Materials Science-Poland, Vol. 25, No. 2, 2007

Modelling of thermomagnetic curves obtained with Mössbauer spectrometry for two-phase nanocrystalline alloys

T. SZUMIATA*, M. GZIK-SZUMIATA, K. BRZÓZKA

Department of Physics, Technical University of Radom, ul. Krasickiego 54, 26-600 Radom, Poland

Thermomagnetic curves obtained with Mössbauer spectrometry for two-phase nanocrystalline alloys have been analyzed theoretically. The main goal was to understand a slope jump in the temperature dependence of the hyperfine field for crystalline phase of higher Curie temperature at the Curie point of the amorphous phase. We propose a simple model introducing an effective exchange integral for one phase depending on mean spin value in the other phase. We also consider a strong spin polarization of the amorphous phase by penetrating field originating from nanocrystallites. Results of numerical calculations within the mean field approximation (MFA) reproduce qualitatively the experimental curves for nanocrystalline FINEMET and Fe–Nb–B alloys.

Key words: *nanocrystalline alloy; thermomagnetic curve; two-phase coupled system; MFA approximation; Mössbauer spectrometry*

1. Introduction

Nanocrystalline magnetic alloys of two-phase structure have recently been the object of intensive investigations due to their great application potential as soft magnets. The interactions between grains determine the thermomagnetic properties of nanocrystalline alloys which cannot be explained just as a combination of the magnetism of the independent crystalline and amorphous constituents. The main goal of this work is to analyse peculiarities in the thermomagnetic curves of the nanocrystalline phase when exceeding the Curie temperature of the amorphous matrix which is significantly lower than Curie temperature of the crystalline phase. The experimental data [1–5] obtained with Mössbauer spectrometry are interpreted within a simple thermodynamical model with effective exchange interactions considering both spin relaxation effects and spin polarization of the amorphous matrix induced by nanocrystallites.

*Corresponding author, e-mail: t.szumiata@pr.radom.pl

2. Theoretical model

Thermomagnetic behaviour of a ferromagnetic grain immersed in a weakly ferromagnetic matrix has been systematically investigated by Monte Carlo simulations [6]. However, this analysis was limited to the case of low temperature spin ordering. Moreover, a single-grain approximation provided a good description for the matrix only, whereas it did not properly consider possible spin relaxation effects (like superparamagnetism and superferromagnetism), important for nanocrystalline grains. Thus in our work we have implemented a simple phenomenological model which takes into account changes of inter-grain coupling caused by the weakening magnetism of the amorphous matrix at higher temperatures.

We assume that in the system composed of two magnetically coupled phases of distinctly different Curie points, an effective exchange integral (say, for the second phase) takes the form:

$$J_2^{\text{eff}} = J_2(1 + q_2 < S_1^z > /S_1)/(1 + q_2) \tag{1}$$

where J_2 denotes the exchange integral for the second phase (a crystalline one) in a bulk form, $< S_1^z >$ and S_1 signifies the mean value of spin projection and spin number of the first phase (i.e., amorphous matrix), respectively, and q_2 is the dimensionless coupling coefficient which depends on the magnitude of possible spin relaxation and surface effects. At low temperatures $< S_1^z > /S_1 \to 1$ and $J_2^{\text{eff}} \to J_2$, because the entirely ordered magnetic system of the matrix suppresses spin relaxation of the strongly coupled grains. On the other hand, at temperatures above the Curie point T_{C1} of the matrix, $< S_1^z > /S_1 = 0$ and $J_2^{\text{eff}} \to J_2/(1+q_2)$, which means that due to spin relaxation effects the effective exchange integral value drops by the factor $1+q_2$.

The analytical calculations of the mean spin values $< S_1^z >$ and $< S_2^z >$ within the mean field approximation (MFA) applied to Ising spin system lead to the following equations:

$$\begin{aligned} < S_1^z > &= B_{S_1}\left(\frac{z_1 S_1 J_1 \cdot < S_1^z > \cdot (1 + q_1 \cdot < S_2^z > / S_2)/(1 + q_1)}{kT}\right) \\ < S_2^z > &= B_{S_2}\left(\frac{2 z_2 S_2 J_2 \cdot < S_2^z > \cdot (1 + q_2 \cdot < S_1^z > / S_1)/(1 + q_2)}{kT}\right) \end{aligned} \tag{2}$$

where B_{S1} and B_{S2} are the Brillouin functions, z_1 and z_2 are the numbers of the nearest neighbours of the spins in the first and the second magnetic subsystem, respectively, T denotes absolute temperature and k is the Boltzman constant.

In some nanocrystalline alloys the magnetization of the amorphous matrix has been observed not to vanish up to the Curie point of the grains [2–4, 6]. This phenomenon can be explained in terms of magnetic polarization of amorphous residual ma-

trix by penetrating exchange fields (of exponential decay) arising from nanocrystalline grains [6–8]. In our model, we consider these phenomena assuming that effective mean spin field felt by spins in the amorphous matrix is given by:

$$< S_1^z >^{\text{eff}} = < S_1^z > + q_1 < S_2^z > \tag{3}$$

in which q_1 (dimensionless quantity) describes the strength of the penetrating exchange field. Equation (3) has been introduced to the first dependence of Eqs. (2).

3. Model fitting to experimental data

The Mössbauer spectrometry (MS) provides information about magnetization state for various phases of the magnetic system, as well as for different magnetic sublattices within a given phase. Thus, this experimental technique is a very effective tool in the investigation of magnetically coupled systems such as nanocrystalline alloys. We have analyzed the MS thermomagnetic data available in literature for selected nanocrystalline materials and interpreted them in terms of our theoretical model. We have applied a simultaneous fitting procedure of theoretical curves with complete set of parameters for amorphous and nanocrystalline phases. Curves are the result of the numerical solution of the equations system (2) with fixed point method. For simplicity, we set spin numbers for both phases as $S_1 = S_2 = 1$ and coordination numbers as $z_1 = z_2 = 8$.

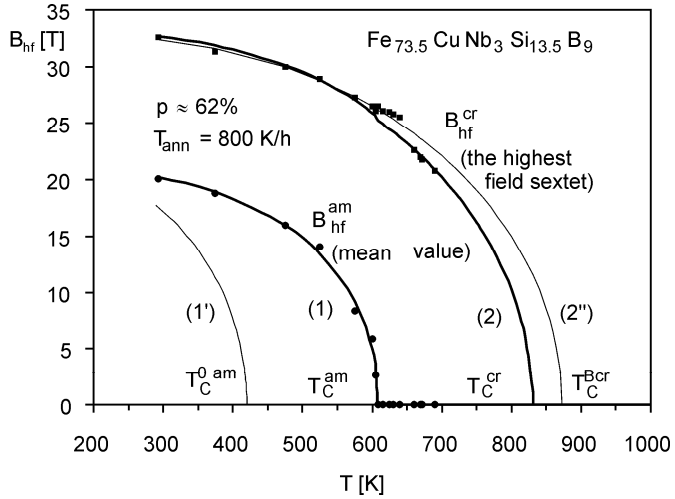

Fig. 1. Mössbauer experimental data [1] (points) and theoretical fits (thick solid lines) of thermal dependence of hyperfine magnetic fields for amorphous (1) and nanocrystalline phases (2) in FINEMET alloy. Additional thin solid line (1′) corresponds to the case of unpolarised amorphous matrix and line (2′′) is for the bulk crystalline phase

First, we examined a typical nanocrystalline FINEMET alloy of nominal composition $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$. The sample was obtained by the controlled isothermal annealing of metallic glass ribbons rapidly quenched at 803 K during one hour [1]. The crystalline volume fraction was estimated with Mössbauer spectrometry as p = 62%. Temperature dependences of hyperfine fields are shown in Fig. 1. For the amorphous matrix, mean values of broad hyperfine field distributions were calculated from MS spectra. Fe–Si nanocrystalline grains of the disordered DO_3 structure are represented in the MS spectra by several sharp sextets. In Figure 1, only the sextet of the maximum hyperfine field is considered (which corresponds to the Mössbauer nuclei surrounded by 8 iron atoms as their nearest neighbours). Since magnetic phase transition of the amorphous matrix occurs at well defined Curie point ($T_C^{am} \approx 609$ K), a model with an effective exchange interaction of the form (1) for both phases was applied in the fitting procedure. The estimated value of coupling parameter for the amorphous matrix is very high ($q^{am} \approx 0.6$), which means that without the ferromagnetic crystalline phase a Curie temperature of the amorphous matrix would be much lower ($T_C^{0\,am} \sim 420$ K – see Fig. 1). The experimental temperature dependence of hyperfine field for nanocrystallites shows a peculiar behavior in the vicinity of T_C^{am} of the amorphous matrix. The theoretical curve reproduces the main feature, i.e. a change of decay rate of hyperfine field with increasing temperature in the region above T_C^{am}, which can be interpreted as a signature of the spin relaxation effects in the grains. Though the estimated value $q^{cr} \approx 0.051$ seems to be relatively small, it results in a noticeable reduction of "bulk" value of the Curie temperature extrapolated from the region $T < T_C^{am}$ (i.e. $T_C^{B\,cr} \approx 873$ K) to the value $T_C^{cr} \approx 831$ K extrapolated from high temperature part of experimental data set (see Fig. 1). The former value corresponds to the Curie temperature of the bulk Fe–Si alloy of about 22% silicon content, which coincides with Si content in the grains determined on the basis of relative absorption areas of Mössbauer subspectra [1]. However, the theoretical model does not explain the question why the observed drop of the hyperfine field occurs not exactly at T_C^{am} (the hyperfine field almost does not change at all up to the temperature higher by about 30 K with respect to T_C^{am}). We suppose that the crucial role in this phenomenon could be played by the interface region between the grains and the amorphous remainder and it should be considered a third phase in the magnetically coupled system. However, in the case of FINEMET it is very difficult to separate the contribution of the interface layers because of the complexity of the Mössbauer spectra [1, 3, 10].

Another material analyzed in terms of thermomagnetic properties was the nanocrystalline $Fe_{80.5}Nb_7B_{12.5}$ alloy obtained by annealing of as cast amorphous ribbons for 1 hour at 783 K [4]. In the considered material, the grains are simple α-Fe phase of *bcc* structure. Thus they contribute to the Mössbauer spectra as a single Zeeman sextet, whereas the amorphous matrix is represented by very broad hyperfine field distribution (HFD). The volumetric fraction of crystalline phase was determined

as $p \approx 26\%$. High-temperature part of the hyperfine field evolution is presented in Fig. 2, for both the amorphous matrix (mean value of HFD) and nanocrystalline grains.

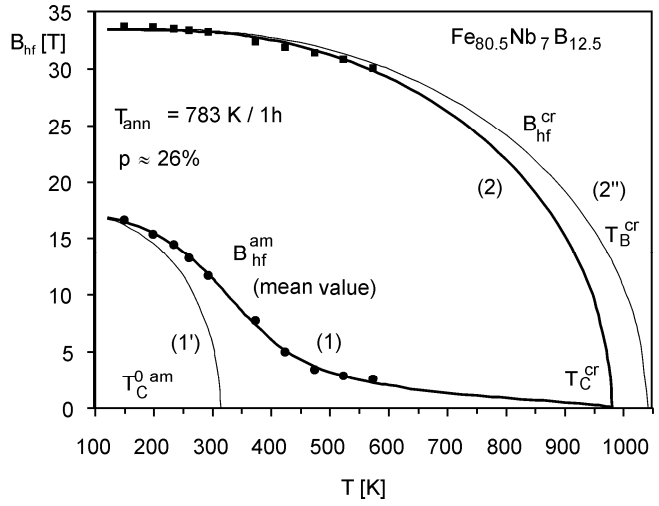

Fig. 2. Mössbauer experimental data [4] (points) and theoretical fits (thick solid lines) of thermal dependence of hyperfine magnetic fields for amorphous (1) and nanocrystalline (2) phases in Fe–Nb–B alloy. Additional thin line (1′) corresponds to the case of unpolarised amorphous matrix and line (2″) is for the bulk crystalline phase

A very distinct feature is that hyperfine field (and magnetization) of the amorphous matrix does not fall to zero in the temperature range covered in the experiment. This suggests that spin polarization of the matrix by penetrating exchange field resulting from grains is very strong and deep. Thus we applied a model which assumes that an effective mean spin field in the amorphous matrix takes the form of Eq. (3). This model fits very well the experimental points corresponding to the amorphous matrix for $q^{am} \approx 0.13$. Within our model the Curie temperature for amorphous matrix $T_C^{0\,am}$ without inter-phase magnetic coupling would be only about 313 K (Fig. 2), whereas predicted hyperfine magnetic field of amorphous matrix polarized by grains completely vanishes only at the Curie temperature of the crystalline phase. The theoretically estimated $T_C^{0\,am}$ well corresponds to the point above which an experimental thermomagnetic curve for nanocrystallites changes the rate of decay. However, this phenomenon is not as pronounced as in FINEMET because of muddy magnetic phase transition in the amorphous phase. The theoretical curve for grains generally reproduces this feature, the quality of the fit, however, is not perfect. Introducing into the model an experimental value of the Curie temperature for a bulk α-Fe phase ($T_C^{B\,cr}$ = 1041 K) we have estimated the value of the Curie temperature of the grain as $T_C^{cr} \approx 980$ K and the value of parameter $q^{cr} \approx 0.063$.

4. Conclusions

Our simple MFA model describes main features of thermomagnetic behaviour of nanocrystalline alloys considered as a magnetically coupled two-phase system in which both spin polarization of the amorphous matrix by the grains and spin relaxation effects in nanocrystallites are important. We obtained satisfactory fits of the theoretical model to the experimental data provided by the Mössbauer spectrometry for FINEMET and Fe–Nb–B alloys. The model qualitatively predicts the experimentally observed change of the slope of thermomagnetic curve for nanocrystallites above Curie temperature of the amorphous matrix, however it does not reproduce all details in the vicinity of this point (in particular, in the case of FINEMET). It also describes not vanishing magnetism of the amorphous matrix in Fe–Nb–B nanocrystalline material up to the Curie temperature of the strongly ferromagnetic grains. It is worth noticing that in Fe–Zr–B (NANOPERM) nanocrystalline materials magnetization of the amorphous material falls down even slower then in Fe–Nb–B [2] which cannot be explained in terms of the developed model. We intend to improve the model by considering the interface region as a third component of magnetically coupled nanocrystalline system as well as some inhomogeneity of the amorphous remainder. Both these factors are recognized as very important in the description of the magnetic properties of nanocrystalline alloys [2–6, 9, 10].

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Received 7 May 2006
Revised 1 September 2006