IMPACT OF PHOSPHORUS FOR BORON SUBSTITUTION ON MAGNETIC PROPERTIES OF MAGNETOSTRICTIVE FINEMETS

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ABSTRACT

Reduction of Si percentage in Fe-Nb-Cu-B-Si alloys known as Finemets results in 1.5 T saturation, surpassing so the standard Si-rich compositions. However the other soft-magnetic properties are worse due mainly to magnetostriction and the consequences of so-called macroscopic heterogeneity. Therefore phosphorus has been added to the detriment of boron to test, whether this could be the way to suppress the undesired properties of Si-poor Finemets. Phosphorus appears to reduce the vulnerability of the ribbon surfaces to environmental influences at non-vacuum annealing and improves parameters like coercivity and magnetic anisotropy. Crystallization kinetics character remains preserved and critical temperatures change only negligibly.

Keywords: *magnetic properties, nanocrystalline alloys, soft-magnetic materials, surfaces*

1. INTRODUCTION

Soft- magnetic materials produced by rapid quenching from the melt known as Finemets (basic composition Fe-Nb-Cu-B-Si) are already of interest for a lot of researchers and electrotechnical developers because of their widely used magnetic properties [1]. Magnetic properties of specific compositions greatly profit from thermal treatment resulting in partial crystallization when nanoscale crystalline grains are embedded in the amorphous rest of the alloy. Apart from the "classic" Finemet composition containing 13.5-15.5 at% of Si, new alternatives are sought to obtain higher saturation induction (B_s) without much sacrifice of increasing coercivity and magnetostriction. Whereas the earlier development line exchanged metals and their percentage (Co for Fe), the other way is to try also exchanging metalloids and/or glass-formers. One of the latest achievements of the later way is B_s as high as 1.8 - 1.9 T shown by a composition with P addition and reduced Si percentage [2]. So far less attention has been paid to the consequences of so-called macroscopic heterogeneity (MH), which builds up preferentially during the thermal treatment of magnetostrictive Si-poor compositions [3] devoted for nanocrystallization. The MH goes along with mutual stress between surfaces and ribbon interior and shows significant effect on the resulting magnetic anisotropy – characteristic hard-ribbon-axis (HRA) contribution appears [4]. The above-mentioned quest for the improvement of saturation without significant collateral detriments to other properties, MH inclusive, led us to the choice of a Si-poor Finemet with partial substitution of B by P to study how P affects the properties of higher-B_s Finemets. Our work on the "parent" Si-poor material (without P) points to the presence of surface oxides [5] capable of supporting MH and so the question how can phosphorus affect the MH is opened by the P for B substitution too.

2. MATERIALS AND METHODS

Planar-flow casting on air was used to prepare the ribbons of 10 mm width and 18 – 26 μm thickness following in the text, labels to identify the composition are used as follows:
$Fe_{78}Nb_3Cu_1B_{13.5}Si_{4.5}$ - FM(Si4.5),
$Fe_{74}Nb_3Cu_1B_{13}Si_9$ - FM(Si9),
$Fe_{78}Nb_3Cu_1P_3B_{10}Si_5$ – FM-P(Si5),
$Fe_{74}Nb_3Cu_1P_3B_{10}Si_9$ – FM-P(Si9).

Amorphous ribbons were submitted to differential scanning calorimetry (DSC) in Perkin-Elmer DSC7 under Ar atmosphere to determine the temperature of crystallization onset T_x, temperature of first crystallization T_p and Curie temperature T_C. Thermo-gravimetric analysis (TGA) at applied magnetic field was performed to check more details of T_C. The nanocrystalline state and ensuing magnetic properties were obtained by annealing at 500 and 540°C for 1 hour in vacuum and in Ar (without preceding furnace evacuation). We measured the hysteresis loops of 10 cm long strips at 21 Hz sine-H excitation in Helmholtz coils. Raman spectroscopy investigation of strip surfaces used the confocal system with 632.8 nm monochromatic laser radiation. Capacitive sensor measured the magnetostrictive strain to facilitate the determination of coefficients of saturation magnetostriction λ_s.

3. RESULTS AND DISCUSSION

3.1. Structure and transformation

Very similar transformation process has been observed for P-containing as well as for P-free ribbons by DSC measurement at 10 K/min and 40 K/min rate. As it is seen from Fig. 1, all the curves show the typical regions: structural relaxation, Curie temperature, structural rearrangement at 350-450°C [6] and the first crystallization peaks, which are merely few degrees lower for the P-containing alloys when compared to the P-free alloys. Nanocrystallization process is governed by grain-growth kinetics, which is often observed in Finemet-type alloys [7]. Si-poor Finemets crystallize to the bcc-Fe(Si) phase moreover, the alloy with 9 at. % Si provides additionally the DO_3 superstructure too [3]. The comparison of critical temperatures and Curie temperatures measured by DSC method at the two rates is shown in Table 1.

Table 1 Critical temperatures calculated form DSC measurements

Alloy	T_x[°C]	T_p[°C]	T_C[°C]
10K/min			
FMP(Si5)	455	472	269
FMP(Si9)	493	504	365
40K/min			
FMP(Si5)	470	490	265
FM(Si4.5)	479	493	273
FMP(Si9)	509	522	361
FM(Si9)	517	539	302

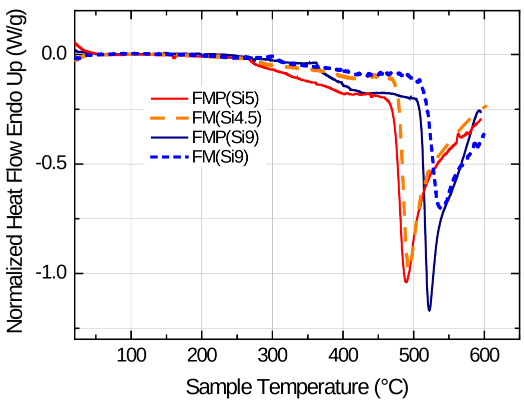

Fig. 1 DSC measurements at 40 K/min of Finemets with and without P

Curie temperatures of FM-P alloys determined from DSC are lower by about 2°C when compared to TGA measurement. We can hypothesize, that the applied field affected the structural relaxation at TGA. The TGA results are seen in Fig. 2. Considerable increase of T_C is noted for FM-P(Si9) alloy as compared to FM(Si9) (see Table 1).

3.2. Magnetic properties

Hysteresis loops at 21 Hz for FM-P(Si5) and FM(Si4.5) strips annealed 500°C and 540°C in vacuum during 1 hour. The loop shape is very similar but significant decrease of coercivity (from 16.8 to 6.7 A/m and from 11.3 to 4.8 A/m) was found for both the annealing temperatures if FM and FM-P are compared, respectively. The comparison of loops for all alloy compositions after annealing at 500°C is shown in Fig.3. For alloy FM-P(Si9) is the effect of P for B substitution different as to the impact on magnetic properties. Hysteresis loops after vacuum annealing show modest increase of coercivity (~ 3 A/m) but higher saturation induction (B_s = 1.36 T) than FM(Si9).

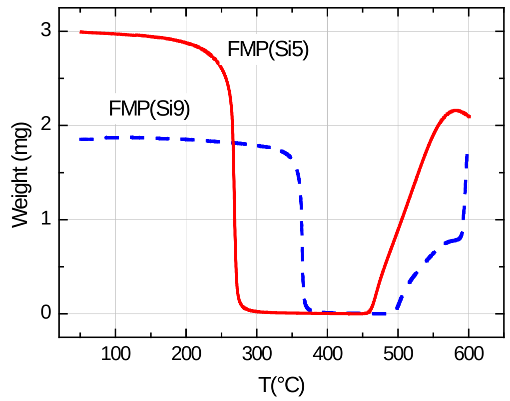

Fig. 2 TGA measurements of the indicated Finemets with P at 10 K/min rate

Annealing in Ar is the treatment that supports MH buildup more than vacuum annealing. Generally, the characteristic HRA anisotropy contribution is seen on a loop as its tilt. The lower temperature (500°C) Ar annealing results in tilted loops as seen in Fig.5. The tilt increases after higher annealing temperature 540°C (not shown). Still, FM-P(Si5) exhibits less-slant loops than FM(Si4.5) for both the annealing temperatures. We assume that this is due to a reduced impact of MH in P-containing alloys. Actually, FM-P(Si9) does not show the characteristic HRA tilt after 500°C Ar anneal, somewhat rounder knees are only visible (see Fig. 4). However the 540°C annealing lets the phosphorus to reduce MH effects in FM-P(Si9) no more – the coercivity increases significantly and the tilt appears. The reason is to be sought possibly in a diverse crystallization – see Fig. 1. The details are unavailable so far.

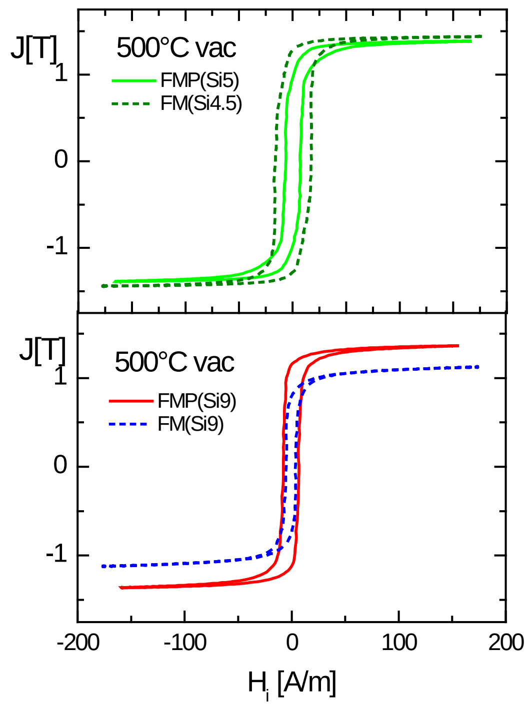

Fig. 3 Comparison of hysteresis loops of FM-P and FM alloys annealed at 500°C for 1 hour in vacuum

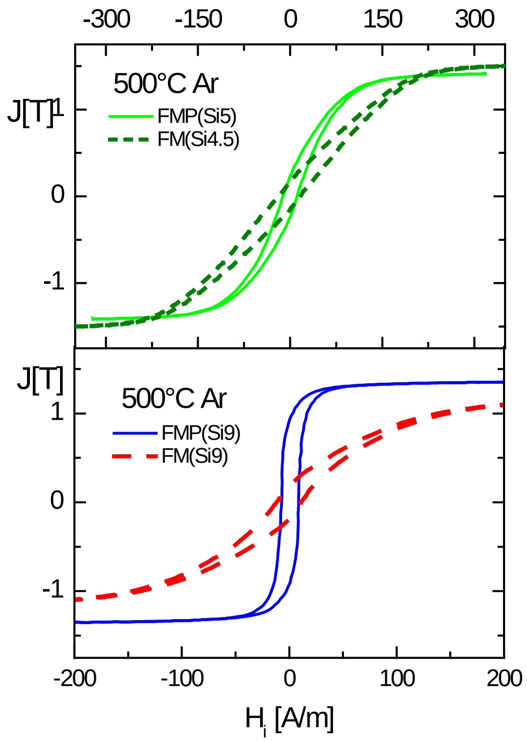

Fig. 4 Comparison of hysteresis loops of FM-P and FM alloys annealed at 500°C for 1 hour in Ar atmosphere

3.3. Raman spectroscopy

Neither side (air- or wheel-) of vacuum-annealed strips show a well-resolved Raman spectrum. Only for sporadic dark spots graphitic double peak at 1300 and 1600 cm^{-1} was recorded [5]. However, on the strips annealed at Ar atmosphere we observed well-expressed peaks on both sides (more intensive on air side) after 500°C and 540°C anneal of FM-P(Si5), and after 540°C anneal of FM-P(Si9). The characteristic Raman spectra (see Fig. 5) correspond with bands of oxides Fe_2O_3 and Fe_3O_4 as it was previously studied on FM(Si4.5) ribbon [5].

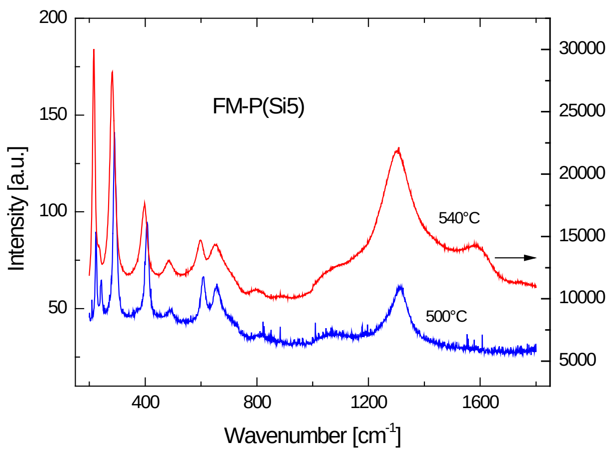

Fig. 5 Raman spectra of Finemet containing 5 at. % Si with substituted P (air side) after different- temperature annealing as is indicated above. The applied beam was ~4 mW power

3.4. Magnetostriction

All the Si-poor Fe-based Finemets show considerable magnetostriction – e.g. FM(Si4.5) λ_s ~ 25 ppm and FM(Si9) λ_s ~ 19 ppm in the as-cast state. These "isotropic" numeric values for the coefficient of saturation magnetostriction are gained by the standard evaluation based on the formula:

$$\lambda_s = \tfrac{2}{3} (\lambda_{\parallel} - \lambda_{\perp}) \qquad (1)$$

where the symbol meaning external magnetizing field oriented parallel (||) and transverse (⊥ = 90°) to the ribbon axis. Apart from some uncertainty at judging of saturation to obtain λ_s, the orthogonal components plotted together provide the helpful information about magnetic anisotropy, which is not always available from hysteresis loops. In particular, as-cast FM-P(Si5) was observed to saturate poorly and anisotropically. Whereas FM-P(Si5) shows some reduction of its λ_s = 21.7 ppm if compared with its FM counterpart, FM-P(Si9) with λ_s = 19.5 ppm does the other way. Thus – no significant difference of as-cast magnetostriction is due to the phosphorus presence in the alloys. The magnetostriction of the P-free Finemets decreases markedly (more than by 50%) due to annealing. Similar behaviour is expected for the FM-Ps although FM-P(Si9) shows surprisingly weakly tilted loop – see Fig. 4. Since magnetoelastic anisotropy is proportional to the product of stress and magnetostriction coefficient, it remains to be disclosed, whether this response to annealing is due to lower MH-coupled stress or to lower magnetostriction.

4. CONCLUSIONS

Substitution of phosphorus for boron has produced marked effects on the magnetic properties of Si-poor Finemets. No impact of the substitution on structural transformation to nanocrystalline state was identified.

Significant decrease of coercivity and better soft magnetic properties were observed for alloy with 5 at. % Si, especially after vacuum annealing. Higher saturation magnetic induction B_s (1.36 T) and increased T_C was found for the higher-Si alloy. The effects of macroscopic heterogeneity after Ar annealing appear significantly reduced by phosphorus, especially after 500°C annealing. Although showing considerable magnetostriction and not free of macroscopic heterogeneity, the substitution of phosphorus for boron brings better soft-magnetic properties useful in the production of electrotechnical devices.

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Pavol Butvin born 1948 in Bratislava studied physics, specialized in solid state physics and graduated from Faculty of Natural Sciences, J.A. Comenius University Bratislava in 1971. He joined the Institute of Physics, Slovak Academy of Sciences (SAS) Bratislava the same year and he is still active there as department deputy head and principal investigator of various projects. In 1980, he acquired his RNDr and CSc (=PhD) degrees from the University and SAS, respectively. He was a member of the group awarded by the State Prize in 1988. From 1973 on, his interests are in magnetism of metals as well as in applied research of novel magnetic materials. In the recent years, he specializes in less-common properties (heterogeneity) of modern soft-magnetic materials.

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