Materials Science and Engineering A 375–377 (2004) 219–222

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Superparamagnetic behaviour of $Fe_{80}B_{12}Zr_7Cu$ alloys with different fractions of primary nanocrystalline phase

T. Kemény [a,*], L.F. Kiss [a], D. Kaptás [a], J. Balogh [a], L. Bujdosó [a], J. Gubicza [b], I. Vincze [a]

[a] *Research Institute for Solid State Physics and Optics, P.O. Box 49, H-1525 Budapest, Hungary*
[b] *General Physics Department, Eötvös University, Budapest, Hungary*

Abstract

The superparamagnetic behaviour of nanocrystalline (nc) $Fe_{80}B_{12}Zr_7Cu$ alloys, having different amounts of body centred cubic (bcc) fraction controlled by DSC heat treatments was studied by high temperature SQUID magnetometry and Mössbauer spectroscopy. The granule diameter calculated from magnetic measurements is significantly higher than the X-ray determined grain size but is proportional to that value. The superparamagnetic behaviour is observed at substantially lower temperatures by the Mössbauer spectroscopy than by the macroscopic magnetisation studies, which means that the applied magnetic field significantly influences the superparamagnetic behaviour.

Keywords: Nanocrystal; Superparamagnetic relaxation; Magnetic properties; Mössbauer study

1. Introduction

One of the most intensively studied topics of solid state physics and material science is the magnetism of nanoscale systems. Superpara-magnetism (SPM) which is characteristic for nanosized magnetic particles is quite important in this respect [1]. Nanocrystalline (nc) samples, produced by the controlled crystallisation of amorphous ribbons, are especially useful since fully compact probes are produced with easy control of particle size and packing fraction. Some reports of superparamagnetic behaviour in this type of alloys were already published [2–4]. These results, however, refer only to low nanocrystalline fractions. Since SPM behaviour is observed in a fully nanocrystallized $Fe_{80}B_{12}Zr_7Cu$ sample [5] it has became possible to study the magnetic behaviour between wide limits of nanocrystalline fractions and with different experimental probes, which is the aim of the present work.

2. Experimental

The amorphous $Fe_{80}B_{12}Zr_7Cu$ alloys were melt quenched in vacuum to typically 2 mm wide and 20 μm thick ribbons. A characteristic two-stage crystallisation process was observed where the first step is the formation of the nano-sized body centred cubic (bcc) Fe-rich alloy in the remaining amorphous matrix. Samples with controlled crystalline fractions were prepared in a Perkin-Elmer DSC2 calorimeter: the fully nanocrystalline sample was heat treated to the end of the first stage, i.e. to 100% nanocrystallization of the primary phase. Smaller nanocrystalline fraction samples were defined by the corresponding fraction of the evolved energy.

The nanocrystalline structure has been studied by X-ray diffraction (XRD) using a Philips X'pert diffractometer. The grain size has been determined by a modified Williamson–Hall procedure [6]. ^{57}Fe Mössbauer spectroscopy measurements were carried out between 12 and 750 K in a closed cycle cryostat below room temperature and in a special furnace at higher temperatures by using a conventional constant acceleration spectrometer with a 50 mCi ^{57}Co*Rh* source at room temperature. It is well known that the bcc contribution to the Mössbauer spectrum is composed of at least two six-line patterns [7] (i.e. Fe atoms with and without impurities in the first two co-ordination spheres). The resolution of this structure for lower bcc fraction samples and at higher temperatures is, however, increasingly difficult. It is even more complicated due to the broadening of the Mössbauer lines caused by the superparamagnetic relaxation. For this reason the bcc spectra are described in this work by a single six-line pattern with somewhat larger linewidth values.

* Corresponding author. Tel.: +36-1-395-9220; fax: +36-1-395-9278.
E-mail address: kemeny@szfki.hu (T. Kemény).

0921-5093/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2003.10.101

The magnetic behaviour was studied by a Quantum Design MPMS5 SQUID magnetometer up to 5 T between 4.2 and 750 K with a special high temperature inset. The magnetisation curve is described in the superparamagnetic regime by the sum of the Langevin curve and a normal paramagnetic contribution (i.e. which is linearly dependent on external magnetic field).

3. Results and discussions

The Mössbauer spectra of the samples with different nanocrystalline fractions are shown in Figs. 1 and 2 at 300 and 500 K, respectively. At 300 K the spectra show the well-known structure consisting of the bcc sextet (denoted by the broken line in Fig. 1) and the broad lines of the residual amorphous phase which is ferromagnetic (FM) at this temperature. Despite the systematic error due to the fitting of a single six-line pattern to the bcc contribution of the Mössbauer spectra [7], the degree of nanocrystallization defined by the evolved energy (DSC data) corresponds well to the bcc fraction determined by Mössbauer spectroscopy. The 500 K spectra, however, show a dramatic increase of the linewidth of the bcc contribution to the extent that no magnetic contribution of the bcc phase is resolved in the 10% nanocrystalline fraction sample. This behaviour is characteristic of the superparamagnetic relaxation of small particles, which is also observed in SQUID magnetometry, albeit in general at higher temperatures.

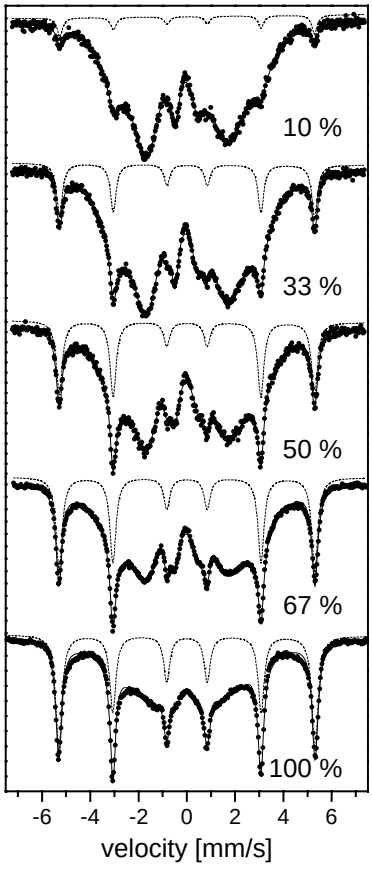

Fig. 1. Room temperature Mössbauer spectra of the different nanocrystalline fraction $Fe_{80}B_{12}Zr_7Cu$ samples. The full line is the fitted curve, the broken line is its bcc component.

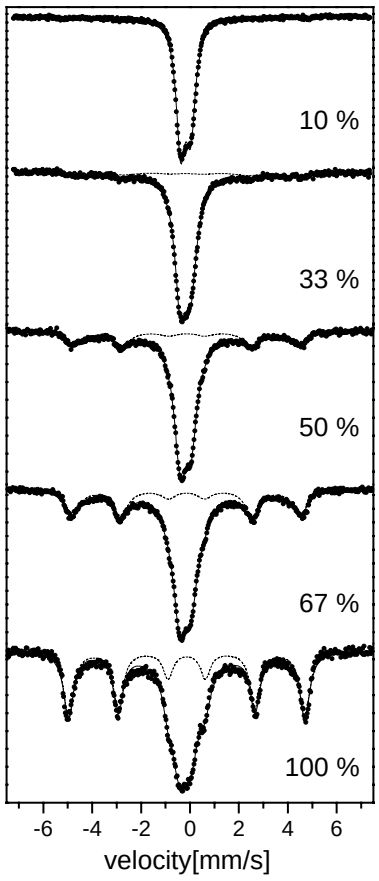

Fig. 2. Mössbauer spectra of the different nanocrystalline fraction $Fe_{80}B_{12}Zr_7Cu$ samples measured at 500 K. The full line is the fitted curve, the broken line is its bcc component. In the case of the 10% nc fraction sample no magnetic hyperfine splitting is observed and the bcc component is overlapped with the contribution of the residual amorphous phase.

The magnetisation curves of the 10% nanocrystalline fraction sample are shown in Fig. 3 at different temperatures. In contrast to the normal ferromagnetic behaviour observed at 300–400 K, the higher temperature regime shows a qualitatively different superparamagnetic dependence [8]. The higher nanocrystalline fraction samples show similar behaviour (not displayed in this paper), the SPM range is, however, shifted to higher temperatures. SPM behaviour is difficult to observe by magnetisation studies at and above 67% nanocrystalline fraction below 650 K; measurements at higher temperatures are complicated by the thermal decomposition of the nanocrystalline structure. The Langevin function fitted to the magnetisation curves in the SPM temperature range yields an average magnetic moment for clusters (which decreases slowly with increasing temperature) and their number. The magnetic moment of the cluster was converted to granule size using the values

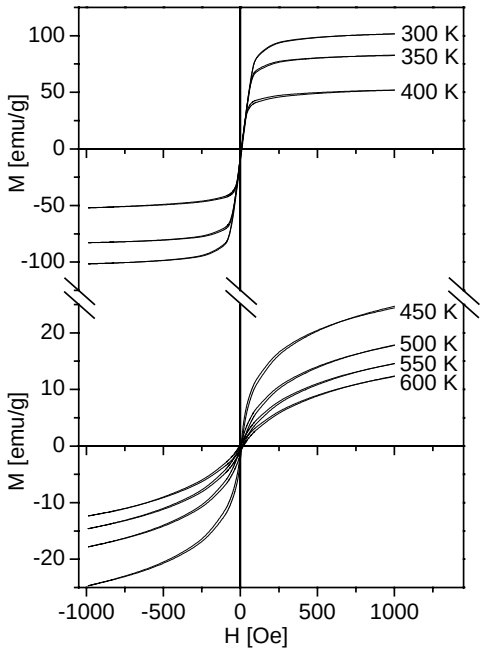

Fig. 3. The magnetisation of the 10% nanocrystalline fraction sample in the ferromagnetic and in the superparamagnetic temperature ranges in the upper and in the lower panel, respectively.

of the bcc magnetic moment obtained from the temperature dependence of the hyperfine field measured by Mössbauer spectroscopy. Fig. 4 shows that the magnetic size is proportional to that derived from the X-ray diffraction while its absolute value is significantly higher.

A basic difference is found, however, between the magnetic and the Mössbauer results. As is shown in Fig. 2 the Mössbauer spectra of all investigated samples show an enhanced bcc linewidth, which is clear evidence for superparamagnetic behaviour. On the other hand, it is shown in Fig. 3 that, even for the 10% fraction sample, the dominant magnetic character is ferromagnetic up to 400 K, see the de-

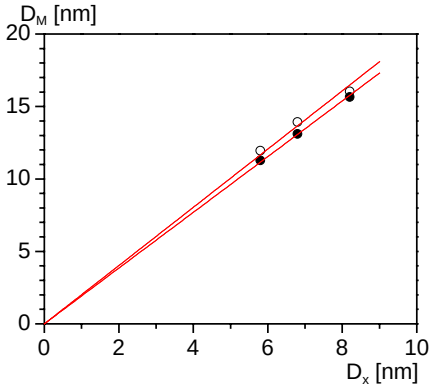

Fig. 4. The diameter of the bcc granules, D_M, determined from the Langevin fitting of magnetisation at 500 K (circles) and 550 K (dots), respectively, vs. the size, D_X, obtained from X-ray results for the 10, 33 and 50% nanocrystallized samples. The full lines show the proportionality of D_M and D_X.

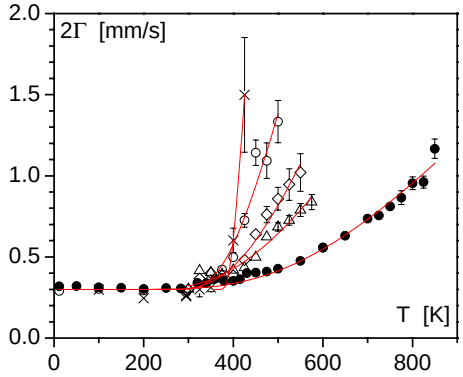

Fig. 5. Temperature dependence of the full linewidth at half maximum (2Γ) of the bcc component of the Mössbauer spectra in the 10% crystalline fraction (crosses), the 33% (circles), the 50% (diamonds), the 67% (triangles) and the 100% fully nanocrystalline samples (dots). Full lines are the Vogel–Fulcher type fits.

magnetisation controlled temperature independent slope at lower fields. This ferromagnetic-like behaviour is retained up to more elevated temperatures at higher nanocrystalline fractions, despite the SPM relaxation indicated by the significant broadening of the Mössbauer bcc lines. It seems that even a moderate magnetic field is capable of retarding the superparamagnetic precession by aligning the moment of the bcc granules.

The temperature dependent excess width of the bcc contribution to the Mössbauer spectra for the different nanocrystalline fraction samples is shown in Fig. 5. In the simplest approach this broadening may be described by an Arrhenius-type form, $2\Gamma = 2\Gamma_0 + Ae^{-\Delta E/k_B T}$, where $2\Gamma_0$ is the full linewidth without SPM relaxation, $\Delta E = KV$ the energy gap assuming uniaxial anisotropy (K is the magnetic anisotropy constant and V is the volume of the particle) and A the usual pre-factor [5]. This description applies reasonably for the 100% nc sample but it is inadequate for the low crystalline fraction samples as the fast increase of 2Γ for those samples shows. It seems that at low nanocrystalline fractions the stray magnetic field of the remaining amorphous matrix has a dominant influence on the relaxation behaviour. This influence may be taken into account by a Vogel–Fulcher type function, i.e. $2\Gamma = 2\Gamma_0 + Ae^{-\Delta E/k_B(T-T_0)}$, where T_0 is the characteristic temperature of this description. The fitting must be made with pre-determined values of A, as simultaneous fitting of all parameters is numerically unstable. The increase of T_0 with decreasing nanocrystalline fraction is shown in Fig. 6a, it approaches the Curie temperature of the residual amorphous phase obtained from the extrapolation of its low temperature hyperfine field values.

The activation energy, ΔE is, on the other hand, approximately proportional to the particle volume as is displayed in Fig. 6b. When the particle volume is determined from the XRD grain size, as is done in Fig. 6b, the derived anisotropy constant is 6.3×10^4 J/m^3 somewhat higher than the room temperature value for pure bcc Fe. This value is, however,

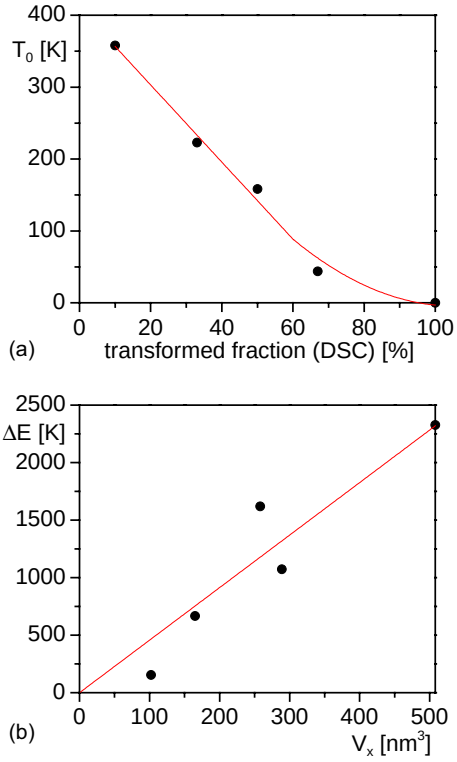

Fig. 6. (a) The characteristic Vogel–Fulcher temperature, T_0 determined by fitting the excess broadening of the bcc Mössbauer lines for the different nanocrystalline fraction samples. The line is guide for the eye. (b) The activation energy of the above mentioned fitting vs. the volume of the bcc granules as determined from the X-ray measurements for the different nanocrystalline fraction samples. The line shows the proportional dependence.

lower by almost an order of magnitude if the significantly higher magnetic grain size is used.

4. Conclusions

High temperature SQUID magnetometry and Mössbauer spectroscopy have been employed to observe the superparamagnetic relaxation behaviour in samples with different fractions of primary nanocrystalline phase. It was established that the magnetic cluster size determined from the superparamagnetic Langevin fit is proportional to the bcc grain size determined from the X-ray line broadening but it is significantly larger than this XRD value. The broadening of the Mössbauer line characteristic to superparamagnetic relaxation is observed at substantially lower temperatures than the superpara-magnetism detected in magnetic studies. The activation energy-determined by a Vogel–Fulcher type fit of the Mössbauer linewidth—is proportional to the volume of the magnetic granules. The superparamagnetic behaviour is only observed in magnetic measurements at higher temperatures due to the dominant influence of the external magnetic field absent in the Mössbauer spectroscopic studies.

Acknowledgements

The co-operation of V. Franco, whose stay is financed by WP9 of the Budapest Condensed Matter Research Centre, useful advises of Prof. T. Ungár and the financial support of OTKA T-30753 and T-038383 appreciated.

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