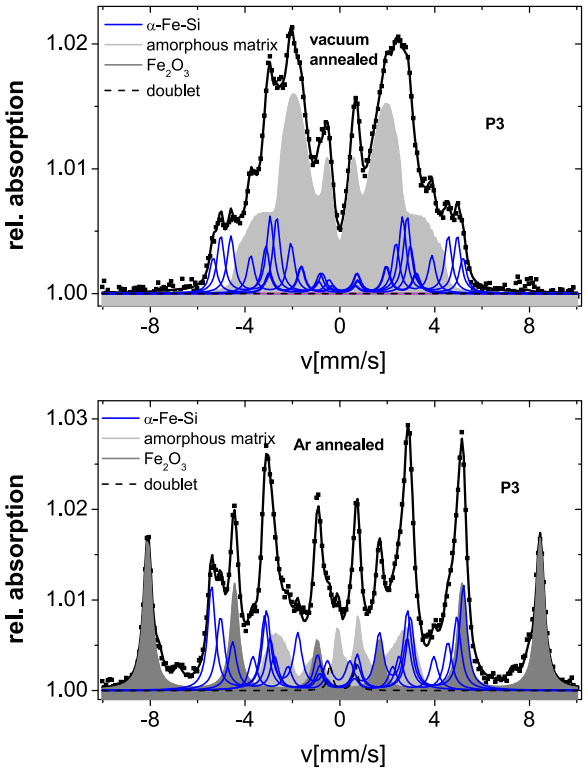

Fig. 2. CEMS spectra of air side of P3 samples annealed at 540 °C 1 h in different atmosphere (vacuum (a) and Ar (b)). Light gray fill – amorphous rest, dark gray fill – Fe_2O_3, Fe_3O_4 – omitted. Doublet present, but negligible after vacuum annealing.