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Dynamic coercivity of Mo-doped FINEMETs

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ABSTRACT

The structure and the dc magnetic behavior of FINEMET-type alloys doped with molybdenum have been recently reported. Most commercial applications of these materials are, however, not at dc but at high magnetizing frequencies. Therefore, we report a study of the frequency dependence of coercivity, $H_c(f)$, in amorphous and nanocrystalline ribbons of composition $Fe_{73.5}Si_{13.5}Nb_{3-x}Mo_xB_9Cu_1$ ($x=0$, 1.5 and 3) in the frequency range from 0.5 to 1.3 kHz. The nature of $H_c(f)$ measurements revealed the influence of eddy currents in the magnetization of samples. The frequency dependence of coercivity did not vary with the molybdenum content in the amorphous samples. All the alloys exhibited a systematic improvement in the coercivity after nanocrystallization and it was found that this improvement was better as more Nb was replaced by Mo.

1. Introduction

Over the past decades, there has been an immense interest in nanocrystalline soft magnetic materials due to their attractive magnetic properties compared to conventional crystalline alloys. In 1988 Yoshizawa et al. [1] developed the first nanocrystalline alloy, called FINEMET ($Fe_{73.5}Si_{13.5}Nb_3B_9Cu_1$), with low coercivity, saturation magnetization and high resistivity. The outstanding properties of FINEMET are due to its special two-phase structure, i.e., α''-$Fe_{1-x}Si_x$ crystals of 10–20 nm size embedded in an amorphous ferromagnetic matrix. This material is usually fabricated by a controlled annealing of an amorphous precursor, previously casted by the melt-spinning technique in the form of a ribbon. FINEMET-like alloys are suitable for a wide range of applications, particularly in ac field such as transformer cores, inductive devices, sensors, etc. [2]. It is therefore important to know the frequency dependence of their magnetic properties.

The coercive field or coercivity (H_c) is defined as the field at which the magnetization is reduced from remanence to zero. For a magnetization loop with peak magnetization M_{max}, $4H_cM_{max}$ gives the order of magnitude of the loop's area. Thus, H_c is a measure of the energy that is dissipated as heat in each magnetization cycle. The losses can be conventionally divided into three categories: hysteresis, classical eddy current and anomalous or excess components (Fig. 1). This division is artificial, since they actually do not arise from different sources, but allows treating loss mechanisms occurring on different space–time scales separately as if they were independent of each other. This subject is treated in detail in Refs. [3,4]. Hysteresis loss is due to the Barkhausen jumps between local energy minima, it is determined from the area of the static hysteresis loop and is assumed to be independent of the frequency of magnetization. The classical eddy current loss per cycle, which varies linearly with frequency, can be calculated from Maxwell's equations for a perfectly homogeneous material with no domain structure, where the boundary conditions of the problem are given by the geometry of the specimen. The so-called anomalous or excess loss increases with frequency but not linearly; it usually exhibits a rapid increase at low frequencies and then an almost constant positive slope. This component appears because the classical calculation of eddy current loss ignores the presence of domains and domain walls motion, which is damped by the eddy currents. As observed earlier, the three contributions to the energy loss have different dependences on with the magnetizing frequency. In spite of this, the total coercivity or loss has been sometimes approximated to one frequency dependent term $\sim f^{\alpha}$ [5–8].

In previous works, the structure and some magnetic properties of a series of FINEMET-like alloys with a partial replacement of Nb by Mo were studied. In Ref. [9] the magnetostrictive behavior of these samples was investigated, but no influence of the refractory elements exchange on the saturation magnetostriction (λ_s) was observed either for the as-quenched ($\sim$19 ppm) or for the annealed samples ($\sim$2 ppm). The phase transformations occurring during the crystallization process of the alloys were studied

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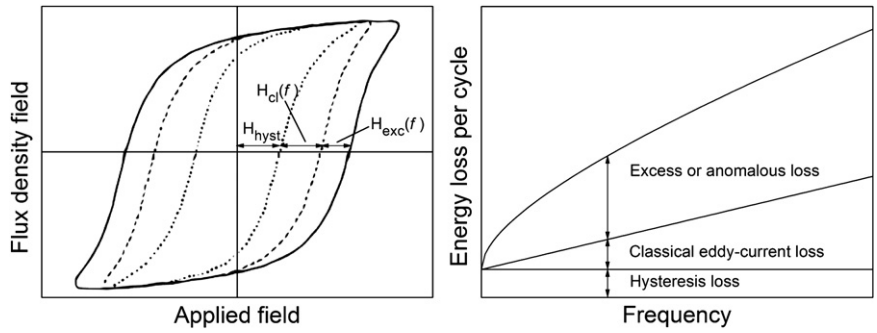

Fig. 1. Left: contributions to the coercivity in the hysteresis loop—static hysteresis, classical eddy currents and anomalous or excess field (modified from Ref.[3]). Right: contributions to the energy loss per cycle as a function of the frequency of the magnetizing field.

in Ref. [10] by a variety of techniques, including differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetric analysis (TGA) under a magnetic field, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The thermal stabilities of both the ferro-paramagnetic transition of the amorphous phase and the precipitation of the α''-$Fe_{1-x}Si_x$ phase were found to deteriorate when Nb was gradually replaced by Mo. Since Mo has a smaller atomic size than Nb, the Fe–Fe interatomic distances in the as-quenched amorphous samples became shorter when Nb was replaced by Mo. This explains why the exchange interaction among Fe atoms and therefore the Curie temperature of the amorphous phase, decreased after the substitution. Furthermore, the inhibition of diffusion of Fe and Si atoms was systematically weakened and thus, α''-$Fe_{1-x}Si_x$ crystallization began at lower temperatures for the same continuous heating runs. For 1 h isothermal annealing at 813 K, a linear increase of the mean grain size was observed with the addition of Mo (from 9.1 to 11.6 nm). The samples annealed at 813 K for 1 h were also studied in Ref. [11] by means of Mössbauer spectroscopy and quasistatic magnetic measurements. In that work, the fractions of various phases were estimated and it was observed that, when Nb was replaced by Mo, the crystalline fraction increased from 55 ± 2 to 66 ± 1 at%, in agreement with the thermal stability deterioration reported in Ref. [10].

The aim of this work is to present a study of the frequency dependence of the coercivity in as-quenched (amorphous) and isothermally annealed (nanocrystalline) samples of composition $Fe_{73.5}Si_{13.5}Nb_{3-x}Mo_xB_9Cu_1$ ($x=0$, 1.5 and 3), which will be called Mo0, Mo1.5 and Mo3, respectively. Some data on the magnetic properties of the amorphous magnetic alloys have already been reported with dc [12–13] or low frequency [14] magnetizing field. However, most of the commercial applications of these materials require higher frequencies. Therefore here we present coercivity measurements in the frequency range from 0.5 to 1.3 kHz, where the frequency dependence of coercivity is almost linear.

2. Experimental

Ingots of homogeneous compositions were prepared in an induction furnace. The amorphous samples were obtained in the form of ribbons $\sim$20 μm thick and $\sim$10 mm wide by planar flow casting in air at the Institute of Physics of the Slovak Academy of Sciences (Bratislava, Slovakia) with the help of RNDr. Dušan Janičkovič. The amorphous structure of the samples was checked by XRD. The composition of the samples was analyzed by inductively coupled plasma spectroscopy to confirm that the intended compositions were achieved. Finally, an isothermal annealing at 813 K for 1 in vacuum was performed to induce the precipitation of α''-$Fe_{1-x}Si_x$ nanocrystals.

Dynamic coercivity was measured from hysteresis loops (magnetic polarization, $J=\mu_0 M$, *vs.* applied magnetic field, H_a) with a specially designed experimental setup based on the inductive method [15]. The magnetic field was applied along the length of the samples with a sinusoidal waveform frequencies within the range 0.5–1.3 kHz and amplitude $\sim$4200 A/m (large enough to magnetically saturate the sample).

3. Results and discussion

The magnetic hysteresis loops of the alloys Mo0, Mo1.5 and Mo3 were recorded at different frequencies of the applied magnetic field in their as-quenched state (with amorphous structure) and after controlled annealing (with nanocrystalline structure). As an example, the loops measured for Mo3 at 0.5 and 1.3 kHz are shown in Fig. 2. It was observed that the as-quenched Mo3 did not saturate completely even at the maximum applied magnetic field (Fig. 2 left), whereas annealed Mo3 reached its magnetic saturation at quite low fields at all the measured frequencies, revealing the magnetic softening achieved after the controlled heat treatment (Fig. 2 right).

H_c was found to be higher at 1.3 than at 0.5 kHz both in as-quenched and annealed samples (Fig. 2). The frequency dependence of H_c exhibited an almost linear increase with frequency of the magnetizing field (Fig. 3).

All the as-quenched samples had approximately the same structural disorder and this was reflected in their similar magnetic behavior. The measured saturation magnetostriction was high ($\lambda_s \sim 19$ ppm) [9] and their domain structure was heterogeneous (it exhibited wide curved in-plane domains as well as island-like fingerprint domains with the magnetization oriented out of the plane of the ribbon [13]). In the present work, no appreciable difference among the H_c *vs.* frequency curves of the as-quenched samples was found (Fig. 3). The continuous increase of coercivity with increasing frequency was due to the eddy currents. When a magnetic field H_a is applied along a body, a flux density field B is induced in the material. If H_a varies with time, B and therefore the flux (ϕ) vary as well through the cross-section of the body. Thus, according to Faraday's law, an electromotive force (emf) will be induced in the specimen proportional to $d\phi/dt$ and, if the material is a conductor, this emf will cause an eddy current. The maximum of the applied field was kept constant in our measurements, so the flux rate increasedonly when the frequency of H_a was increased. During each cycle, as H_a increases, the eddy currents generate a magnetic field (H_{ec}) antiparallel to H_a. The resulting field will be the sum of both fields, H_a and H_{ec}. It follows that the true field acting on the material the interior of the specimen, where the contributions of all the eddy currents are added, becomes weaker. Hence the higher the frequency, the larger the eddy currents and the H_{ec},

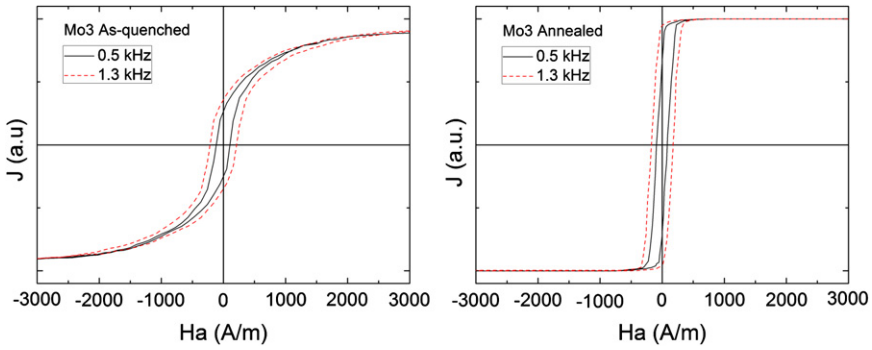

Fig. 2. Hysteresis loops at a frequency of 0.5 kHz (black solid line) and 1.3 kHz (red dashed line) of $Fe_{73.5}Si_{13.5}Nb_{3-x}Mo_xB_9Cu_1$ ($x=3$). Left: as-quenched ribbon. Right: annealed ribbon. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

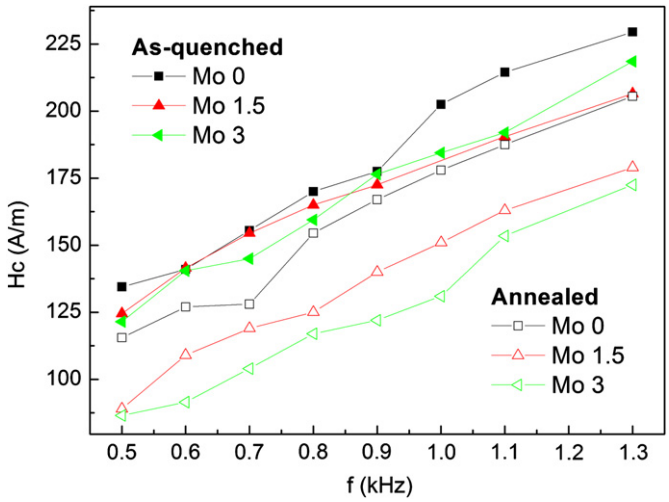

Fig. 3. Coercivity as a function of the frequency of the applied field for as-quenched (solid symbols) and annealed (empty symbols) samples. Lines between experimental points are drawn as guides for the eyes.

and the weaker the effective field. That is why the measured H_c was found to increase with increasing frequency.

Eddy currents can also give rise to other effects when a magnetic structure is present. It is well known that common ferromagnetic materials are subdivided into magnetic domains. In Ref. [13], detailed images of the complicated magnetic domain structures at the surface of a FINEMET ribbon were reported. The dominant mechanism driving the magnetization of the material under an externally applied field is the motion of the domain walls. The eddy currents are localized at the moving domain walls and are sometimes referred to as micro-eddy currents to distinguish them from the already described macro-eddy currents, although the latter are actually simply the vector sum of the former. Because the resulting field acting on the walls is less than H_a due to the eddy currents, the velocity of the walls is less than it would be if the eddy currents did not exist; that is, the wall motion is damped. But the damping effect is not linear with frequency. Strong eddy current effects may lead to drastic deformations of the moving domain walls; the wall tends to move ahead at the surface, where the eddy current field is small. Additionally the eddy current pressure may favor activation of otherwise pinned walls and/or break a wall, giving rise to new active domains, i.e., domains participating in the magnetization reversal processes. The mechanisms of wall bowing and dynamical wall multiplication increase the density of walls, which in turn decreases the velocity of every wall for a given flux change. Since the eddy current losses depend on the square of the domain wall velocity, these mechanisms reduce losses compared to rigidly moving walls. Evolution in the domain structure and the increase the activity of domain walls with increasing frequency were observed [16–19] and are the cause for the non-linear dependence of H_c and losses with increasing frequency. Within the range of frequencies studied in the present work, the number of active domains appears to have already been saturated since $H_c(f)$ had an almost constant slope. This is in agreement with Ref. [20], where the threshold of saturation in Fe-based amorphous ribbons was also reported to be at several hundred of Hz.

After the heat treatment was performed, the dynamic H_c decreased. The decrease of quasistatic H_c after the nanocrystallization of FINEMET is well known and has already been measured [12,13]. Such phenomenon may be partially ascribed to the structural relaxation, but the deepest magnetic softening is due to the α''-$Fe_{1-x}Si_x$ nanograins precipitation. As explained by Herzer [21] with the extended random anisotropy model, when the grain dimensions are kept below the ferromagnetic exchange length, the anisotropy of the homogeneously distributed nanocrystals averages out to zero. In addition, the composite structure leads to the compensation of λ_s between the amorphous (positive contribution) and the crystalline (negative contribution) phases, decreasing the magnetoelastic energy [9]. Therefore, the material is magnetically even softer than in the as-quenched state.

In annealed ribbons, dynamic H_c increased with increasing frequency with a slope close to that of as-quenched ribbons again because of the eddy currents. It seems quite reasonable that both kinds of samples, as-quenched and annealed, showed similar behavior, since the classical eddy current loss depends on the geometry of the sample, which barely changed after the heat treatment.

In Ref. [13] the static domain structure was found to change after the annealing and it was much more ordered due to the reduction of the magnetoelastic energy (because of the relaxation of the remaining stresses from the rapid quenching and the very low λ_s). As in the static case it is probable that under dynamic magnetization the nanocrystalline ribbons have a domain structure with smaller anisotropy than the as-quenched ribbons and, therefore, less pinning centers to overcome, resulting in smaller dynamic H_c and losses.

Contrary to the $H_c(f)$ plots of the as-quenched series, which did not change with chemical composition, the $H_c(f)$ curves corresponding to the annealed series showed improvement with increasing Mo content. The differences in the dynamic H_c of the ribbons should be due to different excess losses because hysteresis losses are very small and the contribution of the classical eddy currents should be similar for all the samples, as in the as-quenched series. The lower

dynamic coercivity or total loss was ascribed to stronger domain wall multiplication in materials with lower anisotropy. However, the magnetoelastic anisotropy is vanishingly small for all the ribbons and the remaining magnetocrystalline anisotropy should be higher for Mo-rich alloys since they have larger grains and larger crystalline fraction. The explanation of the dynamic coercivity improvement with increasing Mo is therefore still uncertain.

4. Conclusions

The frequency dependence of coercivity was studied in amorphous and nanocrystalline Mo-doped FINEMET ribbons. H_c was found to increase almost linearly with frequency for all the samples. The Mo content did not affect significantly the nature of the dependence of $H_c(f)$ in the amorphous samples. However, the alloys showed a systematic improvement in dynamic H_c after nanocrystallization and the improvement was better the larger the Nb replacement by Mo.

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