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Magnetic and thermal studies of nano-size Co and Fe particles

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Abstract

The thermal and magnetic properties of nanocrystalline Fe, $CoFe_2$, and Co particles as well as their bulk samples were studied between room temperature and 900°C. From the thermogravimetric analyzer measurements, we have observed that near 200°C an endothermal signal occurs abruptly within 10°C for nanocrystalline Fe, and then this signal decreases with increasing temperature and shows a kink near 550°C. However, an exothermal signal starts near 200°C for nanocrystalline Co and $CoFe_2$, and it stops to decrease near 310°C and 440°C for Co and $CoFe_2$, respectively. Both endo- and exo-thermal effects near 200°C are related to the aggregation and oxidation of the ultra-fine particles. The kink near 550°C for Fe is related to the Curie temperature of Fe_3O_4. The magnetization of the ultra-fine particles was slightly smaller than that of the bulk samples, and it decreased very fast with increasing temperature between 100°C and 200°C. The coercivity of nanocrystalline $CoFe_2$ is roughly 1780 Oe, and is larger than that of Co ($H_c \sim 1198$ Oe) and Fe ($H_c \sim 883$ Oe). After annealing in air, the content of oxygen in nanocrystalline particles increases roughly to 40% for Fe particles, and roughly to 30% for $CoFe_2$ and Co particles. The oxidation is manifestly reduced after adding the Co element into Fe nanoparticles.

Keywords: Nanocrystalline; Ferromagnetism; Thermal property

1. Introduction

In recent years, research of ultra-fine magnetic particles has been active because of the potential applications in high density magnetic recording media. A large fraction of the atoms in ultra-fine particles are surface atoms; this has a significant influence on the thermal and magnetic properties [1–5]. Many investigations on the low temperature physical properties of the nano-size ferromagnetic particles have been reported [6–12]. Comparatively little effort has been devoted to the physical properties of these nano-particles at high temperatures. Therefore, it is very interesting to study the properties of these nano-size ferromagnetic particles at high temperatures. In this study, we report on studies of the calorimetric and magnetic behaviors at high temperatures for nano-size Fe, $CoFe_2$, and Co particles with average particle sizes of 20 nm as well as bulk Fe and Co.

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2. Experimental

The ultra-fine particles of Fe, $CoFe_2$, and Co with averaged particle sizes of about 20 nm were prepared by evaporation technique or bought from commercially available source. Powder X-ray diffractometer and transmission electron microscope (TEM) were used in crystal structure and particle size analyses. A thermogravimetric analyzer (TGA) with a permanent magnet system was used for thermal study measured in argon gas with flowing rate of 2 kg f/cm^2. The magnetization was studied by a vibrating sample magnetometer and a quantum interference device (SQUID).

3. Results and discussion

From the X-ray diffraction studies, the crystal structure of the nano-size Fe, $CoFe_2$, and Co agreed well with their bulk materials. From the TEM study we observed that the particle sizes were roughly 20 nm. According to the elements index analyses, the ratio of

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Co and Fe in nano-size Co–Fe particles was 1–2, and a very thin layer of oxide of the element was coated on the surface of the nano-size particles [13]. Fig. 1 shows as an example the powder X-ray diffraction patterns of nanocrystalline and bulk Fe samples. Both curves show almost the same peak positions (1 1 0) and (2 0 0) for α-Fe, except that the width of the peaks for nanoparticles is broadened than that of the bulk sample, and a (3 1 1) Fe_3O_4 peak has been observed near 36.82° for nanoparticles. In general, from the broadening of the peak of X-ray diffraction patterns, the size of nano-particles can be estimated, and it was obtained roughly 20 nm in average, which is the same value observed by TEM.

The thermal and magnetic properties of nanocrystalline Fe, $CoFe_2$, and Co particles as well as their bulk samples were studied between room temperature and 900°C. Fig. 2 shows the TGA measurements for three nanocrystalline Fe, $CoFe_2$, and Co particles. The TGA with a permanent magnet system is a powerful tool to observe many phase change effects including the ferromagnetic phase change. We have observed that near 200°C an endothermal signal occurs abruptly within 10°C for nanocrystalline Fe, and then this signal decreases with increasing temperature and shows a kink near 550°C. However, an exothermal signal starts near 200°C for nanocrystalline Co and $CoFe_2$, and it stops to decrease near 310°C and 440°C for Co and $CoFe_2$, respectively. Both endo- and exo-thermal effects near 200°C are related to the aggregation and oxidation of the ultra-fine particles. The kink near 550°C for Fe is related to the Curie temperature ($\sim$585°C) of Fe_3O_4. The magnetization of the ultra-fine particles was slightly smaller than that of the bulk samples, and it decreased very fast with increasing temperature between 100°C and 200°C. The endothermal signal for nanocrystalline Fe near 200°C indicated that Fe was easily oxidized during the aggregation process. As shown in Fig. 2, for Co and $CoFe_2$, an exothermal effect was mainly accompanied with the aggregation process. For all the bulk samples, the signal of TGA curves was almost temperature-independent below 850°C.

We measured $M-H$ hysteresis loop for all the samples under the following conditions: we heated the sample to a temperature T in a furnace under the air environment, and kept it at T for about 10 min. We allowed the sample to cool down to room temperature, and measured its $M-H$ loop at room temperature. The magnetization of the ultra-fine particles was a little smaller than that of its bulk samples, and it decreased very fast with increasing annealing temperature between 100°C and 200°C for all the samples. As an example, Fig. 3 plots the magnetization at room temperature as a function of applied magnetic field up to 0.8 T for Fe nano-particles after annealing. It shows that two drops of the magnetization: one between 100°C and 200°C related to aggregation and oxidation processes, and the

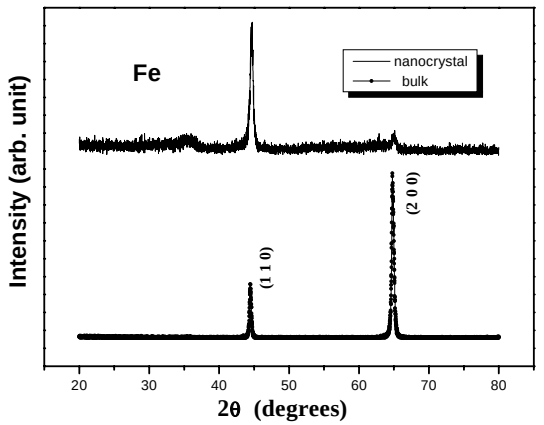

Fig. 1. Powder X-ray diffraction patterns of nanocrystalline and bulk Fe samples.

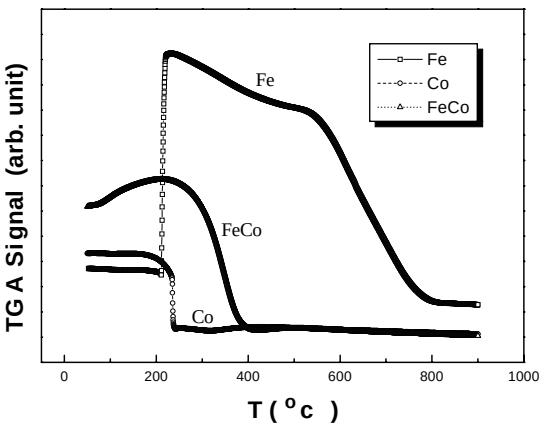

Fig. 2. The TGA measurements for nanocrystalline Fe, CoFe, and Co particles between room temperature and 900°C.

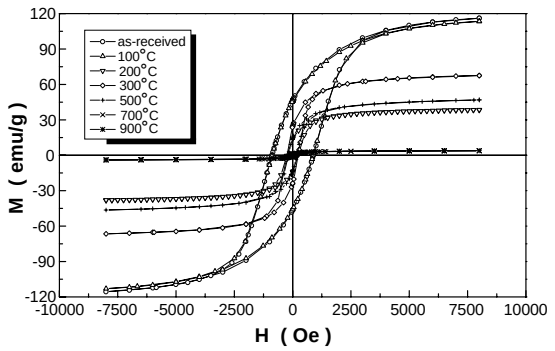

Fig. 3. The magnetization as a function of applied magnetic field up to 0.8 T for the nanocrystalline Fe particles.

other between 500°C and 700°C related to the Curie temperature (~585°C) of Fe_3O_4. The coercivity of Fe particles is reduced after high temperature annealing, this also indicates the aggregation effect of the particles after annealing above 200°C. For Co nanoparticles, its room temperature saturation magnetization is very small after annealing above 200°C. This is due to the antiferromagnetic property of CoO above room temperature. For FeCo system, its room temperature saturation magnetization increased monotonically with increasing annealing temperature from 200°C to 900°C. This indicates that the magnetic properties of the FeCo system is more stable than that of the Fe and Co systems. From the elements index analyses of TEM studies for samples after annealing, we found that the content of the oxygen in samples increased from roughly below 10% for all the nano-size particles before annealing to roughly 30% for $CoFe_2$ and Co nanoparticles, and roughly 40% for Fe nanoparticles after annealing for temperatures above 300°C. And these oxygen content in the samples after annealing between 300°C and 900°C is almost the same. This indicates that a fixed thickness of the surface oxidized layer for all the nanocrystalline particles will protect the particles for further oxidation. By comparing the magnetic data and the oxygen content data, we conclude that the oxidation is manifestly reduced after adding the Co element into Fe nanoparticles.

Fig. 4 shows the normalized magnetization as a function of the applied magnetic field for nanocrystalline Fe, $CoFe_2$, and Co particles. The coercivity of nanocrystalline $CoFe_2$ ($H_c \sim 1780$ Oe) is larger than that of Co ($H_c \sim 1198$ Oe) and Fe ($H_c \sim 883$ Oe). We believe that the high magnetic anisotropy of $CoFe_2$ may be responsible for the enhancement of coercivity in the Co–Fe alloy samples.

In summary, the thermal and magnetic properties of nanocrystalline Fe, Co, and $CoFe_2$ particles have been studied between room temperature and 900°C. From the TGA measurements, we have observed that near 200°C an endothermal signal occurs abruptly within 10°C for nanocrystalline Fe, and then signal decreases with increasing temperature and shows a kink near 550°C. However, an exothermal signal starts near 200°C for nanocrystalline Co and $CoFe_2$, and stops to decrease near 310°C and 440°C for Co and $CoFe_2$, respectively. Both endo- and exo-thermal effects near 200°C are related to the aggregation of the ultra-fine particles. The kink near 550°C for Fe is related to the Curie temperature of Fe_3O_4. The magnetization of the ultra-fine particles decreased very fast with increasing temperature between 100°C and 200°C. The coercivity of nanocrystalline $CoFe_2$ is roughly 1780 Oe, and is larger than that of Co ($H_c \sim 1198$ Oe) and Fe ($H_c \sim 883$ Oe). The high magnetic anisotropy in $CoFe_2$ may be responsible for the enhancement of coercivity in the Co–Fe alloy samples. After annealing in air, the content of oxygen in nanocrystalline particles increases roughly to 40% for Fe particles, and roughly to 30% for $CoFe_2$ and Co particles. The oxidation is manifestly reduced with adding the Co element in Fe nanoparticles. Further quantitative analyses are under processing and will be reported later.

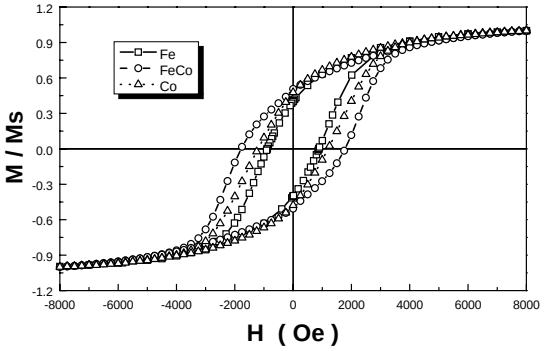

Fig. 4. The normalized magnetization as a function of the applied magnetic field up to 0.8 T for nanocrystalline Fe, $CoFe_2$, and Co particles.

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