Effect of hydrogen plasma treatment on reduction process of iron oxide nanoparticles

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Abstract. Fe3O4 nanoparticles coated with oleic acid as a surfactant were reduced by hydrogen plasma generated by 13.56 MHz Radio-Frequency (RF). With increasing input RF power to the inductive coil, Fe3O4 nanoparticles could be transformed to almost single phase of Fe3C and finally to α-Fe. The average grain sizes of Fe3C and α-Fe nanoparticles are 19 - 23 nm and 52 - 59 nm, respectively. Saturation magnetizations of Fe3C and α-Fe nanoparticles at 5 K were almost same as those of bulk Fe3C and α-Fe. Field cooling procedure from room temperature to 5 K in the magnetic measurement revealed a formation of FeO phase from Fe3O4 by weak reduction. The desired ranges of electron temperature and electron density in order to obtain Fe3C and α-Fe phases were determined by investigating plasma characteristics.

1. Introduction
Iron-based magnetic nanoparticles (NPs) such as iron oxide, carbide, nitride and metal have been studied for newly developing high performance magnetic materials. Various methods for fabricating iron-based NPs have been reported, which are mainly separated into two processes: reaction with gas phase (dry process)[1,2] and chemical synthesis in solution (wet process)[3,4]. In dry process, reaction gases are provided as stable molecules such as H2 and CH4, thus the reaction generally needs high temperature. High temperature treatment promotes sintering and grain growth of NPs, which brings about difficulty of controlling phases and nanostructures.

Low-temperature plasma treatment is well known as a useful method to improve surface property/activity of materials because of higher reactivity of exited elements than gas phase[5]. In addition, this method is expected to be suitable for treating NPs because it acts more effective to NPs having wide surface area than bulk materials. In this study, we apply hydrogen plasma treatment to the reduction of iron oxide NPs for developing high performance magnetic NPs with well-controlled phases and nanostructures.

2. Experimental procedures
Fe3O4 NPs were prepared by thermally decomposing iron pentacarbonyl (Fe(CO)5) in the atmosphere. 5 mmol of Fe(CO)5, 10 mmol of oleic acid (OA) and 30 ml of octyl ether were added into a flask. Then the solution was heated to 280 °C and kept for 1.5 h with stirring. After cooling down to the room temperature, the synthesized NPs were precipitated by adding acetone and separated by
centrifugation. The precipitation and the centrifugation processes were repeated four times and the NPs were re-dispersed in hexane without any precipitation. For spatially homogeneous irradiation of hydrogen plasma to the NPs, the SiO$_2$ substrate was dipped into the hexane solution with Fe$_3$O$_4$ NPs and withdrawn at the rate of 4.5 mm/h. After evaporation of hexane at the interface between solution and atmosphere, NPs were adhered to the substrate. By withdrawing the substrate from the solution at a constant speed, NPs could be deposited on the substrate uniformly in thickness.

The NPs coated with OA on the substrate were inserted into the plasma treatment apparatus, which is shown schematically in figure 1. Hydrogen and argon gases were introduced into a quartz furnace tube with an inductive coil, and a steady gas flow was realized by pumping using a rotary pump. After pumping to a pressure under 1.0 Pa, hydrogen gas was introduced and the hydrogen plasma was generated by 13.56 MHz radio-frequency (RF). The input RF power for generating plasma was changed from 50 W to 450 W and the hydrogen gas pressure and the treatment time were fixed at 6.0 Pa and 1 h, respectively. The sample position in the tube was at the center of the coil as shown in figure 1. After plasma treatment, the samples were cooled in an argon atmosphere and directly carried to a glove box in order to prevent re-oxidation.

Crystalline structure of NPs was characterized by an X-ray diffraction (XRD) and a transmission electron microscopy (TEM). Thermal analysis was performed by a thermogravimetry (TG). The weight of Fe in the NPs was estimated by using a X-ray fluorescence (XRF)[6]. The hysteresis loops of the samples were measured at 5 K with a superconducting quantum interference device (SQUID) after field cooled (FC) procedure from room temperature to 5 K under magnetic field of 4 T. In order to prevent re-oxidation during the magnetic measurement, samples were sealed by laminated films in the glove box. Plasma parameters were measured using a Langmuir probe that was installed at the center of the coil, which is the same position of samples.

3. Results and discussion

Figure 2 shows XRD patterns of NPs with various input RF power, $P$. As-prepared NPs were single phase of Fe$_3$O$_4$. Fe$_3$C phase appeared with residual Fe$_3$O$_4$ phase at $P = 100$ W and Fe$_3$O$_4$ phase was disappeared for $P \geq 150$ W. When $P = 150 - 200$ W, the NPs were supposed to be almost single phase of Fe$_3$C. From the TG measurement, the amount of OA covering the Fe$_3$O$_4$ NPs was estimated as 9.2
Therefore, the molar ratio between Fe and C was calculated as 2 : 1, suggesting that an enough amount of C to carbonize the Fe existed in the NPs. From these results, within the intermediate range of input power, it was suggested that the decomposition of OA, reduction of Fe$_3$O$_4$, and carbonization to Fe$_3$C occurred almost at the same time. At $P = 250$ W, $\alpha$-Fe began to appear with some additional Fe$_3$C. For $P \geq 300$ W, the peak intensity originating from $\alpha$-Fe became dominant and that from Fe$_3$C negligible. This suggested that the hydrogen plasma excited by larger $P$ could decompose Fe$_3$C to $\alpha$-Fe.

Figure 3 shows the relationships between the grain size, $D_S$, of NPs and $P$. The $D_S$ was estimated by the Scherrer’s equation,

$$D_S = \frac{K\lambda}{\beta \cos \theta},$$  \hspace{1cm} (1)

where $K$ is a shape factor, $\lambda$ is the wavelength of the X-ray, $\beta$ is the half-value width of the diffraction, and $\theta$ is the Bragg angle. In this paper, the value of $K$ was 0.94[7]. For $P \leq 100$ W, the $D_S$ calculated from Fe$_3$O$_4$(311) peak was around 10 nm. For $P = 200 - 250$ W, the $D_S$ was increased to 19 nm - 23 nm, that was calculated from Fe$_3$C(210) peak. For $P \geq 300$ (W), the main phase became $\alpha$-Fe and $D_S$ further increased to 52 nm - 59 nm, which was calculated from $\alpha$-Fe(110) peak. The average grain sizes of NPs, $D_T$, that were estimated from TEM images shown in figure 4, were also presented in figure 3. The $D_T$ increased discontinuously with increasing $P$ from 100 W to 350 W, and this tendency was in good agreement with that of $D_S$.

The structural transformation discussed above was also supported by the magnetic measurement. Figure 5 shows variation of the saturation magnetization, $M_s$, per unit weight of the Fe in the NPs, the coercivity, $H_{ch}$, and the exchange-anisotropy field, $H_{ex}$ with the RF power $P$ at 5 K. The procedure to determine $H_{ch}$ and $H_{ex}$ were described elsewhere[8]. With increasing $P$ up to 250 W, $M_s$ increased from 118 A·m$^2$/kg$_{Fe}$ to 160 A·m$^2$/kg$_{Fe}$. This was mainly caused by the phase transition from Fe$_3$O$_4$ to Fe$_3$C. The saturation magnetization of the bulk Fe$_3$C is 137 - 141 A·m$^2$/kg at room temperature[9], and these values can be converted to 147 - 151 A·m$^2$/kg$_{Fe}$ (per unit weight of Fe). $M_s$ increased with increasing $P$ from 300 W to 450 W and $M_s$ reached 210 A·m$^2$/kg$_{Fe}$ at $P = 450$ W. This value is close to the $M_s$ of the bulk $\alpha$-Fe, thus almost all of the NPs were transformed to $\alpha$-Fe from Fe$_3$C. $H_{ch}$ took a maximum at $P = 150 - 250$ W. This could be attributed to the larger magnetocrystalline anisotropy field, $H_a$, of bulk Fe$_3$C.
Fe$_3$C ($H_a = 324 - 333$ kA/m[9, 10]), compared to that of the bulk Fe$_3$O$_4$ ($|H_a| = 38$ kA/m[11]) and the bulk $\alpha$-Fe ($H_a = 45$ kA/m[12]). Furthermore, $H_{ex}$ slightly increased at $P = 100 - 150$ W from those of as-made Fe$_3$O$_4$ NPs shown at $P = 0$. This would be a consequence of exchange-coupling between ferromagnet and antiferromagnet, thus the NPs were suggested to contain antiferromagnet FeO phase that was formed by a weak reduction of Fe$_3$O$_4$ phase.

Figure 6 shows electron temperature, $T_e$, and electron density, $n_e$, as a function of $P$. $T_e$ increased from 4.2 eV to 8.9 eV with increasing $P$, $n_e$ also increased from $6.1 \times 10^9$ cm$^{-3}$ to $2.9 \times 10^{10}$ cm$^{-3}$ with increasing $P$ in the range of $P \leq 250$ W, while $n_e$ became constant when $P \geq 300$ W. From these results, in the case of hydrogen plasma treatment for 1 h, the proper values of the plasma parameters for the transformation of 10 nm Fe$_3$O$_4$ NPs into 20 nm Fe$_3$C NPs were determined to be $T_e = 6$ eV and $n_e = 2 \times 10^{10}$ cm$^{-3}$. Similarly, it is necessary to apply plasma with $T_e \geq 7.5$ eV and $n_e = 2 \times 10^{10}$ cm$^{-3}$ in order to produce the transformation of 10 nm Fe$_3$O$_4$ NPs into 50 - 60 nm $\alpha$-Fe NPs. $T_e$ represents kinetic energy of electrons that collide with sample and heat it up. On the other hand, $n_e$ represents the amount of excited ions, which is involved in activity of plasma. Therefore, when $T_e$ and $n_e$ have large values in the hydrogen plasma treatment, the reactivity between the hydrogen and the NPs become high by two effects: increased temperature of the NPs and high activity of the hydrogen plasma. It is suggested that this high reactivity induced the reduction and/or the carbonization of the NPs.

4. Conclusion
Fe$_3$O$_4$ NPs coated with OA as a surfactant was reduced by hydrogen plasma. By changing input RF power to the inductive coil, Fe$_3$C NPs that have 20 nm of average grain size and $\alpha$-Fe NPs that have 50 - 60 nm of average grain size were obtained with almost single phase, respectively. The desired values of $T_e$ and $n_e$ have been also determined. These results suggest that the hydrogen plasma treatment can be useful to control the phase formation in Fe-based NPs.

5. References
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