Size effect of magnetic properties in Fe–Al₂O₃ granular solids

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Abstract

Ultrafine Fe particles of nanometer size in Al₂O₃ insulating material have been obtained by rf magnetron sputtering. The structure of Fe particles is body-centered cubic, the same as α -Fe. However, small peaks corresponding to α -Fe₂O₃ diffraction start to appear at smaller Fe concentration and become more apparent as the Fe concentration decreases. The magnetic results indicate that the specific magnetization (σ_s) of iron particles for $x > 0.3$ at 5 K almost independent of Fe concentration. However, as x is below 0.30, σ_s shows a reduction. The saturation magnetization for $x = 0.10$ is only approximately 65% of pure iron. It is believed that a thin layer of non-magnetic α -Fe₂O₃ is formed on the surface of the Fe particle. Furthermore, Mössbauer spectra confirm the existence of α -Fe₂O₃ phase in the sample.

1. Introduction

Granular Fe solids have been studied extensively in the last few years [1]. This is because ultrafine Fe particles exhibit many magnetic properties that are quite different from those of bulk Fe. For example, a large coercivity of one magnitude higher than that of bulk Fe has been found for Fe granules [2]. In this work we describe the variation of magnetic properties when the particle size or dimension of ultrafine Fe particles in the insulating Al₂O₃ matrix is reduced.

2. Experiment

Granular Fe_x(Al₂O₃)_{1-x} films, where x denotes the relative volume fraction of Fe, were prepared by rf magnetron sputtering using composite targets. In order to be used for Mössbauer experiments, kapton foils were chosen as the substrates of films. The thickness of granular films were estimated to be several μ m.

After sputtering, the granular film structure was determined by X-ray diffraction and the microstructure of granules was investigated by TEM. The Fe composition was checked by electron probe X-ray microanalyzer (EPMA). The magnetic measurements were performed on a superconducting quantum interference device magnetometer (SQUID) as well as on a Mössbauer spectrometer between 5 and 300 K.

3. Results and discussion

In Fig. 1, examples of X-ray diffraction patterns for granular Fe–Al₂O₃ are shown. It indicates that a broad peak at $2\theta \approx 45^\circ$ has been observed, which is identified from the reflection of α -Fe phase. From the Scherrer formula, a broad peak indicates the appearance of fine crystallites in the film [3]. The width of this peak becomes larger as x is decreasing. This is consistent with the TEM results which show the reduction of particle size with x . Furthermore, additional peaks start to appear as x is smaller than 0.45 and become more apparent as x is

Fig. 1. Representative X-ray diffraction patterns for granular Fe_x(Al₂O₃)_{1-x} films.

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further decreased. These peaks can be attributed to the α -Fe₂O₃ phase.

The dependence of specific magnetic saturation magnetization (σ_s) at 5 K is plotted in Fig. 2. For $x > 0.30$, σ_s is almost independent of Fe concentration. As x decreases from 0.30, σ_s starts to fall and it drops to only 65% of $x > 0.30$ when x is 0.10. The values from our data for $x > 0.30$ are about 10% higher than that of α -Fe. In reality these values should be equal to that of bulk Fe, which is 218 emu/g. This is because an infinite network of connecting Fe granules is realized as x exceeds the percolation threshold [4]. This disagreement is probably caused by the uncertainty encountered in determining the mass of samples after removal from the substrates. As to the reduction of σ_s ; it is due to the formation of a thin layer of non-magnetic α -Fe₂O₃ on the surface of Fe particles. It should be noted that a clear-cut boundary between metal particle and insulating Al₂O₃ matrix material has been found previously [5]. However, this is not true in our case. Besides, it has been shown that Fe₃O₄ or γ -Fe₂O₃ phases exist on the surfaces of Fe particles prepared from evaporation in inert gas or intensively exposed in air [6]. This situation is also not discovered in our sample. From TEM results, the Fe granules can be reasonably assumed to be spheres with the mean radius r which is 50 and 70 Å for $x = 0.10$ and 0.30, respectively. The thickness t of the oxide layer was estimated from the reduction of σ_s as well as r . We obtain about 5 Å for t for all Fe concentrations, which is much smaller than the thickness of iron-oxide shell for Fe particles in the past [7]. The small amount of surface layer might cause the difficulty in detecting α -Fe₂O₃ in Ref. [5].

Representative Mössbauer spectra for granular Fe-Al₂O₃ at 300 K is shown in Fig. 3. For comparison, the spectrum of bulk Fe is also included in the figure. The spectrum for larger Fe concentration with $x > 0.45$ is essentially similar to that of pure iron. But the width of the absorption peaks becomes wider as x is closer to 0.45, the

Fig. 2. Specific magnetic saturation magnetization versus Fe volume fraction x for granular Fe_x(Al₂O₃)_{1-x} films.

Fig. 3. Representative Mössbauer spectra at 300 K for granular Fe_x(Al₂O₃)_{1-x} films.

percolation threshold. This result indicates a narrow distribution of the magnetic hyperfine field in the solid. The 6-peak spectrum collapses, becoming almost a single peak for $x = 0.40$ and a doublet for 0.10. The singlet for $x = 0.40$ is from the contribution of a small magnetic hyperfine field. The doublet is the result of superposition from a doublet of ultrafine Fe particles and another doublet of α -Fe₂O₃ on the surface. As is known, Fe particles behave superparamagnetic as the measurement temperature is higher than the blocking temperature of the sample. The blocking temperature, T_B has been determined below 300 K for $x \leq 0.30$ [3]. As a result, the ultrafine Fe particles should give a doublet Mössbauer spectrum. In order to clearly separate the contribution from Fe and α -Fe₂O₃, respectively, the Mössbauer measurement has to be taken at low temperatures, which is under investigation.

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