Effect of Ambient Gas Temperature on Synthesis of Fe-N Nanosized Powders by Pulsed Wire Discharge

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Keywords: Fe-N nanosized powders, ambient gas temperature, Pulsed Wire Discharge

In recent years, with the progress in the miniaturization of magnetic recording apparatus, it is required to increase the saturation magnetization and the chemical stability of the magnetic particles in magnetic recording media. Therefore, attention has been paid to Fe-N nanosized powders as a possible candidate. It is well known that some of the iron nitrides are unstable at higher temperature. Therefore, the synthetic methods using high temperature processes such as plasma and arc discharge methods have not yet been applied. For instance, pulse wire discharge (PWD) is one of these methods that can synthesize different nanosized powders of metals or compounds by cooling high-temperature plasma in ambient gas.

We have succeeded to synthesize γ'-Fe₄N nanosized powders using PWD by optimizing the synthetic conditions, i.e., gas molecules and gas pressure. However, powders with single-phase γ'-Fe₄N was not obtained, because non-nitride phases of α-Fe and γ-Fe₄N were remained in the synthesized powders.

Since γ'-Fe₄N phase is stable below 680 °C, it may be possible to increase volume fraction of that with increasing the holding time below 680 °C. The synthesis conditions for obtaining iron nitride were optimized by varying the ambient gas temperature. The synthesized powders were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

The results of XRD revealed that the powders synthesized from room temperature (R.T.) to 450 °C consisted of α-Fe, γ-Fe₄N, γ'-Fe₄N and ε-Fe₄N. The volume fractions of α-Fe, γ-Fe₄N, γ'-Fe₄N and ε-Fe₄N in the synthesized powder were calculated from XRD patterns. The volume fractions are plotted as a function of ambient gas temperature in Fig. 1. The volume fraction of γ-Fe₄N decreased rapidly above 300 °C. On the contrary, those of α-Fe and γ'-Fe₄N were increased. The volume fraction of ε-Fe₄N was independent on ambient gas temperature. This results suggests that γ-Fe₄N was transformed into α-Fe and γ'-Fe₄N above 300 °C. From the results, it was found that volume fraction of low temperature phase such as α-Fe and γ'-Fe₄N was possible to rise by increasing ambient gas temperature up to the decomposition temperature.

Figure 2 shows the size distribution of nanosized particles synthesized at different ambient gas temperature obtained from the TEM images. The experimental results were fitted with a log-normal distributions which were plotted by dotted lines in Fig. 2. The median size of the synthesized powders at R.T. was approximately 23.0 nm. The median size of synthesized powders increased with the increasing ambient gas temperature and reached 30.9 nm at 450 °C. This result suggested that particles were either sintered or grown in the ambient gas.

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![Fig. 1. Volume fraction of α-Fe, γ-Fe, γ'-Fe₄N and ε-Fe₄N in synthesized powders as a function of ambient gas temperature](image)

![Fig. 2. Diameter distribution of synthesized powder at ambient gas temperature of (a) R.T., (b) 150 °C, (c) 300 °C and (d) 450 °C](image)
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Fe-N nanosized powders successfully were synthesized in ambient ammonia (NH₃) gas at different temperature by pulsed wire discharge (PWD). The powders were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results of XRD revealed that the powders synthesized from room temperature (R.T.) to 450 °C was α-Fe, γ-Fe(N), γ'-Fe₄N and ε-Fe₃N. The volume fraction of γ-Fe(N) decreased rapidly above 300 °C. On the contrary, those of α-Fe and γ'-Fe₄N were increased. The volume fraction of ε-Fe₃N was independent on ambient gas temperature. The median size of the synthesized powder observed by TEM increased with increasing ambient gas temperature.

Keywords: Fe-N nanosized powders, ambient gas temperature, pulsed wire discharge

1. Introduction

In recent years, with the progress in the miniaturization of magnetic recording apparatus, it is required to increase the saturation magnetization and the chemical stability of the magnetic particles in magnetic recording media. Therefore, the development of a new magnetic material has been pursued in order to improve the properties in the magnetic particles. In particular, attention has been paid to iron nitrides as a possible candidate.

In the Fe-N system, there exist many phases including α-Fe(N), γ-Fe(N), α’-martensite, γ’-Fe₄N, ε-Fe₂₃N and ε-Fe₃N. Amongst these phases, α’-Fe₃C₅N₂, γ’-Fe₄N, ε-Fe₂₃N and ε-Fe₃N exhibit ferromagnetism at room temperature(12). In particular, the α’-Fe₃C₅N₂ phase displays the saturation magnetization higher than that of pure iron(3). In addition to the magnetic properties, the iron nitrides also exhibit good corrosion durability, surface hardness and wear resistance(4).

It is well known that some of the iron nitrides are unstable at higher temperature. Therefore, low temperature synthetic techniques such as chemical vapor deposition, mechanical alloying, reactive gas evaporation and vapor-liquid chemical reaction have been used for obtaining iron nitrides(5-7). In contrast, the synthetic methods using high temperature processes such as plasma and arc discharge methods have not yet been applied. For instance, pulse wire discharge (PWD) is one of these methods that can synthesize different nanosized powders of metals or compounds by cooling high-temperature plasma in ambient gas(8).

We have succeeded to synthesize γ’-Fe₄N nanosized powders using PWD by optimizing the synthetic conditions, i.e., gas molecules and gas pressure(9)(10). However, powders with single-phase γ’-Fe₄N was not obtained, because non-nitride phases of α-Fe and γ-Fe(N) were included in the synthesized powders. On the basis of the phase diagram of the Fe-N system, it has been known the γ-Fe with N content of 8.8 at.% is stable above 592 °C(11). The result suggested that nanosized powders of high temperature metastable phases could be synthesized by PWD in which high-temperature plasma was cooled rapidly. Therefore, it seemed that synthesis of the low-temperature phase such as γ’-Fe₄N is difficult. Since γ’-Fe₄N phase is stable below 680 °C, it may be possible to increase volume fraction of that with increasing the holding time below 680 °C.

In this research, synthesis of the iron nitride nanosized powders was attempted by PWD. The synthesis conditions for obtaining iron nitride were optimized by varying the ambient gas temperature. We discussed an effect of ambient gas temperature on Fe-N nanosized powders synthesized by PWD on the basis of the morphology and the phases of synthesized nanosized powders as well as the electric discharge characteristics.

2. Experimental Procedure

The experimental setup for PWD is shown in Fig. 1. The basic electric discharge system comprised an electrical heating furnace and simple electric discharge circuits, which consisted of a high-voltage power supply, a capacitor and a gap switch. The typical experimental conditions are summarized in Table 1. In Table 1, The evaporation energy was defined as the enthalpy change of the whole wire from the solid state at R.T. to the gaseous state at the boiling point. The evaporate energy was calculated to be a sum of the following four terms; the enthalpy change of solid state from R.T. to the melting point, the heat of fusion, the enthalpy change of the liquid state from the melting point to the boiling point and heat of evaporation(12). An iron wire (99.5% in purity) of 0.3 mm in diameter and 100 mm in length was located between electrodes in the combustion tube filled with ammonia (NH₃) gas at 750 Torr. The evaporation
energy and heat of evaporation of the wire were 484 J and 348 J, respectively. The ambient gas temperature was changed from R.T. to 450 °C. After charging a capacitor, the capacitor was discharged though the wire by closing the gap switch. After the discharge, the floating particles in the tube were collected on a filter by flowing the gas.

The discharge current and voltage drop across the wire were measured by an oscilloscope, and the deposited energy in the wire was calculated by integrating the electrical power.

The phases in the synthesized powders were characterized by X-ray diffraction (XRD) using Cu-Kα radiation (0.15406 nm). Furthermore, the volume fractions of the phases in the powder were calculated by the following way. First, the peaks in XRD pattern were deconvoluted assuming Gaussian distribution curves. Secondly, intensities of the peaks were measured by integrating the curves. Finally, volume fractions of the phases were determined by the ratio of the measured intensities and the theoretical intensity calculated from structure, multiplicity and Lorentz polarization factors. The morphology of the synthesized powders was observed by transmission electron microscopy (TEM) and the particle size of the synthesized powders was evaluated on the basis of bright-field images.

3. Results and Discussion

3.1 Current and Voltage Waveforms Figure 2 shows typical waveforms of the applied voltage and discharge current in the wire at different ambient gas temperature. The distinctly noticeable features in the current and voltage waveforms were the drop in current and the rise in voltage, which are indicated in Figs. 2 by arrows. This current drop arose from the increase in resistance of the wire due to melting or vaporization, and the voltage rise was caused by the current flow in the high resistive state of the wire. The current amplitude dropped to zero for a while, and the current flows again, as shown in Fig. 2. It seemed that the flow of current was intercepted due to high-resistance of the metal vapor, and then the dielectric breakdown occurred due to the electrons/ions in the vapor were accelerated by electric field between the electrodes. The duration of zero current is shortened with increasing ambient gas temperature as shown in Fig. 2. It can be thought that the dielectric breakdown is easily taken place in high-temperature vapor.

The deposited energy in the wire, which was estimated until the time shown by the arrow, was calculated from current and voltage waveforms. The deposited energy in the wire was plotted as a function of the ambient gas temperature in Fig. 3. The deposited energies stayed constant up to 375 °C but slightly decreased at 450 °C. From the discussion above, it was expected that the deposited energy decrease at ambient gas temperature of 450 °C.
The peaks of the patterns matched with those of the International Center for Diffraction Data (ICDD) for α-Fe, γ-Fe, γ'-Fe₃N and ε-Fe₃N. The XRD patterns showed the peak position of γ-Fe shifted to the lower angle. The result indicated that some atoms dissolved in the γ-Fe. Although, no chemical analysis was carried out, the dissolved atoms should be nitrogen which was dissociated from NH₃.

The nitrogen content in the γ-Fe(N) was calculated from lattice constant of γ-Fe(N) (10). The calculated nitrogen content plotted as a function of ambient gas temperature is shown in Fig. 5. The nitrogen contents were comparable to 10.3 at.% which was solid solubility limit for bulk of γ-Fe(N).

The volume fractions of α-Fe, γ-Fe(N), γ'-Fe₃N and ε-Fe₃N in the synthesized powder were calculated from XRD patterns. The volume fractions are plotted as a function of ambient gas temperature in Fig. 6. The volume fraction of ε-Fe₃N was kept constant up to 450 °C. The reason seems to be due to ε-Fe₃N is stable from R.T. to 1000 °C as show in the phase diagram of the Fe-N system (10). Thus, the volume fraction of ε-Fe₃N was independent on ambient gas temperature. On the other hand, as shown in Fig. 6, the volume fraction of γ-Fe(N) unchanged up to 300 °C, above which it decreased abruptly. In addition, the volume fractions of α-Fe and γ'-Fe₃N showed nearly constant up to 300 °C, above which it increased. The volume fraction of γ'-Fe₃N reached a maximum of 45.5 vol.% at an ambient gas temperature of 450 °C. This result suggests that γ-Fe(N) was transformed into α-Fe and γ'-Fe₃N above 300 °C. This fact was in good agreement with phase transformation in the phase diagram.
be almost spherical. The size of most of the synthesized particles was less than 100 nm. Figure 7 (b), (c) and (d) show the synthesized powder at ambient gas temperature of 150 °C, 300 °C and 450 °C, respectively. These powders included large particles whose grain sizes were above 100 nm. Moreover, the number of submicron-sized particles increased with increasing ambient gas temperature. Previously, it was reported that the formation of submicron-sized particles in the PWD process was controlled by the energy deposited in the wire\(^{(10)}\). According to ref. 13, the number of submicron-sized particles decreased with increasing the deposited energy. In this experiment, the deposited energies at different ambient gas temperature were constant. From the results, it was found that ambient gas temperature affected the formation of submicron-sized particles.

Figure 8 shows the size distribution of nanosized particles synthesized at different ambient gas temperature obtained from the TEM images. The diameter distribution followed a log-normal distribution plotted by dotted line. The median size of the synthesized powders at R.T. was approximately 23.0 nm. The median size of synthesized powders increased with the increasing ambient gas temperature and reached 30.9 nm at 450 °C. This result suggested that particles were either sintered or grown in the ambient gas.

4. Conclusion

The synthesis of the Fe-N nanosized powders using PWD was studied. The synthesis of iron nitride has been optimized by varying ambient gas temperature. The characterization of powder has been conducted using XRD and TEM. From these results, the following conclusions were obtained.

1. The dielectric breakdown easily happens in high-temperature vapor with increasing ambient gas temperature. The deposited energy in the wire stayed constant from R.T. to 375 °C, but decreased at 450 °C.

2. In ambient gas at low temperature, the volume fraction of the low-temperature phase such as γ'-Fe3N increased.

3. The number of submicron-sized particle including the synthesized powder and median size of nanosized particles was increased with increasing ambient gas temperature.

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References

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