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MAGNETIC PROPERTIES OF GRANULAR Fe-SiO FILMS

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Abstract - Granular Fe-SiO films were prepared by co-evaporating in a vacuum. Magnetic properties of the films were investigated by Mössbauer and magnetization measurements. The Mössbauer data suggest that the films consist of amorphous Fe-Si alloy particles with the size of nanometers. Superparamagnetic magnetization curves were well reproduced by considering the distribution of particle size and the magnetic dipole interaction between particles treated as the mean field.

I. INTRODUCTION

Magnetic properties of ferromagnetic fine particles embedded in insulating materials have been extensively investigated from viewpoints of both fundamentals and applications. It has been shown that metal particles in insulating materials such as oxides and fluorides can be prepared by co-sputtering or co-evaporation of two materials [1-3]. In this work, we show that amorphous Fe-Si alloy particles are prepared by co-evaporating Fe and SiO. The films of Fe-SiO were investigated by Mössbauer spectroscopy and magnetization measurements. Mössbauer spectroscopy was also used to examine the chemical state of Fe and showed that a Fe-Si alloy is formed. Magnetization curves in the superparamagnetic state were analyzed by considering the distribution of particle size and the magnetic dipole interaction between particles.

II. EXPERIMENTAL

The samples were prepared by co-evaporating two sources of Fe and SiO in a vacuum better than 5×10^{-6} Pa. The films were deposited onto polyimide films placed on a holder cooled by liquid nitrogen during the deposition. Deposited amount of each material was monitored independently by two quartz oscillators. The volume fraction x_v of Fe was calculated from the deposited amount of each material. The thickness of the films is typically 0.5 μm.

Small flakes were prepared by scratching the films for TEM observations. Transmission Mössbauer spectra were recorded at temperatures from 4.2 K to room temperature by using a conventional constant-acceleration spectrometer with a ^{57}Co/Rh source. Magnetization was measured with an alternating force magnetometer at temperatures from 10 K to room temperature. Magnetic fields up to 1.0 T were applied for the measurements in the directions parallel and perpendicular to the film plane.

III. RESULTS AND DISCUSSION

We show the results of TEM, Mössbauer and magnetization measurements for two samples: A, x_v=0.25 and B, x_v=0.50. The substrate temperature during the deposition was about 110 K.

Granular structure was observed by TEM as shown in

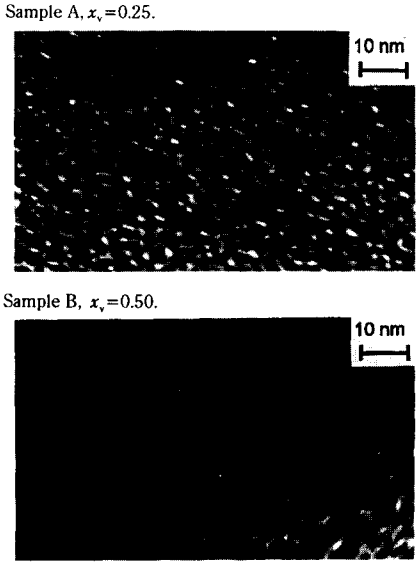

Fig. 1 TEM micrographs for indicated volume fractions x_v of Fe.

Fig. 1. It was found that the grain size is approximately 2 nm in sample A and 4 nm in sample B. The electron diffraction for each sample showed a halo pattern typical for amorphous structure.

Figure 2 shows Mössbauer spectra for sample A. The spectra show that the sample is superparamagnetic around room temperature. Hyperfine splittings appear with decreasing temperature. The blocking temperature T_B is estimated to be about 80 K.

The spectra in the superparamagnetic state clearly show quadrupole splittings. As shown in Fig. 2(a), the spectrum at 293 K is mostly reproduced by superposing two symmetric doublets. The obtained Mössbauer parameters are summarized in Table I. The spectrum at 4.2 K contains no superparamagnetic component and have broad lines indicating the

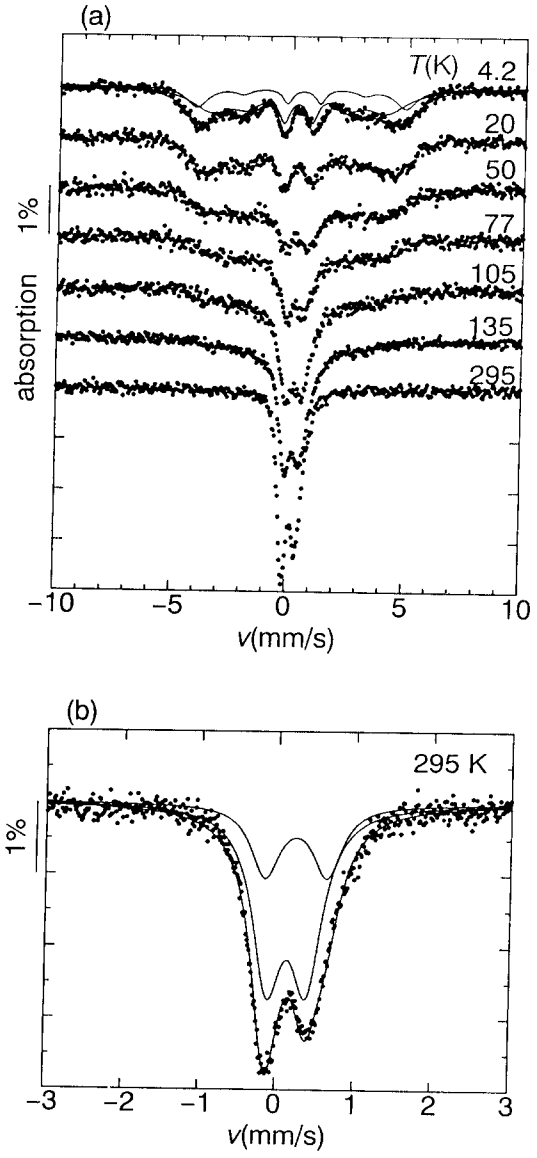

Fig. 2 Mössbauer spectra of sample A (x_v=0.25) at indicated temperatures.

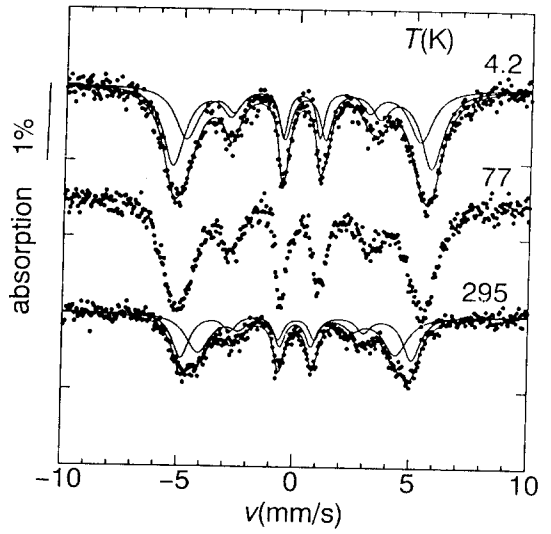

Fig. 3 Mössbauer spectra of sample B (x_v=0.50) at indicated temperatures.

Table I. Mössbauer parameters for each component at indicated temperature T: isomer shift IS in mm/s, quadrupole splitting QS in mm/s, hyperfine field B_{hf} in T and relative area in %. The values of IS are relative to α-Fe at room temperature.

Sample A, x_v=0.25.

T	IS	QS	B_{hf}	Area
295	0.13	0.51	---	71
	0.24	0.80	---	30
4.2	0.25	0.04	23.5	70
	0.41	-0.12	27.9	30

Sample B, x_v=0.50.

T	IS	QS	B_{hf}	Area
295	0.08	0.05	26.3	54
	0.09	-0.01	30.8	46
4.2	0.18	0.09	31.2	42
	0.25	-0.11	34.4	58

Journal of Korean Magnetics Society, Volume 5, Number 5, October 1995

distributed hyperfine field B_{hf}. For evaluating the Mössbauer parameters, we tentatively made the fitting of the spectrum by two components. The value of B_{hf} at 4.2 K on average was obtained to be 25 T, which is pronouncedly smaller than that of bulk Fe, 34 T. It is to be noticed that the small value of B_{hf} is not from superparamagnetic fluctuations [4] because the spectra at 4.2 K and 20 K have similar B_{hf}.

Sample B with x_v=0.50 shows ferromagnetically split spectra at all temperatures as shown in Fig. 3. The result shows that T_B is higher than room temperature because of the larger particle size than sample A. The broad lines indicates the distributed B_{hf}. The average value of B_{hf} at 4.2 K was calculated to be 33 T, which is still smaller than that of bulk Fe. For each sample, we find no sign of the formation of iron oxide, which has B_{hf} larger than 40 T.

It has been reported that, in Fe-Si alloys, Si atoms reduces B_{hf} of Fe atoms in the surrounding sites [5]. In amorphous Fe-Si alloys, B_{hf} is continuously reduced by increasing the concentration of Si [6]. Thus, the small value of B_{hf} in our samples is most reasonably understood by considering that Fe is in an amorphous Fe-Si alloy, resulting from the chemical reaction of Fe with SiO. The amount of Si in the alloy particles seems to increases with decreasing the Fe fraction. The spectra in the superparamagnetic state, indicating quadrupole splittings, are also reasonable for an amorphous Fe-Si alloy.

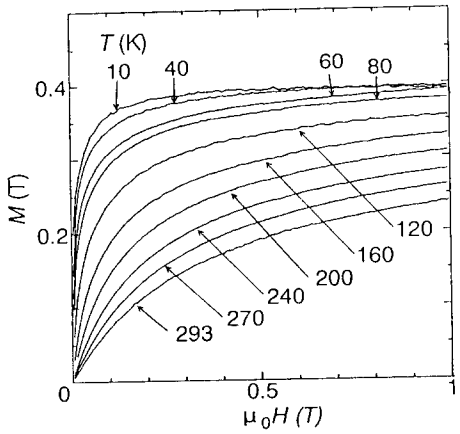

Fig. 4 Magnetization curves of sample A at each temperature. Date were taken with decreasing magnetic field applied in the direction parallel to the film.

It is to be noticed that the intensities of the 2nd and the 5th lines of the ferromagnetic spectra are weak. The results suggest that the perpendicular anisotropy is induced in this material. The intensity ratio of the 1st and the 2nd lines was calculated to be about 3:1 for both samples at 4.2 K, while 3:2 is expected for the case that the direction is random. The perpendicular anisotropy possibly comes from some configuration of the particles. It seems to occur that the particles forms chains perpendicular to the film plane, for example. Detailed investigations, however, are needed to clear this problem.

In Fig. 4, we show magnetization curves for sample A with x_v=0.25 measured in parallel fields. Superparamagnetic behavior was also observed in the magnetization measurements. The blocking temperature T_B, above which no hysteresis is observed, is estimated to be 60 K, consistently with the results of Mössbauer spectroscopy. Coercivity increases with decreasing temperature. The value at 10 K is $\mu_0 H_c$ = 4.4×10^{-3} T in parallel and 1.3×10^{-2} T in perpendicular fields. In contrast, magnetization curves of sample B with x_v=0.50 have hysteresis in the temperature range below room temperature. Coercivity at 10 K was $\mu_0 H_c$ = 1.2×10^{-2} T in parallel and 3.2×10^{-2} T in perpendicular fields. Thus, we find the effect of the perpendicular anisotropy as larger H_c in the perpendicular fields.

The magnetic moment per Fe atom was calculated from the magnetization in the field of 1.0 T applied parallel to the film at 10 K, taken for the saturation magnetization. The obtained values are $1.5\mu_B$ for sample A and $2.1\mu_B$ for sample B. The moment in sample A is remarkably reduced comparing with the value of bulk Fe, $2.22\mu_B$. The result corresponds to that of hyperfine field.

We analyzed the superparamagnetic magnetization curves of sample A in the following way. Analyses were made for the curves measured in parallel fields, shown in Fig. 4. We assumed the logarithmic normal distribution function for the magnetic moment m of each particle. The distribution function is expressed by,

$$P(\ln m) = \frac{1}{\sqrt{2\pi}s}\exp-\frac{(\ln m-\ln m_0)^2}{2s^2}, \qquad (1)$$

where m_0 is the median and s is the dispersion of the distribution. The magnetization M per unit volume of the film at the temperature T is then expressed by,

$$M = N\int d(\ln m)P(\ln m)\cdot m\,L\left(\frac{mH_{eff}}{k_B T}\right), \qquad (2)$$

where N is the number of particles in the unit volume, k_B the Boltzmann constant and L the Langevin function. For including the magnetic dipole interaction between particles, we tried the mean field approximation by assuming the mean field to be the Lorentz field. Then the effective field H_{eff} is expressed by, $H_{eff} = H+M/3\mu_0$, where H is the applied field. The demagnetization field is not to be considered because the field is parallel to the film plane. We first evaluated H_{eff} from the experimental data and determined the parameters by using the eq. (2). We put a realistic restriction that s and N are temperature independent. Thus, only m_0 was taken as a temperature dependent parameter. The obtained values are $N=1.9\times10^{19}/cm^3$ and $s=0.84$. The value of m_0 is $1420\mu_B$ at 293 K and increases with decreasing temperature to $1820\mu_B$ at 60 K. By assuming that the particles are spherical α-Fe and using the moment per atom obtained from the saturation magnetization, the diameter corresponding to m_0 is calculated to be 2.5 nm. Although the size is ambiguous because the particles consist of a Fe-Si alloy, the composition of which is uncertain, the estimated size is consistent with the TEM observations.

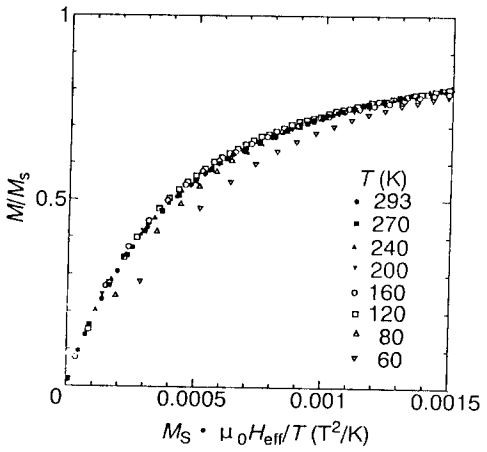

Fig. 5 Magnetization curves of sample A in parallel fields. M/Ms is plotted against $M_s\mu_0H_{eff}/T$ at each temperature T.

In Fig. 5 M/M_s at each temperature is plotted against $M_s\cdot\mu_0H_{eff}/T$, where the saturation magnetization M_s is calculated by the relation, $M_s = Nm_0\cdot\exp(s^2/2)$. We find the data at each temperature are mostly on the same curve, as expected for superparamagnetism. Although the M vs. H/T plot is usually used to show superparamagnetism, we need to include M_s for compensating the temperature dependence of the magnetic moment in this material. The points taken at 60 K and 80 K, however, show some deviation from the common curve. This seems to show that the mean field approximation is inapplicable at low temperatures. It is to be noted that no reasonable fitting was obtained if we do not account for the mean field $M/3\mu_0$, i.e., the dipole interaction.

IV. SUMMARY

Granular Fe-SiO films prepared by co-evaporation were examined by TEM, Mössbauer spectroscopy and magnetization measurements. It was shown that the films consist of fine particles of amorphous Fe-Si alloys with the size of nanometers. Perpendicular anisotropy was observed in Mössbauer spectra. The hyperfine field and the magnetic moment of Fe decrease with decreasing the fraction of Fe, because the content of Si in alloy particles increases. Magnetization curves in the superparamagnetic state were well reproduced by accounting for the magnetic dipole interaction by the mean field approximation. The distribution of the particle size was also considered in the analysis.

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