Magnetic anisotropy in Fe nanocrystals fabricated by GDM

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Abstract.

Ferromagnetic nanocrystals composed of nano-sized grains show excellent soft magnetic characteristics and their mechanism is explained by a random anisotropy model (RAM). We have been studying nanocrystal systems with ferromagnetic 3d elements to understand the RAM. Fe nanocrystals were fabricated with a gas condensation and deposition method (GDM). The oxygen content in an as-deposited Fe nanocrystal was about 20%. Hysteresis loop shifts observed in magnetic field cool measurements suggest the presence of antiferromagnetic oxides. Dependence of room temperature coercive forces on the grain size ($D$) is not $D^6$ but $D^{3.4}$. Magnetization curves often seen in thin films with stripe domain structures were observed at room temperature irrespective to the sort of substrates. The presence of perpendicular magnetic anisotropy was suggested.

1. Introduction

The discovery of superior soft magnetic properties in thermally recrystallized amorphous materials has accelerated researches of ferromagnetic nanocrystalline materials.[1, 2, 3] The coercive force was decreased with the decrease of grain sizes and this tendency was interpreted by Herzer using the random anisotropy model (RAM)[2]. The model clearly supports the theorem that the coercive force $H_C$ is proportional to $D^6$ of the grain size $D$ when the magnetic anisotropy is averaged in the magnetically coherent area including a large number of crystallites.

The RAM is based on a simple average of magnetic anisotropy over single phase grains. It has been extended to systems with two separated phases and systems accompanied by uniform uniaxial magnetic anisotropy.[3] Such extended models are suitable for practical materials made by thermal treatments of amorphous materials.[4] To understand the RAM in detail, for example the role of averaging of crystalline anisotropy, complicated systems are not suitable and studies on single element and single phase nanocrystals is desired. Fe and Ni nanocrystalline materials prepared using a gas condensation and compaction technique[5] have been reported, however, the results were not well supported by the simple RAM.

A gas condensation and deposition method (GDM) has been developed for the production of ferromagnetic nanocrystalline materials.[6] In the GDM, a simple process enables to prevent the surface contamination of ferromagnetic grains and single phase metallic nanocrystals can be produced. We demonstrated clear $D^6$ dependence of coercive force on the grain size of single
phase n-Ni prepared using GDM in the previous paper.[7] In this paper, structural and magnetic properties of Fe nanocrystals prepared by the GDM are reported.

2. Experimental procedure
Fe nanocrystals were produced with the GDM.[8] Ultra fine particles(UFPs) were prepared by heating Fe metal using a carbon crucible in an evaporation chamber keeping the He gas pressure at 500 - 760 Torr. The UFPs were transferred into a deposition chamber by the He gas flow resulting from the pressure difference and were deposited on a substrate up to several µm in thickness. In this process, nanocrystals are formed within a few milliseconds after generating UFP and the oxidization can be suppressed. Polyimide(@kapton) films, SiO$_2$ glass plates, MgO and NaCl single-crystal wafers were used as substrates.

X-ray diffraction (XRD) studies were carried out with a conventional diffractometer (Rigaku RINT 2000) with Cu-Kα radiation. The oxygen content was examined with Auger electron spectroscopy(AES). Thermal annealing was carried out in vacuum to increase grain sizes.

Magnetization curves were obtained using a vibrating sample magnetometer(VSM) at room temperature. In order to confirm the existence of exchange bias, magnetization measurements were carried out between 5 K and room temperature after magnetic field cooling from room temperature to 5 K.

![Figure 1](image1.jpg)

**Figure 1.** Effect of thermal annealing on the grain size of an Fe nanocrystal film prepared with GDM. Grain sizes are deduced from X-ray diffraction patterns with Scherrer’s equation (○) and Wilson’s method(△).

![Figure 2](image2.jpg)

**Figure 2.** Magnetization curves for as-prepared Fe nanocrystals measured at room temperature. Samples were prepared on the various substrates, Polyimide (Kapton®) films, SiO$_2$ glass plates, MgO and NaCl single-crystal wafers where the grain sizes were 9.5, 11, 7.8 and 7.8 nm, respectively.

3. Results and Discussion
The Fe nanocrystals prepared with the GDM have the bcc crystal structure same as that of bulk Fe metal and no trace of oxides was detected in as-prepared samples while 20% of oxygen atoms in the films was found by the AES study. This amount is remarkably higher than 5 at% of Ni nanocrystals[6] prepared with the same GDM. After thermal annealing, weak peaks of Fe
oxides may be observed in an X-ray diffraction pattern and the amount of oxygen atoms increased to \( \sim 29\% \) (AES).

Thermal annealing for 10 min was successively carried out on the sample to increase the grain size. Scherrer’s equation and Wilson method were adopted to evaluate the grain sizes from the X-ray diffraction patterns.[9] The typical results are plotted in Fig. 1. The sizes deduced by both methods showed almost the same values and increased with the increase of annealing temperature. We used the grain sizes obtained from Scherrer’s equation for convenience.

Magnetization was measured at room temperature for as-prepared samples grown on four kinds of substrate, Polyimide (Kapton®) films, SiO\(_2\) glass plates, MgO and NaCl single-crystal wafers. (See Fig. 2.) All curves have similar shapes which are often seen in thin films with a stripe domain structure. It is suggested that a weak perpendicular magnetic anisotropy exists. For Ni nanocrystals prepared with GDM, only the sample prepared on the SiO\(_2\) glass plates shows such a curve, while samples prepared on the polyimide film and KBr do not. The saturation fields are depend on the sort of substrates, while coercive forces are almost the same in amplitude.

![Figure 3](image1.png)  
Figure 3. Coercive forces of Fe nanocrystals plotted as a function of grains sizes. The fitting of coercive forces for regions, higher and lower than \( D_0 = 18 \) nm, leads to the index of - 2 and 3.4 for \( D^\delta \) relation, respectively. Solid lines show the result of the fit.

![Figure 4](image2.png)  
Figure 4. Hysteresis loop shift, \( \Delta H_C \), measured at the final temperature of magnetic field cooling. Samples of as-prepared, annealed at 300 and 450 °C were cooled from room temperature to the final temperature in a magnetic field of 2.5 kOe.

Coercive forces measured at room temperature are plotted against the grain size in Fig. 3. The coercive force increases as the grain size decreases and has a peak \( D_0 = 18 \) nm. Further decrease in grain size causes remarkable decrease in coercive force. This tendency is qualitatively resemble to those of nanocrystal magnets with random magnetic anisotropy. Coercive force were numerically fit to the relation of \( D^\delta \) and results were also plotted with solid lines. For the smaller grain size region, \( D^\delta \) was obtained to be 3.4 which was not coincide with 6 expected for regular RAM system, and rather close to 3, which is suit for the RAM system with universal anisotropy uniaxial anisotropy.[3] In the larger grain size region, \( \delta \) was obtained to be -2 and is not compatible to those from domain wall motion generally expected.

Coercive forces of Fe nanocrystals prepared with a compaction technique was reported.[5] The data clearly showed a peak of coercive force at around 30 nm and coercive forces decreased on
the both side. The tendency on the grain size is similar to the present result and determination of the index \( \delta \) seems to be difficult. In the case of Fe nanocrystals prepared by the compaction method, \( 6 \sim 12 \% \) of oxygen was found in the sample and may influence to the magnetic characteristics.

From the result of AES, it was confirmed that about \( 20 \sim 29 \at\% \) of oxygen atoms were included in the present sample. Mössbauer study on GDM Fe nanocrystals did not show clear evidence of paramagnetic and/or ferromagnetic Fe oxides in room temperature spectra and saturation magnetic moment was more than \( 90 \% \) of bulk Fe.[10] It implies that a part of the oxygen atoms detected by AES may not be coupled with Fe atoms.

To understand the influence of oxygen atoms, we have measured magnetization curves after magnetic field cooling from room temperature to the measuring temperature \( (T_m) \). Hysteresis loop shifts, \( \Delta H_c (= (|H_{c1}| - |H_{c2}|)/2) \) were plotted against \( T_m \) in Fig. 4. Here, \( H_{c1} \) and \( H_{c2} \) mean coercive forces for positive magnetic field and negative magnetic field, respectively. The hysteresis loop shifts increased below \( T_m < 50 \) K. This result indicates that some oxygen atoms form Fe oxides and it magnetically orders below 50 K. It is noted that the starting temperature of shifts slightly moved to higher, about 80 K, for the sample annealed at 450 °C, however, the amplitudes did not change much after annealing. It suggests that the number of oxygen atoms coupled with Fe atoms dose not change much and the crystalline state of the oxides become more sable by the thermal annealing. The starting temperature must be related to the sort of oxides, however, bulk antiferromagnetic Fe oxides such as Hematite \( (T_N = 950 \) K\) and FeO \( (T_N = 198 \) K\), have much higher ordering temperature than the starting temperature \( \sim 80 \) K\) which obtained in the present study. It is naturally observed in systems with thin oxide layers with small volume of antiferromagnetic materials.[11]

The Fe nanocrystals produced with GDM were found to include about 20 at\% of oxygen at the as-prepared state. The exchange bias was observed in the magnetic field cool magnetization measurements and it supports the presence of antiferromagnetic phase. From the magnetization curves, weak perpendicular magnetic anisotropy was indicated to present. This anisotropy may originate from the structure of grains or stress induced by the grain formation. Room temperature coercive forces have a \( D^{3.4} \) relation with the grain size \( (D) \), however its reason is not clear at the present stage.

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