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STRUCTURAL, MAGNETIC AND THERMAL CHARACTERIZATIONS OF Fe_2O_3 NANOPARTICLE SYSTEMS

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Abstract

X-ray, magnetic and differential thermal analysis and thermogravimetric (DTA-TG) measurements of Fe_2O_3 nanoparticles surrounded by amorphous SiO_2 were carried out. The mass loss above 370 K could be attributed to the dehydration. The broadened exothermic peak around 900 K was observed by the DTA analysis. Considering the results of the X-ray and magnetic analyses, this anomaly was interpreted as due to the γ- to α-transition in the present Fe_2O_3 nanoparticle system. The broadness of the peak and thus the gradual progress of the transformation would be attributed to the stress caused by the amorphous SiO_2 network surrounding extremely small particles.

Keywords: DTA-TG, iron oxide, magnetization, nanoparticle

Introduction

Nanoscience or nanotechnology has been one of the most important and interesting topics nowadays. Studies on nanometer-size systems are needed to be developed quickly and extensively. Especially, magnetic nanoparticles with large coercivity at room temperature are expected to realize the new high density magnetic recording materials.

Recently, the authors succeeded in producing Fe_2O_3 nanoparticles surrounded by amorphous SiO_2 networks [1]. In the study, diameters of the particles were confirmed by the X-ray diffraction patterns to be in between 1.3 and 23.1 nm depending on the annealing temperatures. Besides, the crystal structure of Fe_2O_3 nanoparticles changed from a spinel structure to a corundum one at the annealing temperature T_α of 1023 K. The sample annealed below T_α was only composed of γ-Fe_2O_3 particles, while the sample annealed at above T_α additionally contained the α-Fe_2O_3 phase.

As given in [1], the blocking temperatures T_B were obtained from the magnetization measurements, where T_B was defined as the temperature below which the anisotropy energy became larger than thermal energy and the Fe^{3+} magnetic moments in the γ-Fe_2O_3 nanoparticles would be blocked against the external field. The T_B of this system increased with the annealing temperature and annealing time. And the coer-

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cive forces H_c decreased as the annealing temperature increased and disappeared at T_B of 60 K in the sample annealed at 923 K, while it remained at about 1 kOe even at 300 K in the sample annealed at 1023 K for 10 h.

In the present report, the additional structural and magnetic results were given for the Fe_2O_3 nanoparticle system. In order to clarify the transformation process from γ-Fe_2O_3 to α-Fe_2O_3, differential thermal analysis and thermogravimetric (DTA-TG) measurements were also carried out.

Sample preparation

The Fe-hydroxide fine particles were produced by mixing aqueous solutions of $FeCl_2 \cdot 4H_2O$ and $Na_2SiO_3 \cdot 9H_2O$. The obtained precipitates were washed several times with distilled water and dried at about 350 K in the thermostat. They were rapidly oxidized into Fe_2O_3 particles in air through these processes. These samples were crushed in a porcelain mortar, and then baked in air at annealing temperatures of 473, 723, 923, 1023 and 1133 K in a furnace. For each annealing temperature, the annealing times were taken to be 4, 7 and 10 h.

Results and discussion

Preliminary data of CuK_α X-ray powder diffraction patterns are shown in Figs 1(a)–(e) for the samples annealed at 473, 723, 923, 1023 and 1133 K, respectively, for 7 h. The broad peaks at 2θ=35 and 60 degrees in Figs 1(a)–(d) were confirmed to be (311)-reflection and (440)-reflection of γ-Fe_2O_3, respectively, while that below 2θ=30 degree to originated from the amorphous SiO_2 [2]. In Fig. 1(d) for the sample annealed at 1023 K, additionally, broad peaks appeared at 2θ=33 and 61 degrees which corresponded to the (104)- and (214)-reflections of α-Fe_2O_3, respectively. As shown in Fig. 1(e), the sample annealed at 1133 K exhibited rather sharp peaks due to α-Fe_2O_3 particles with larger size, and there the broad peaks due to the γ-Fe_2O_3 nanoparticles clearly disappeared.

Table 1 γ and α mean the γ- and α-Fe_2O_3 phases, respectively. Average diameter (nm) of Fe_2O_3 particles

	4 h	7 h	10 h
473 K an. (γ)	1.5	1.6	1.7
723 K an. (γ)	1.6	1.6	1.7
923 K an. (γ)	1.7	2.0	2.4
1023 K an. (γ+α)	3.7	4.0	6.3
1133 K an. (α)	20.2	27.3	33.3

The average diameters of the particles were evaluated from the half width of X-ray diffraction peaks as given in Table 1. It is found that a larger diameter is obtained by increasing the annealing temperature and by elongating the annealing time.

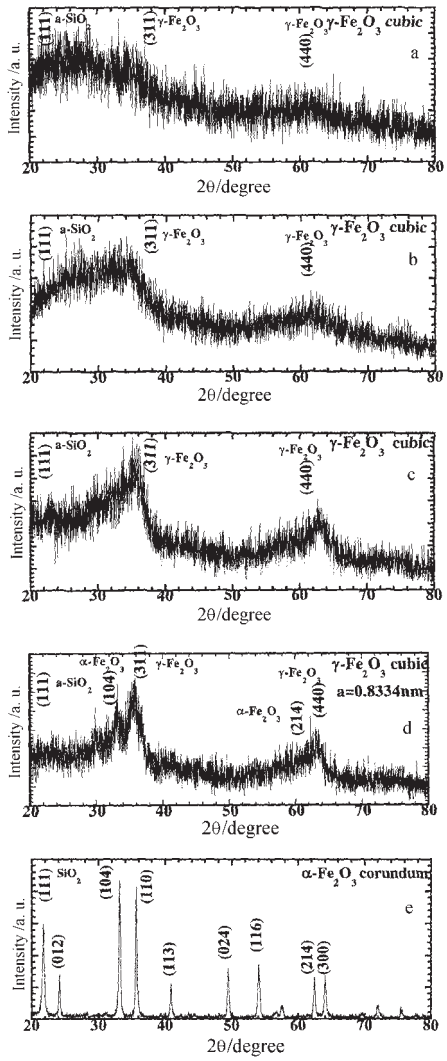

Fig. 1 Powder X-ray diffraction patterns for the samples annealed at 473 K (a), 723 K (b), 923 K (c), 1023 K (d) and 1133 K (e) for 7 h

The magnetization measurements were performed by the Quantum Design's MPMS SQUID magnetometer under the external field between –50 and 50 kOe from 5 to 300 K. For all of the samples, they were measured at 5, 20, 40, 60, 100 and 300 K. For the sample annealed at 1023 K, the *M–H* curves were additionally measured at 110, 120, 130, 140, 150, 200 and 250 K. The coersive force H_c was estimated from each magnetization curve. Temperature dependences of the H_c for the samples at 923 and 1023 K are shown in Fig. 2. The Morin temperature T_M, below which α-Fe_2O_3 re-orders into antiferromagnetic phase, was also indicated.

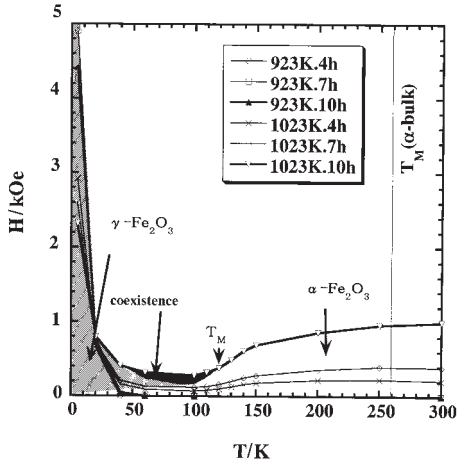

Fig. 2 Phase diagram of Fe_2O_3 nanoparticles concerning coersive force H_c, temperature, annealing time and annealing temperature

It is well known that the γ-Fe_2O_3 (maghemite) orders ferrimagnetically below the Curie temperature of T_C=1020 K, and that the α-Fe_2O_3 shows weak ferromagnetic phase below the Néel temperature of T_N=958 K [3, 4]. As shown in Fig. 2, the coexistence of γ-Fe_2O_3 and α-Fe_2O_3 phases was indicated for the sample annealed at 1023 K for 10 h from the temperature dependence of the coersive force H_c. It is suggestive that the transformation from the γ- to α-Fe_2O_3 is important to elucidate the magnetic behaviors of this sample.

In order to clarify the transformation process, differential thermal analysis and thermogravimetric (DTA-TG) measurements were carried out by ULVAC 700-RH under air circumstances, where the commercial bulk γ-Fe_2O_3 reagent was used as the standard sample. The measured temperature region was between room temperature and 1173 K.

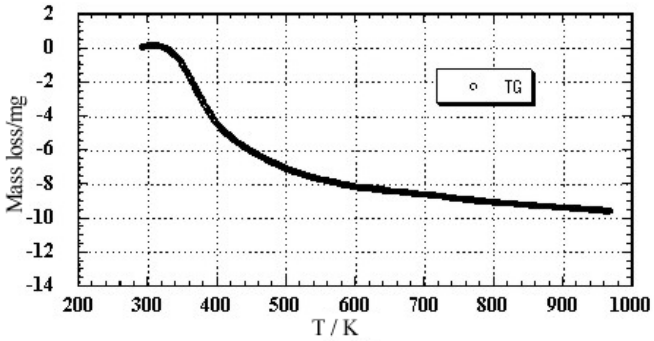

Fig. 3 TG curve of Fe_2O_3 nanoparticles measured under air

In the TG curve, the mass loss by dehydration was observed above 370 K, and then the sample mass gradually decreased at higher temperatures up to 1173 K, as shown in Fig. 3.

As for the DTA curve in Fig. 4, a broad endothermic peak was observed at around 363 K, corresponding to the above dehydration, while the two very broad exothermic peaks were observed at around 550 and 900 K, respectively. Considering the results of the X-ray and magnetic analyses, a DTA anomaly by the transformation from γ-Fe_2O_3 nanoparticle to bulk α-Fe_2O_3 can be expected to appear between 723 and 1133 K. Therefore the broadened 900 K peak was interpreted as caused by the γ- to α-transition in the present Fe_2O_3 nanoparticle system. Though the transformation from Fe_3O_4 to γ-Fe_2O_3 was reported for the acicular type Fe_3O_4 at 523 K [5], such a phenomenon could not be observed in the magnetization, X-ray and TG results for our nanoparticle system. So the origin of the broad peak at 550 K in DTA is unknown at present.

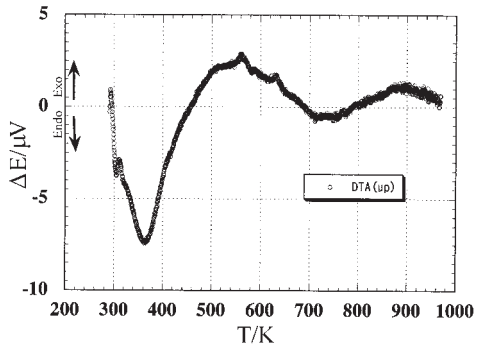

Fig. 4 DTA curve of Fe_2O_3 nanoparticles measured on heating under air in the temperature range between room temperature and 973 K

Now more detailed X-ray analysis should be needed for our samples annealed below 700 K. The broadness of these DTA peaks, namely, a very gradual progress of the transformation is probably due to the stress caused by the amorphous SiO_2 network surrounding these extremely small particles. To examine the above possibilities, the XAFS measurements are now prepared, and the successive results shall be reported in the near future.

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