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Size dependence of coercivity in nanostructured soft alloys

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An increase of coercive field with decreasing particle size has been observed in a ball milled nanocomposite consisting of Fe rich nanocrystals embedded in an amorphous matrix. This type of behavior can be caused by two different effects: the introduction of strong lattice strain fields and structural defects with milling and a dependence of coercivity with particle size. Both effects have been analyzed. It was found that they both likely contribute to the increase of coercivity and, therefore, to a deterioration of the outstanding soft magnetic properties of the mother material.

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Nanocrystalline melt-spun ribbons consisting of Fe-based crystallites embedded in a soft amorphous phase present excellent soft magnetic properties.[1] Due to the almost vanishing magnetostriction and anisotropy, nanocrystalline powders could be thought as materials, with more adjustable size than the ribbons, to be used as the basis of performing magnetic flux multipliers nucleus in devices working at a range of high frequencies. However, as will be shown in this Brief Report, the decrease of the sample dimensions leads to a magnetic hardening that in principle could be ascribed to an intrinsic random anisotropy effect as well to an increase of residual stresses and structural defects introduced during milling. The influence of these effects has been experimentally studied and it is reported below.

A relevant soft magnetic material is the two-phase system formed by α-Fe(Si) nanocrystals (around 12-nm grain size) that are randomly oriented and embedded in a soft ferromagnetic amorphous matrix.[2] The low coercivity ($H_c < 0.01$ Oe) and high susceptibility ($\chi \propto 10^5$) have been successfully explained as a consequence of the random anisotropy characteristic of these systems[3–5] that reduces dramatically the effective anisotropy of the material.

Some attempts of preparation of nanocrystalline Fe-Cu-Nb-Si-B by mechanical alloying have been reported in the literature.[6] Nanocrystalline $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy was synthesized by using a Spex vibratory ball mill. This alloy exhibited a bcc phase characterized by a mean crystallite of 10 nm and rms strains of 1%. There was no evidence for the formation of an amorphous phase. This sample coercivity of 130 Oe and magnetization of 150 emu/g were measured after 60 h of mechanical alloying. The coercivity of mechanically alloyed powder is much larger than that of the melt-spun ribbons, although the saturation magnetization was the same. This was ascribed to the absence of grain boundaries in the amorphous ferromagnetic phase resulting in a weakening of the exchange coupling between the nanograins. In any case, similar microstructures obtained after annealing Fe-Si-B-Cu-Nb wires at 600 °C show higher coercivity values than the partially nanocrystalline samples annealed at 550 °C but one order of magnitude lower than in the corresponding powders.[7] An alloy with the same composition was studied by Baricco *et al.*[8] After thermal treatment of amorphous ribbons, the nanocrystalline bcc phase with a grain size of the order of 15 nm was found embedded in the amorphous matrix. A single bcc solid solution was obtained by ball milling the ribbons. Garitaonaindia *et al.*[9] studied the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ and $Fe_{73.5}Cu_1Nb_3Si_{16.5}B_6$ alloys prepared in a Retsch planetary ball mill (up to 120 h of processing). The resulting products were crystalline FeSi compound and an amorphous phase. The lower coercive field obtained, after 40 h of milling, was 28 Oe.

In order to analyze the possibility of maintaining this excellent magnetic softness after reducing the particle size we performed the following experimental study. A nanocrystalline powder of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ was produced by ball milling partially nanocrystalline ribbons (obtained initially as amorphous and nanocrystallized by annealing at 550 °C for 1 h). A Fritsch Pulverisette P5 ball mill was used for the size reduction. The following parameters were used: 250 rpm, ball-to-powder weight ratio 10:1, mass of milled material 10 g. Stainless steel vials and balls (10 mm diameter) were used. The mill operated in the sequence 15 min work–5 min stop, in order to avoid overheating the powders. Small amounts of the material were withdrawn from the vials after various milling times for structural and magnetic characterization. All powder handling was performed in a glove box under an argon atmosphere. For x-ray diffraction measurements (XRD) Philips PW 1830 diffractometer, with Cu $K\alpha$ radiation, was employed. The values of lattice parameters were calculated applying $\cos^2\theta/\sin\theta$ function. Crystallite size and lattice strain were calculated adopting the Williamson-Hall[10] approach. Magnetic measurements were carried out in a standard vibrating sample magnetometer.

The structure of the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy after isothermal nanocrystallization (at 550 °C for 1 h), and ball milling has been examined using x-ray diffraction and transmission electron microscopy. The XRD patterns recorded for ball milled $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ ribbon (previously nanocrystallized at 550 °C for 1 h) after various milling times (from 10 min up to 10 h) are presented in Fig. 1(a). The pattern for initial (mother) sample is also included, verifying the two-phase structure: nanocrystalline Fe(Si) solid solution + amorphous. The volume contribution of the amorphous phase was estimated as 20–25 %. The nanocrystalline

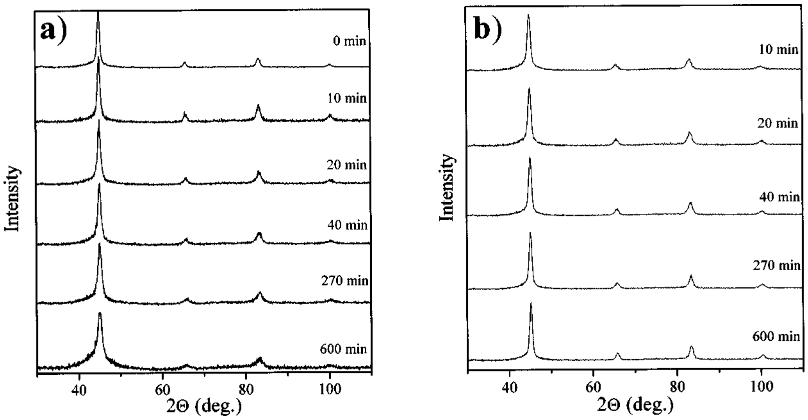


FIG. 1. XRD patterns for as-milled samples (a) and for annealed samples at 575 °C (b).

Fe(Si) solid solution was characterized by a lattice parameter of 0.283 nm (almost unchanged with milling) and crystallite size around 20 nm. Increasing milling time resulted in broadening of the diffraction lines of Fe(Si) and after 10 h of processing the Fe-based solid solution was characterized by an average crystalline size of 12 nm and rms strain of 0.6%. It can be concluded that the broadening of the diffraction lines is mostly due to the significant increase of lattice strain, while the crystallite size remains constant. Figure 1(b) shows the influence of annealing at 575 °C on samples milled between 10 min and 10 h. An average grain size about 15–20 nm is observed in all cases.

Figure 2 reveals that the grain size after the set of treatments is between 12 and 18 nm. The alloy consists of α-Fe(Si) nanocrystals embedded in an amorphous matrix. No traces of other phases were seen in the electron diffraction patterns. Therefore, the structure of the powder is practically the same as the structure of the nanocrystalline ribbon before milling.

Ball milling is known to introduce high density dislocations and structural defects that are expected to increase H_c. Therefore, in order to ascertain the possible influence of residual stresses introduced during the size reduction process all the samples were submitted to an annealing treatment at 575 °C for 1 h.

X-ray diffraction observations point out that the increase of milling time t_m results in the decrease of particle size d as shown in Table I, where the dependence of different structural parameters is also indicated. Note that the grain size D is almost constant and ranges between 12 and 18 nm, whereas the lattice strain ε grows with milling time.

The experimental dependence of H_c on milling time, for as-milled and postannealed samples, is plotted in Fig. 3. An increasing hardening exhibiting two different slopes is observed for increasing t_m. For t_m lower than 50 min, H_c increases very fast evolving toward a lower increasing rate for longer t_m. Smaller H_c values, but of the same order of magnitude, are observed by the annealed samples and should be associated with stress relaxation. Therefore, the lattice strain contributes to H_c. However, other effects introduced by milling should also contribute to an increase in H_c. As indicated in Table I the increase of t_m leads to an increase of ε but also to a decrease of d and, presumably, to an increase of the total number of structural defects.

According to the Neel[11] theory, randomly distributed internal stresses σ introduced by milling in a sample with local[12] magnetostriction constant λ are expected to increase

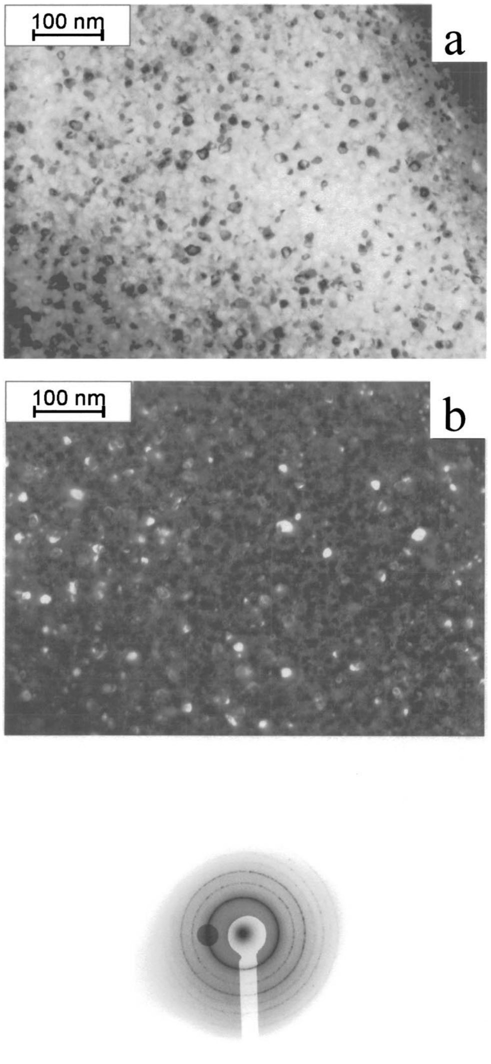


FIG. 2. TEM micrographs of Finemet $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ powders obtained from nanocrystalline ribbon after ball milling for 10 h. (a) Bright field image. (b) Dark field image obtained using part of the first ring—(110) bcc Fe. (c) SADP (selected area diffraction pattern).

TABLE I. Influence of milling time t_m on particle size d, lattice strain ε, lattice constant a, and grain size D for as-milled and annealed samples. The different parameters were obtained from x-ray diffraction patterns (Refs. 14 and 15).

		As-milled			Annealed		
t_m (min)	d (μm)	ε (%)	a (nm)	D (nm)	ε (%)	a (nm)	D (nm)
1	170	0,142	0,28352	19	0,115		
5	100	0,183	0,28349	21	0,118		
10	70	0,209	0,28347		0,120	0,28371	17
20	46	0,242	0,28349	21	0,130	0,28371	16
40	31	0,302	0,28344	18	0,107	0,28379	15
90	25	0,392	0,28341	20	0,135	0,28377	
270	22	0,492	0,28342		0,200	0,28389	16
600	21	0,600	0,28344	12	0,424	0,28415	23

H_c. If the magnetoelastic energy $\lambda\sigma$ is larger than the anisotropy energy, H_c is predicted to be proportional to the strain as $v^*(\lambda Y\varepsilon)/M_s$, where v^* is the strained volume fraction and Y the elastic constant. Figure 4(a) shows the dependence of ε on t_m. Figure 4(b) illustrates the H_c dependence on the strain. It is obvious that at high strain levels, above 0.13% for annealed and 0.29% for as milled particles, H_c shows a linear dependence with strain independently of the particle size. The linear behavior points out that magnetoelastic energy density is higher than the structural anisotropy and consequently H_c is governed almost exclusively by strain. However, at constant ε, according to Fig. 4(b), H_c of as-milled and annealed samples are indeed different. H_c is larger for annealed samples when ε is below 0.25% but lower when ε is above 0.25%. Consequently, it can be inferred that the strain is not the only parameter governing H_c. Since the grain size D has been observed not to change with annealing, it can be concluded that H_c also depends on other parameters as the total number of defects or the particle size d.

In a magnetically soft random anisotropy system the crys-

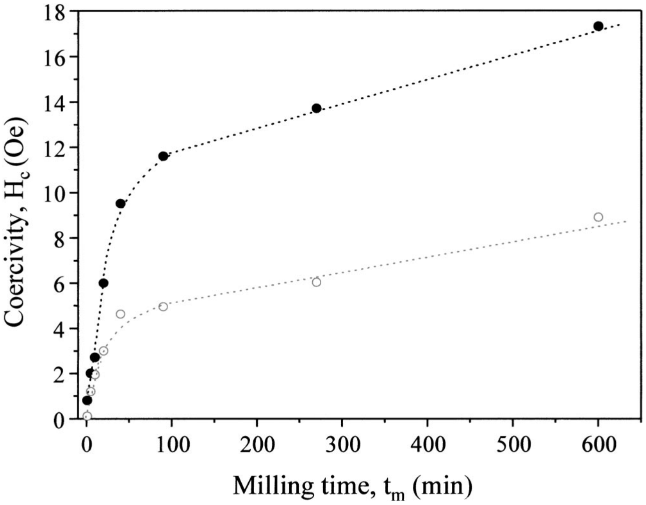
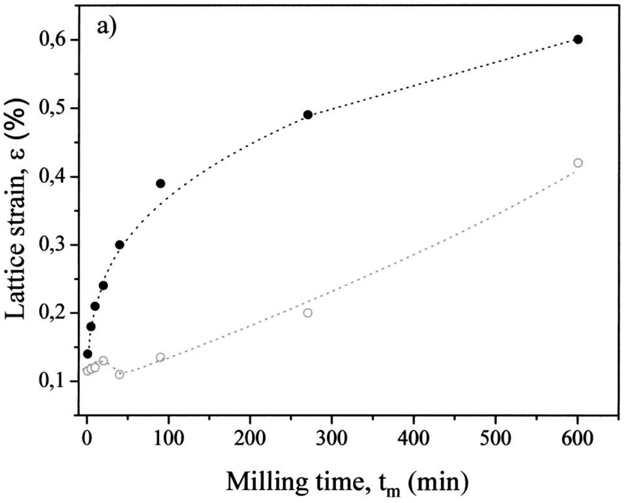


FIG. 3. Dependence of coercivity, H_c on milling time t_m for as-milled (●) and 575 °C annealed (○) powder samples.



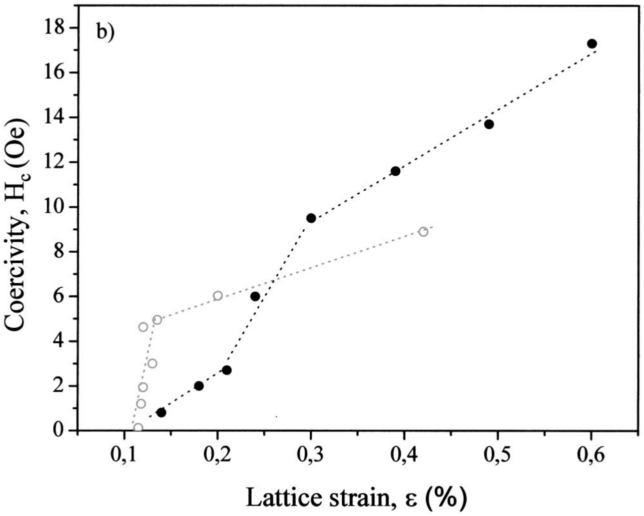


FIG. 4. (a) Influence of milling time t_m, on lattice strain ε and (b) dependence of coercivity H_c one for as-milled (●) 575 °C annealed and (○) powder samples.

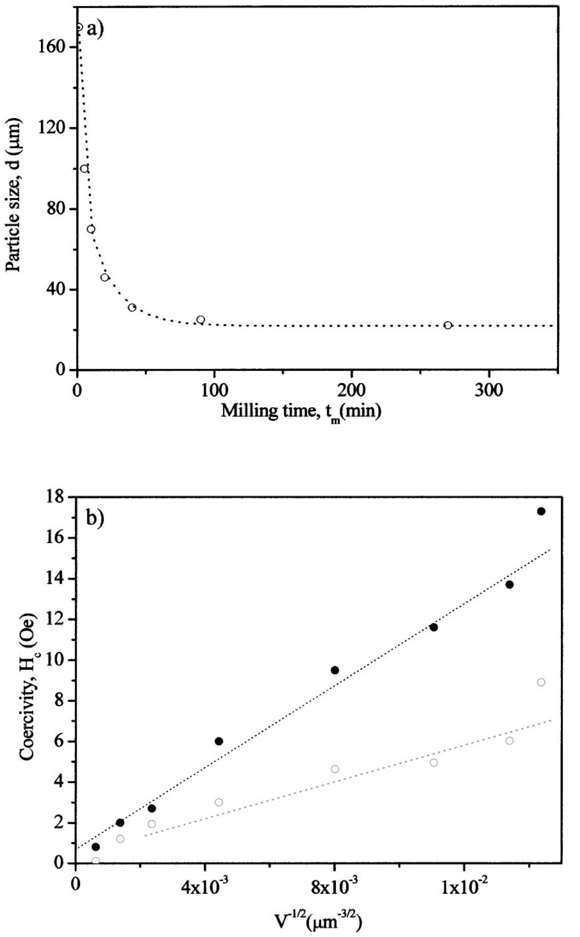


FIG. 5. (a) Influence of milling time t_{m} on particle size d and (b) linear dependence of coercivity H_{c} with $v^{-1/2}$ for as-milled (●) 575 °C annealed and (○) powder samples.

talline anisotropy constant k_1 is reduced by the exchange A to an effective constant $\langle k \rangle$ given by[2,3]

$$\langle k \rangle = \frac{k_1}{\sqrt{N}}, \tag{1}$$

where N is the maximum number of crystallites randomly oriented but ferromagnetically coupled. Even though the theory predicts that N is the number of crystallites contained in a volume with linear dimensions of the order of the exchange correlation length,[4,5] it is obvious that the number of exchange coupled grains is the total number of grains contained within a magnetic domain. An experimental idea about the order of N can be inferred from domain observations[13] that have pointed out the existence of ferromagnetic domains of several hundredths of μm in size. Therefore, when the volume of the sample v is smaller than the size of the domains, the average magnetic anisotropy, according to Eq. (1), should increase with decreasing v as

$$\langle k \rangle = \frac{k_1 D^{3/2}}{\sqrt{\nu}}. \tag{2}$$

Figure 5(a) shows the size dependence on t_{m}. It is worth to note that as Fig. 5(b) indicates H_{c} shows a linear dependence with $v^{-1/2}$ or $d^{-3/2}$ for samples with larger or smaller particle size. This surprisingly excellent fitting to Eq. (2) suggests that for low ε, the increase of H_{c} may be mainly due to the increase of $\langle k \rangle$ as a consequence of the size reduction, as described by Eq. (2).

In summary, we have shown that soft magnetic materials based on random anisotropy systems undergo a remarkable hardening with decreasing particle size by milling. It can be concluded that for high ε the increase of H_{c} is due to the magnetoelastic anisotropy generated by ε. Even though other effects can also be involved, the experimental results seem to indicate that the influence of the particle size on the average structural anisotropy noticeably contributes to the hardening observed for low ε.

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