Thermal behavior for a nanoscale two ferromagnetic phase system based on random anisotropy model

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ABSTRACT

Advances in theory that explain the magnetic behavior as function of temperature for two phase nanocrystalline soft magnetic materials are presented. The theory developed is based on the well known random anisotropy model, which includes the crystalline exchange stiffness and anisotropy energies in both amorphous and crystalline phases. The phenomenological behavior of the coercivity was obtained in the temperature range between the amorphous phase Curie temperature and the crystalline phase one.

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1. Introduction

Over the past few decades nanocrystalline magnetic materials have been investigated for their application in magnetic devices requiring magnetically soft materials such as transformers, induction devices, etc. These materials present optimal magnetic properties because of their microstructure, in which chemistry and structure vary at the nanoscale. The softest nanocrystalline grain structure magnetic materials, known to date, are the FINEMET [1] ($Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$) and NANOPERM [2] ($Fe_{88}Zr_7B_4Cu_1$) alloys. The FINEMET alloy exhibits excellent permeability (10^5 at 1 kHz), almost zero magnetostriction (2×10^{-6}) and high saturation magnetization ($B=1.2$ T). These excellent soft magnetic materials are based on a two phase microstructure consisting of nanocrystalline ferromagnetic grains surrounded by a ferromagnetic amorphous matrix. In order to control and obtain the optimal microstructure and properties, amorphous precursors produced by melt spinning are annealed at nearly 823 K, which is above the primary crystallization temperature of nearly 783 K. Several works have studied the influence of different elements on these alloys [3–8] and the state of the art has been reviewed in different works [9,10].

During the last fifteen years thermal dependence of magnetic properties of these materials has been studied and discussed from the theoretical point of view. Different authors have reported results on the thermal dependence of the coercivity as function of the annealing temperature [11–13]. For values between the

amorphous Curie temperature and the crystalline phase one, they found a singular behavior characterized by a rapid increase of coercivity with temperature. Hernando et al. [12] suggested that this behavior could be explained considering that the sample has two different coercivity contributions, one of ferromagnetic type and the other of superferro-paramagnetic type.

It is well known that the microstructure, magnetostriction, anisotropy, saturation magnetization, and grain size essentially determine the magnetic properties of a ferromagnetic material. The combination of small grain size and soft magnetic properties is surprising and very interesting from theoretical and technological points of view. The origin of the magnetic softness in these materials is due to the condition that the structural correlation length is shorter than the exchange (magnetic) correlation length (L_{exch}) over which spins are coupled via exchange interaction. Alben et al. [14] described the effective energy of the amorphous based on a statistical argument, the so-called random anisotropy model (RAM). This model considers a random anisotropy distribution, which determines an effective random anisotropy energy. In this model, the effective anisotropy density is given by the square root of the mean square fluctuation of the anisotropy within a volume determined by the exchange correlation length. Different authors have used this model to describe and understand the magnetic behavior of soft magnetic materials [12,15–17].

Particularly, Herzer [15] applied the RAM to the dependence of coercivity on the nanocrystals size, D. To do this, he considered an assembly of ferromagnetic coupled grains of size D with magnetocrystalline anisotropies K_{cr} randomly oriented. Based on these assumptions he obtained the effective anisotropy affecting the magnetization process, which can be written as $\langle K \rangle = (4/3)^3$

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$K_{cr}^4 D^6/A_{cr}^3$ where A_{cr} denotes the crystalline exchange stiffness. However, in this approximation the two phases character of the nanocrystalline alloy was neglected.

The aim of this paper is to clarify and improve this phenomenological model by introducing a new approach to the thermal dependence of the coercivity above the amorphous Curie temperature. To do this, a model of single domain ferromagnetic particles embedded in an amorphous paramagnetic matrix was considered. Based on the idea presented by Hernando et al. [12] thermal coercivity dependence studies were performed in the range between amorphous and crystallite Curie temperature.

Based on the approximation made by Herzer, Hernando et al. [17] proposed a phenomenological model but including the two-phase character of the nanocrystalline material. To take into account the influence of the amorphous phase they modified the crystalline exchange stiffness proposed by Herzer as $A_{cr} \rightarrow \gamma_A A_{cr}$ where $\gamma_A = e^{-A/L_{am}}$ is a parameter varying between 0 and 1 and is closely related to the amorphous exchange correlation length L_{am} and where Λ is the average distance between the surfaces of two adjacent crystallites.

Considering that amorphous phase anisotropy cannot be neglected, the anisotropy of the system will be $K = \sqrt{x^2 K_{cr}^2 + (1-x)^2 \langle K_{am} \rangle^2} = \gamma_K K_{cr}$ where $\gamma_K = \sqrt{x^2 + (1-x)^2 (\langle K_{am} \rangle / K_{cr})^2}$, x is the crystalline volumetric fraction and we considered the amorphous anisotropy as the mean value of the anisotropy in the amorphous phase ($\langle K_{am} \rangle$) obtained by Alben et al. [14] based on the random walk principle, being

$$\langle K_{am} \rangle = \frac{K_{am}}{\sqrt{N_{am}}}, \tag{1}$$

where N_{am} is the number of amorphous units surrounding the crystal defined as

$$N_{am} = \frac{(D+\Lambda)^3 - D^3}{\delta^3}, \tag{2}$$

where D is the structural correlation length of the crystalline phase (grain size), $\Lambda = D(1/x)^{(1/3)} - D$ is the distance between the different grains in the alloy and δ is the structural correlation length of the amorphous phase. Considering that

$$x = D^3/(D+\Lambda)^3, \tag{3}$$

and using Eqs. (1) and (2) the $\langle K_{am} \rangle$ can be expressed as

$$\langle K_{am} \rangle = \frac{K_{am}}{\left(\frac{1}{x} - 1\right)^{1/2}} \left(\frac{\delta}{D}\right)^{3/2}. \tag{4}$$

The effective magnetocrystalline anisotropy constant may have other contributions besides the magnetocrystalline anisotropy. The amorphous anisotropy constant is due to the residual stresses and the magnetoelastic coupling. The strength of the local magnetoelastic anisotropy can be written as

$$\langle K_{am} \rangle = \frac{3}{2} \lambda \langle \sigma \rangle, \tag{5}$$

where $\langle \sigma \rangle$ is the average absolute value of the residual stresses, and λ is the saturation magnetostriction of the isotropic amorphous.

The optimal magnetic correlation length (L_{exch}), with $L_{exch} \gg D$, will be determined by the spin fluctuation within the volume element (L_{exch})^3. Considering

$$\gamma_D = \begin{cases} \dfrac{1}{x} & \text{if } x > \dfrac{D^3}{L_{exch}^3} \\[2ex] \dfrac{D^3}{L_{exch}^3} & \text{if } x < \dfrac{D^3}{L_{exch}^3} \end{cases} \tag{6}$$

the effective macroscopic anisotropy $\langle K \rangle$ can be derived from random-walk considerations, in the same form that it was proposed by Alben et al. [14], to be

$$\langle K \rangle = \gamma_K \frac{K_{cr}}{\sqrt{N}} = K_{cr} \gamma_K \frac{\left(\gamma_D^{1/3} D\right)^{3/2}}{L_{exch}^{3/2}}, \tag{7}$$

Hence

$$\langle K \rangle = K_{cr} \gamma_K \gamma_{D^{1/2}} \frac{D^{3/2}}{L_{exch}^{3/2}}, \tag{8}$$

where

$$N = \frac{L_{exch}^3}{(\Lambda+D)^3} = \frac{1}{\gamma_D} \frac{L_{exch}^3}{D^3} = \frac{L_{exch}^3}{\left(\gamma_D^{1/3} D\right)^3} \tag{9}$$

From this last equation and considering the definition of Λ, it is easy to note that γ_D only depends on the volume fraction of the crystallites (x).

Minimization of the sum of exchange and anisotropy energies leads to the corresponding correlation length, which is $L_{exch} = 16A_{am}^2/9K_{am}^2\delta^3$ in an amorphous single phase [14] and $L_{exch} = 16A_{cr}^2/9K_{cr}^2 D^3$ in the case of a single crystalline phase [13].

For a two ferromagnetic phase system L_{exch} is given as

$$L_{exch} = \frac{16}{9} \frac{A_{cr}^2}{K_{cr}^2 D^3} \frac{\gamma_A^2}{\gamma_K^2 \gamma_D} = L_0 \frac{\gamma_A^2}{\gamma_K^2 \gamma_D} = L_0 \gamma_L. \tag{10}$$

This last expression was obtained replacing $A_{cr} \rightarrow \gamma_A A_{cr}$, $K \rightarrow \gamma_K K_{cr}$ and $D \rightarrow \gamma_D^{1/3} D$ in the exchange correlation length of a single crystalline phase and L_0 corresponds to the exchange correlation length of a single crystalline phase system. From Eqs. (7) and (10), the effective macroscopic anisotropy can be written, for $N \gg 1$ or $L_{exch} \gg D$, as

$$\langle K \rangle = \left(\frac{3}{4}\right)^3 \gamma_{eff} \frac{K_{cr}^4 D^6}{A_{cr}^3}, \tag{11}$$

where

$$\gamma_{eff} = \frac{\gamma_K^4 \gamma_D^2}{\gamma_A^3} \tag{12}$$

The γ_{eff} and γ_L are dimensionless coefficients and they are functions of the volume fraction of the nanocrystalline phase and the relative parameters of the material. These coefficients summarize the most important results of the two-phase system coupled through exchange interaction and random orientation anisotropies.

A useful expression to analyze possible influences of some parameters on the coercivity (H_C) of the material can be derived as a function of saturation magnetization (M_S) and the effective anisotropy constant $\langle K \rangle$ as follows:

$$H_C = p_C \frac{\langle K \rangle}{\mu_0 M_S}, \tag{13}$$

where p_C is a coefficient less than one, μ_0 is the vacuum magnetic permeability and M_S is the saturation magnetization of the two-phase material. Eq. (13) represents H_C as a function of crystalline fraction, relative exchange stiffness, relative anisotropies and grain size of the crystallites.

The maximum possible size D^* of the crystallites can be inferred from the assumption that $L_{exch} > x^{-1/3}D$:

$$D^* = \frac{16}{9} \frac{A_{cr}^2}{K_{cr}^2 D^3} x^{1/3} \frac{\gamma_A^2}{\gamma_K^2 \gamma_D} = \frac{L_0 \gamma_L}{x^{-1/3}} = L_{exch} x^{1/3}, \tag{14}$$

where $D^* > D$ is the maximum possible size for different values of exchange stiffness ($A = \gamma_A A_{cr}$) and relative anisotropy ($K_r = K_{am}/K_{cr}$). From Eq. (14) it can be seen that the behavior of this parameter is well related to the exchange length parameter.

It is interesting to note that in the limit when $x \to 1$, γ_D, γ_K and $\gamma_A \to 1$ so $\gamma_{eff} \to 1$ hence

$$L_{exch} = L_0 \approx \sqrt{\frac{K_{cr}}{A_{cr}}}, \tag{15}$$

$$\langle K \rangle = \left(\frac{3}{4}\right)^3 \frac{K_{cr}^4 D^6}{A_{cr}^3} \Rightarrow H_C = \left(\frac{3}{4}\right)^3 \frac{p_C K_{cr}^4 D^6}{\mu_0 A_{cr}^3 M_S}, \tag{16}$$

and

$$D*L_0 = L_{exch}, \tag{17}$$

On the other hand, when $x \to 0$ or $x < D^3/L_{exch}^3$, $\gamma_D = D^3/L_{exch}^3$ and $N=1$ hence

$$L_{exch}^4 = \left(\frac{4}{3}\right) \frac{A_{am}^2}{K_{am}^2} \Rightarrow L_{exch} = \left(\frac{4}{3}\right)^{1/4} \sqrt{\frac{A_{am}}{K_{am}}}, \tag{18}$$

and

$$\langle K \rangle = \langle K_{am} \rangle = \left(\frac{3}{4}\right)^3 \frac{K_{am}^4 \delta^6}{A_{am}^3}, \tag{19}$$

and

$$H_C = \langle K_{am} \rangle = \left(\frac{3}{4}\right)^3 \frac{p_C K_{am}^4 \delta^6}{\mu_0 A_{am}^3 M_S}, \tag{20}$$

which match the value obtained by Alben et al. [14].

Thermal dependence of the coercive field can be divided into two different ranges of temperatures. The first one between 273 K and the ferromagnetic–paramagnetic transition temperature of the amorphous phase ($T_C^{am} \sim 600$ K), and the second between T_C^{am} and 900 K. For temperatures below T_C^{am} the thermal behavior of H_C can be described using Eq. (20) considering $M_S = M_S(T)$. Turtelli et al. [18] propose, for Finemet type alloy, that $M_S(T)$ can be approximated as

$$M_S(T) = x M_S^{cr} \left[1 - \frac{T}{T_C^{cr}}\right]^\beta + (1-x) M_S^{am} \left[1 - \frac{T}{T_C^{am}}\right]^{\beta_{am}}, \tag{21}$$

where M_S^{cr} (M_S^{am}) is the saturation magnetization of the crystalline (amorphous) phase. The dependence on the temperature of $\langle K \rangle$ is principally through the thermal dependence of the amorphous stiffness as was proposed by Herzer [11,15]

$$A_{am} \propto M_{am}^2 \propto \left[1 - \frac{T}{T_C^{am}}\right]^{2\beta_{am}}. \tag{22}$$

For temperatures higher than T_C^{am}, H_C exhibits a singular behavior. The initial coupled system at low temperatures cross over to an *un coupled* system at high temperatures. This behavior is due to the decrease of L with the increase in temperature and the un coupling occurs when $L=D$ (dipolar magnetic interactions are neglected in this approach). This *un coupled* system could be considered as an ensemble of ferromagnetic particles through a paramagnetic phase. We can obtain the temperature dependence on the coercivity for temperature values higher than the Curie temperature of the amorphous inter-grain. To do this we used the general form of the coercivity [19] as follows:

$$H_C = \frac{p_C \langle K \rangle}{\mu_0 M_S(T)} \left[1 - \left(\frac{25 k_B T}{\langle K \rangle V}\right)^m\right], \tag{23}$$

where V is the volume of the crystallites supposed to be single domain particles and m is an exponent less than one.

In our approximation we considered that H_C corresponds to ferromagnetic grains surrounded by a paramagnetic phase. This phase appears due to the fact that L_{exch} diminish as a function of temperature from values higher than D to $L_{exch} = D$ when the amorphous ferromagnetic inter-grain phase is transformed in a paramagnetic phase under the influence of the magnetic mo-

ments of the grains. Replacing L_{exch} by D in Eq. (7) and considering that $\gamma_K = x$ and $\gamma_D = 1$ we obtain the following:

$$\langle K \rangle = \left(\frac{3}{4}\right)^3 x K_{cr}. \tag{24}$$

From this last expression we can observe that the average anisotropy obtained is less than the crystalline one while it is higher than the associated with the nanocomposite at temperatures below Curie temperature of the amorphous matrix, T_C^{am}. This result is well consistent because the anisotropy of the crystallites is averaged over all the volume crystallite plus the paramagnetic matrix. Hence the matrix acts as a reducer of the total anisotropy. Using the last expression given for $\langle K \rangle$ in Eq. (23) the coercivity will be

$$H_C = \left(\frac{3}{4}\right)^3 \frac{p_C x K_{cr}(T)}{\mu_0 M_S(T)} \left[1 - \left(\frac{25 k_B T}{(3/4)^3 x K_{cr}(T) V}\right)^m\right], \tag{25}$$

where $K_{cr}(T)$ is assumed to change as $(M_S^{cr}(T))^n$, $3 \le n \le 10$ for anisotropies between uniaxial and cubic, respectively, [11] and $M_S(T)$ is saturation magnetization of the nanocomposite.

The resulting saturation magnetization $M_S(T)$ can be expressed as

$$M_S(T) = x M_S^{cr}(T) + (1-x) M_S^{para}(T), \tag{26}$$

where $M_S^{cr}(T)$ depends on temperature as follows:

$$M_S^{cr}(T) \propto M_S^{cr} \left[1 - \frac{T}{T_C^{cr}}\right]^\beta, \tag{27}$$

$\beta = 0.36$ being the critical exponent. The saturation magnetization of the paramagnetic amorphous phase in the presence of an external field can be expressed as

$$M_S^{para}(T) = M_0 B_s(T, H_{am}) = N\mu_{am} B_s(T, H_{am}), \tag{28}$$

where $B_s(T, H_{am})$ is the Brillouin function, H_{am} is the field applied on the paramagnetic phase by the grains, N is the number of magnetic moment per unit volume and μ_{am} is the magnetic moment per atom in the amorphous phase. Hence the saturation magnetization of the sample becomes

$$M_S(T) = x M_S^{cr}(T) + (1-x) N\mu_{am} B_s(y), \tag{29}$$

where $y = N\mu_0 g \mu_B S H_{am}/K_B T$ with $H_{am} \propto M_S^{cr}(T)$. When the argument of the Brillouin function is small, the paramagnetic saturation magnetization can be approximated as

$$M_s^{para}(T) = \frac{M_S^{cr}(T) C_1}{T} \tag{30}$$

with $C_1 = c N\mu_0 g^2 \mu_{B^2} S(S+1)/3 k_B$ where μ_B is the Bohr magneton, g is the Landè factor and c is a constant less than one related to the geometric arrangement of the crystals.

Hence the temperature dependence of the coercivity will be

$$H_C \propto \left(\frac{3}{4}\right)^3 p_C \frac{x(M_S^{cr}(T))^{n-1}}{\mu_0 (x + (1-x) C_1/T)} \left[1 - \left(\frac{C_2 T}{(M_S^{cr}(T))^n T_C^{cr}}\right)^m\right], \tag{31}$$

with

$$C_2 = (4/3)^3 25 k_B T_C^{cr}/x D^3, \tag{32}$$

where $V = D^3$ is the volume of the crystallites.

From Fig. 1 we observed that the theory seems to be well consistent with the experimental results reported previously [11]. The results obtained are very interesting from the physical point of view, considering that could provide a useful tool to understand the magnetic behavior of systems such as Finemet and Nanoperm alloys. The crystalline fraction (x) of the material along with C_1 and C_2 determines the thermal dependence of the coercive field. These three parameters depend on thermal treatment and composition. The values of x, C_1 and C_2 in the simulation were
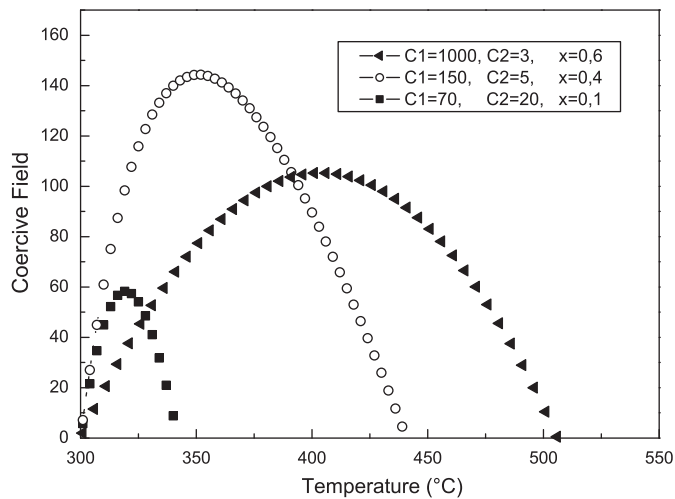
Fig. 1. Coercive field (H_C) as function of temperature, $m=0.5$, $n=4$.

chosen just to consider three possible examples. Eq. (31) reveals the magnetic behavior of the system for $T > T_{am}$. While the approximation reveals the origin of the singular bahavior of the coercive field with temperature, in order to achieve more detailed approximation other contributions need to be considered, for example the magnetic dipolar interaction.

In this paper we present an improved, more detailed, treatment of a two phase soft magnetic system, constituted by crystallites embedded in an amorphous matrix. The analysis is performed within an extended temperature range, both below and above the Curie temperature of the amorphous. Single domain ferromagnetic particles embedded in an amorphous paramagnetic matrix was considered to understand the coercivity behavior between the amorphous (matrix) and the crystalline (core) Curie temperatures. Based on these assumptions we obtained a good approximation to the singular experimental magnetic behavior of these types of materials in this temperature range.

Acknowledgments

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