Magnetic properties of Fe–Ag granular alloys

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A R T I C L E   I N F O

Article history:
Received 30 August 2007
Received in revised form 15 July 2008
Accepted 25 July 2008
Available online 6 December 2008

Keywords:
Granular alloys
Magnetic anisotropy
Mössbauer spectroscopy
Bulk magnetization

A B S T R A C T

A discontinuous Fe/Ag multilayer and a granular alloy, both with the overall nominal composition of Fe10Ag90, were studied by bulk magnetization and Mössbauer spectroscopy measurements. The superparamagnetic blocking temperatures, as measured by the low-field susceptibility, agree quite well but the external-field dependence of the magnetization shows large difference for the two samples at all temperatures and the grain sizes obtained from a Langevin fit to the bulk magnetization differ in almost a factor of two. The discrepancy is attributed to the different directions of anisotropy in the samples, as observed by Mössbauer measurements as well as by comparison of the magnetizations measured in parallel and perpendicular applied fields. Similar grain size is obtained for the two samples by both techniques when a simple large-field approximation (M(H) ~ M(∞)(1 − kTSUB/H)) is applied in the calculations.

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1. Introduction

Granular alloys are nano-scale composites of two non-mixing elements, i.e. of elements with a positive heat of mixing. Thin films of these materials are generally prepared by co-evaporation or co-sputtering of the elements, but discontinuous multilayers or, as these are frequently called, granular multilayers also belong to this category. In case of the Fe–Ag system the nano-size Fe grains show superparamagnetic properties which are basically determined by the size and the density of the Fe-grains. Determination of the size of superparamagnetic Fe clusters from the magnetic properties is an especially challenging task since the commonly used experimental methods (e.g. X-ray diffraction or transmission electron microscopy, TEM) fail to identify the clusters [1,2] when they are in the few nm range. The appearance of a perpendicular magnetic anisotropy below certain grain size [3] is an interesting although not fully understood property of the discontinuous multilayer type samples and it is interesting to see its influence on the evaluation of the magnetic grain size.

2. Experimental

The samples were prepared by evaporation from Knudsen cells in a molecular beam epitaxy (MBE) equipment onto Si(1 1 1) wafer. The Fe/Ag multilayer was prepared with a sequence of [0.2 nmFe/2.6 nmAg]75, which has an overall composition of Fe10Ag90, while the 80 nm thick granular alloy film with the same average composition was fabricated by co-evaporation. The multilayer and the granular film were covered by a 2.4 and 10 nm thick Ag layer, respectively, in order to prevent oxidation. For the purpose of the transmission Mössbauer spectroscopy measurements both samples were removed from the substrates with a Scotch tape and the removed pieces were cut into 8 × 8 mm² squares and stacked. The Mössbauer measurements were performed with a standard constant acceleration spectrometer and a Janis cryostat equipped with a 7 T superconducting magnet. The hyperfine field distributions were evaluated by allowing binomial distribution shapes [4]. For measuring the bulk magnetization, the multilayer sample was removed from the substrate with a Scotch tape and four pieces of 4 × 4 mm² squares were stacked. The granular alloy was measured in the as-received form after co-evaporation together with the substrate and also after removing from the substrate. The results were rather similar, therefore here we will use the magnetization data measured without the substrate. The bulk magnetization was recorded using a Quantum-Design MPMS-5S superconducting quantum interference device (SQUID) in wide temperature (5–300 K) and magnetic-field range (0–5 T).

3. Results and discussion

Fig. 1 shows the Mössbauer spectra of the discontinuous multilayer and the granular alloy measured at 4.2 K and in zero external-field. The spectra allow a separation into two components, as shown in Fig. 1, the ratio of the smaller hyperfine field component being about 53% and 50% for the multilayer and the granular sample, respectively. The low and high hyperfine-field (hf) components were shown to be associated [5] with Fe atoms at the surface and in the volume of the grains. The small difference in the ratio of the surface components (see subspectra in Fig. 1) indicates a smaller than 20% difference of the average grain sizes. The grain size can also be calculated from the external-field dependence of the hyperfine fields [6,7]. Applying the hf(H) ~ hf(∞)(1 − kT/H) approximation for H/kT > 1 (where H is the applied field, k is Boltzmann’s constant, T is the temperature, and μ is the magnetic moment of the cluster),
the estimated magnetic moment of the Fe clusters was also found to be similar [8], about 800 $\mu_B$ for both samples.

From the spectra shown in Fig. 1 conclusions can also be drawn on the anisotropy of the samples. The different intensity ratios of the 2nd and 5th lines in case of the two samples indicate different anisotropies; the spontaneous magnetization of the discontinuous multilayer is oriented close to perpendicular to the sample plane while that of the granular alloy is close to parallel to the sample plane.

Fig. 2 shows the magnetization of the two samples as a function of temperature measured in a magnetic field of 100 Oe during warming after cooling the sample in zero field (ZFC) or in a field of 100 Oe (FC). A cusp-like behaviour characteristic of superparamagnetic particles is observed for the ZFC curves, giving blocking temperatures $T_B = 40$ and 45 K for the multilayer and the granular alloy, respectively. (The as-received granular alloy sample measured with the substrate gives a value of $T_B = 48$ K.) If $T_B \sim V$ is valid, the FC–ZFC curves are in line with the Mössbauer results (see Fig. 1) indicating a less than 20% difference of the cluster volumes.

Fig. 3a compares the magnetization curves of the two samples as a function of the applied field. For the comparison the magnetizations are normalized to the saturation value of the respective sample at $T = 5$ K. It is clearly seen from the measured points that the form of the magnetization curve is different for the two samples. The $M$–$H$ curves of the discontinuous multilayer can be adequately fitted by a Langevin function whereas for a good description of the field-dependent magnetization of the granular alloy, a linear term should be added to the Langevin function. However, the physical meaning of the linear term can be questioned. The grain sizes calculated from these fits differ by almost a factor of two for the multilayer and the granular alloy. Since both the Mössbauer results and the measured blocking temperatures indicate similar average grain size for the two samples, the deviation of the grain sizes calculated from the Langevin fits should be associated with the different
anisotropy directions of the samples. This statement is further supported by Fig. 3b where the magnetizations of the discontinuous multilayer measured in magnetic fields parallel and perpendicular to the sample plane are compared for selected temperatures. $M$ saturates in lower fields in the perpendicular geometry than in the parallel one, in line with the perpendicular magnetic anisotropy indicated by the Mössbauer spectrum for this alloy (Fig. 1a).

In order to get rid of the problem how the anisotropy direction affects the magnetization curves, they were also plotted as a function of the reciprocal applied field, $1/H$ and fitted as $M(H) \sim M(\infty)(1 - kT/\mu H)$, similarly to the Mössbauer studies [4,7]. This formula is the high-field limit of the Langevin function and therefore it is expected to be not influenced by any anisotropy present in the sample. As seen in Fig. 4a and b for the discontinuous multilayer and for the granular alloy, respectively, the linear variation is a good approximation in the field range of 30–50 kOe, depending on the temperature. The calculated cluster moment is fairly constant above 100 K and is almost equal for the two samples (around 430 and 500 µB for the discontinuous multilayer and for the granular alloy, respectively), in accordance with the Mössbauer study and the temperature dependence of the ZFC magnetization.

4. Conclusions

Superparamagnetic samples with equal Fe content (Fe$_{10}$Ag$_{90}$) were prepared both by sequential and co-deposition of the elements. A similar average size of the Fe grains and different anisotropy of the spontaneous magnetization were found by Mössbauer spectroscopy. The difference of the anisotropy directions in the two samples is also reflected in the different field dependence of the bulk magnetization, which prevents a reliable grain size determination from a Langevin-type fit. A simple large field approximation ($M(H_{ext}) \sim M(\infty)(1 - kT/\mu H_{ext})$) is shown to give results consistent with those obtained by Mössbauer spectroscopy.

Acknowledgements

The financial support of the Hungarian Scientific Research Fund OTKA T 46795, T 48965 and OTKA-NKTH K 68612 is highly acknowledged.

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