

Oxidation and Magnetic Properties of Iron-nitride Particles in Fluids

†Hyo Sook Lee and Isao Nakatani*

Korea Research Institute of Geoscience, Mining and Materials, Yusung-ku, Taejon, 305-350, Korea,

**National Research Institute for Materials Science, Tsukuba, 305-0047, Japan*

ABSTRACT

Iron nitride magnetic fluid was oxidized by exposing it to the air under normal atmospheric conditions. After exposure of 3.2 hours, the relative saturation magnetization of the iron nitride magnetic fluid is less than 0.4 compared to the value of the unexposed sample, and it is nearly zero after exposure for 1008 hours. The structure of the oxidized iron nitride is considered to be a non-magnetic hematites. The thickness of the oxidation layers of the iron-nitride particles are nearly the same, about 3 nm, regardless of the different particle sizes.

Key words : Magnetic fluid, Iron nitride, Oxidation, Nano Particle, Magnetization

1. Introduction

Magnetic fluids with high saturation magnetization are now recognized to be important to a wide variety of industrial fields. Attempts have been made to produce magnetic fluids with higher magnetic moments from iron metal or iron nitride particles, instead of from magnetite or ferrite particles¹⁻³⁾ The iron nitride magnetic fluids are anticipated to have greater chemical stability with respect to oxidation than iron particles.¹⁾ However, extensive research has been carried out on the structure and magnetic properties of the oxide layers formed on the iron-nitride particles⁴⁻⁶⁾ Some investigators believe that the iron oxide layers are micro-crystalline Fe_3O_4 or $\gamma-Fe_2O_3$ or a mixture of the two.⁷⁻⁹⁾ Kishimoto suggested that the iron oxide layers are ferromagnetic and have a significant saturation magnetization.¹⁰⁾ On the contrary, Suzuki reported that the iron oxide layer formed on both the metallic iron and iron nitride particles is composed only of Fe_3O_4 and that the oxide layers have nonmagnetic properties¹¹⁾

In this paper we present the results of an investigation into the oxidation product layers of the iron nitride

particles in fluids and magnetic properties of the oxidized iron nitride magnetic fluids produced under atmospheric conditions.

2. Experimental

The iron nitride magnetic fluids were synthesized using kerosene, iron carbonyl and ammonia gas as per the previously reported vapor-liquid chemical reaction method.¹⁾ Just after synthesizing the iron nitride magnetic fluid, it was evenly divided into eight samples of about 6 ml each they were handled under a dry nitrogen atmosphere. Seven samples among eight were exposed to air for 1, 3.2, 14, 37, 101, 360 and 1008 hours, respectively. All exposure tests were carried out with a shaker and the samples were opened to normal atmospheric conditions; the temperature was kept at 23.0~23.2°C and the relative humidity was in the range of 20~40% during the exposure test. One unexposed sample was used as a reference (called the initial sample). Mass changes of the exposed samples were measured by comparison with the initial sample mass and magnetic properties were measured using a vibration sample magnetometer (PAR model 151). A transmission electron microscope (JEOL-200FXII) was used to examine the particle morphology.

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† E-mail: hslee@kigam.re.kr

3. Results and Discussion

The relative mass changes of the iron-nitride magnetic fluids were plotted against exposure times as shown in Fig. 1. The mass of the iron nitride magnetic fluids increased by about 2 % relative to the initial samples with increasing exposure time up to 100 hours. The increasing mass of the iron nitride magnetic fluids is caused by the oxidation of the iron nitride particles. For exposure times greater than 100 hours, the mass of the iron nitride magnetic fluids decreased. This is likely due to the losses by evaporation of kerosene being greater than the increasing mass due to the oxidation of the iron nitride particles. These results suggest that the oxidation reaction of the iron nitride particles will be nearly completed after exposure for 100 hours.

The magnetization curves of the initial and exposed iron nitride magnetic fluids for 3.2 and 1008 hours and at room temperature are shown in Fig. 2. The initial and exposed sample for 3.2 hours show magnetic saturation in a field of 10 kOe strength. The saturation magnetization (M_s) of the initial sample and the iron nitride magnetic fluid after exposure for 3.2 hours are 7.0 emu/g, and 3.1 emu/g, respectively. After exposure for 1008 hours the magnetization of iron nitride magnetic fluids is 0.1 emu/g. This indicates that the iron nitride particles in the fluid were almost fully oxidized into a non-magnetic iron oxide with exposure

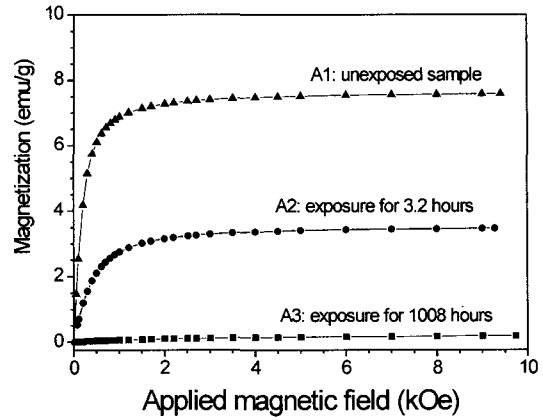


Fig. 2. Magnetization curves of the iron nitride magnetic fluids at room temperature.

of 1008 hours under atmospheric conditions.

Fig. 3 shows the relative saturation magnetization of the exposed iron nitride magnetic fluids with respect to the initial sample versus the exposure times. After exposure for only 3.2 hours, the saturation magnetization of the iron nitride magnetic fluid is less than 0.4, compared to the initial value. The relative saturation magnetization of the iron nitride magnetic fluids rapidly decrease with increasing exposure time until 101 hours. The relative M_s of a sample is less than 0.1 after exposure for 101 hours and it is nearly zero after 1008 hours. From these results the oxidation product of iron nitride particles in the magnetic fluids are

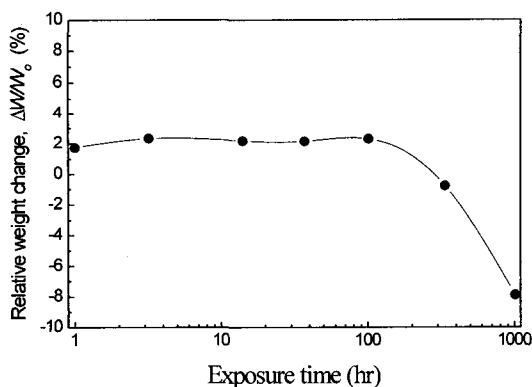


Fig. 1. Relative weight change, $\Delta W/W_0$ (%) vs exposure time, $\Delta W/W_0 = (W_t - W_0)/W_0$
 W_0 : weight of magnetic fluids before exposure.
 W_t : weight of magnetic fluids at exposure time, t.

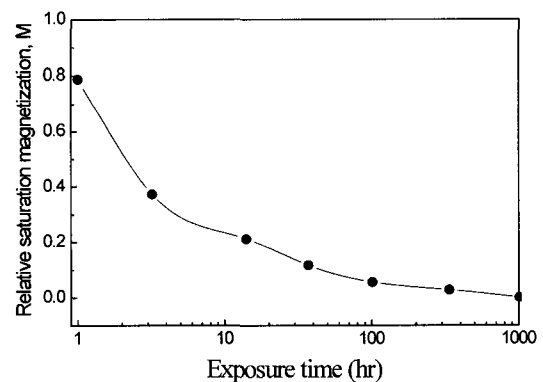


Fig. 3. Relative saturation magnetization vs exposure time, $M = M_{st}/M_{si}$
 M_{si} : initial saturation magnetization.
 M_{st} : saturation magnetization at exposure time, t.

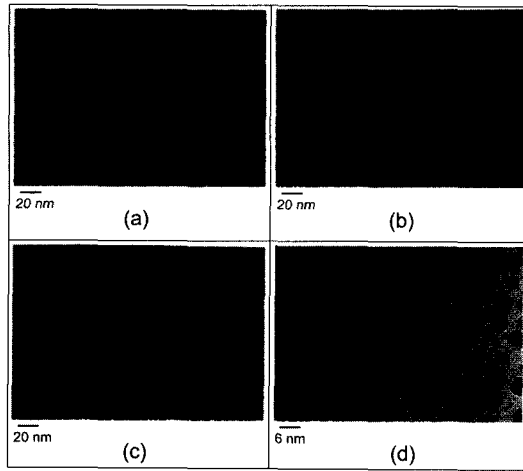
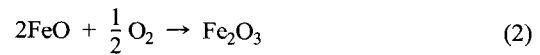
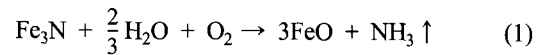


Fig. 4. TEM photographs of iron nitride magnetic fluids (a) unexposed, (b) exposed for 3.2 hours, (c) exposed for 1008 hours and (d) exposed for 1008 hours, magnified three times.

considered to be a non-magnetic material such as hematite (α - Fe_2O_3) rather than magnetite (Fe_3O_4) and/or maghemite (γ - Fe_2O_3). Magnetite and maghemite possess some saturation magnetization, 92 emu/g and 80 emu/g, respectively, albeit less than iron nitride as 192 emu/g.

Fig. 4 reveals the TEM microstructure of the iron-nitride magnetic fluids. The initial, 3.2 hour and 1008 hour exposure samples are shown in Fig. 4(a), (b) and (c), respectively. The iron nitride particles obtained by the vapor-liquid chemical reaction with iron carbonyl and ammonia gas were almost uniformly spherical with 6-9 nm diameters. After the iron nitride particles were exposed for 3.2 hours the particles were covered with an oxide layer which appears less dark in the TEM micrographs compared with the particle core. After exposure for 1008 hours most particles are composed of three different layers. To look at the exposed iron nitride particles in detail, the photo in Fig. 4(c) was enlarged three times [Fig. 4(d)]. As seen in Fig. 4(d) the particles are composed of three layers. At the core of the particles the remaining iron nitride is seen as a black region. The layer next to the core can be seen as the first oxidation product of the iron nitride and the surface layer of the particles can be considered to be a second oxidation layer. The thickness of the oxidation layers of the iron nitride particles are nearly

the same, about 3 nm, regardless of the different particle sizes. The particles of less than 6 nm diameter are completely oxidized but the particles with diameters greater than 6 nm retain the black core of the iron nitride. Also it is apparent that the oxidation of iron nitride particles occurs in two stages, because the particles exposed for 3.2 hours have two layers and those exposed for 1008 hours are composed of three distinctive layers. The second oxidation layer appears more dark than the first one. This means that the second oxidation compound (Fe_2O_3 -rhombohedral) has a more dense structure than the first one (FeO-cubic). The final oxide structure of the iron nitride particles is concluded to be a non-magnetic iron oxide such as a hematite, rather than magnetite and/or maghemite. Therefore, we can consider the oxidation processes of iron-nitride such as the followings:



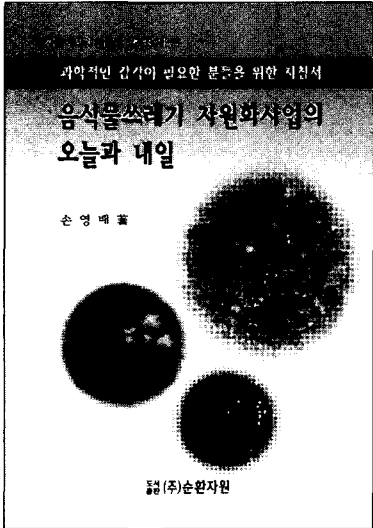
4. Conclusion

The iron nitride particles in fluids are oxidized by oxygen and water in two stages under atmospheric conditions. The thickness of the oxidized layers are almost uniformly the same at about 3 nm, regardless of the particle size. The oxidized iron nitride after exposure to air is non-magnetic and the oxide structure can be considered to be composed of a non-magnetic material such as hematite rather than magnetite and/or maghemite.

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신간 안내

제 목 : **음식물쓰레기 자원화 사업의 오늘과 내일**

저 자 : **손 영 배**

발행처 : 도서출판 (주)순환자원

신국판 216P

정 가 : 1,5000원

본서는 음식물쓰레기처리시설이 현재 어떻게 돌아가고 있는가에 대한 정부의 발표내용에 대한 소개와 이에 대한 필자의 검증부터 시작된다.

제1장은 「음식물쓰레기 사료화편」,

제2장은 「음식물쓰레기 퇴비화편」,

제3장은 「음식물쓰레기 자원화에 대한 개념정리를 위한 제언」으로 구성되어 있으며 저자는 음식물쓰레기의 사료화와 퇴비화에 대해서 지금까지 잘못 알려진 내용을 정리하고 새로운 대안과 지식을 전달하고 있다.