

기계적 합금화법에 의한 준안정 철질화물의 합성 및 자기특성

논문
7-5-5

Syntheses and Magnetic Properties of Metastable Iron-Nitrides Subjected to Mechanical Alloying

이충효, 홍진웅*
(Chung-Hyo Lee, Jin-Woong Hong)

요 약

기계적 합금화방법을 이용 실온에서 철분말의 질화물을 얻을 수 있다. 이때 얻어진 준안정 철질화물은 질소농도가 14.9[at. %N] 이하에서는 bcc 구조의 과포화 고용체가, 그리고 19.4[at. %N] 이상에서는 고온상인 hcp 구조임을 확인할 수 있었다. 또한 bcc 상의 Fe 원자당 Volume은 문헌에 보고된 N-martensite의 것보다 작은 값을 나타내었다. 제조된 철질화물의 실온 포화 자화값은 질소농도가 증가함에 따라 감소하였으며, 이 결과는 bct 구조의 철질화물에서 질소농도가 증가함에 따라 자화값이 증가하는 것과 대조적이었다.

Key Words(중요용어) : Magnetic properties(자기특성), Magnetization(자화), Mechanical alloying(기계적 합금화), Metastable phase(준안정 상).

I. INTRODUCTION

The discovery of giant magnetic moment of the $Fe_{16}N_2$ ¹⁾ and hard magnetic characteristics of the $Sm_2Fe_{17}N_x$ ²⁾ has roused the interest in the magnetic properties and the preparation of ferromagnetic nitrides. Kim et al.¹⁾ reported, for the first time, that the ordered bct iron-nitrides of $Fe_{16}N_2$ exhibit the highest magnetization of 2.8 T at room temperature. Recently, Komura et al.³⁾ have succeeded to produce the single crystalline $Fe_{16}N_2$ films by vacuum deposition and confirmed its large magnetic moment. Nakajima et al.^{4,5)} have employed the multi injection nitrogen ion implantation technique to obtain the ordered and disordered iron nitrides, and they found that the tetragonal axial ratio and magnetic moment increase with increasing N concentration⁶⁾. They also found that the magnetization of the disordered bct nitrides is

almost same as that of the $Fe_{16}N_2$ ⁶⁾. Neither disordered bct iron-nitrides nor the ordered $Fe_{16}N_2$ are produced as a bulk sample with a single phase because of their metastability. They have been obtained as thin films or precipitates in rapidly quenched nitrogen austenite. Therefore, the corresponding magnetic structures are not exactly determined owing to the difficulty in the sample preparation.

From the viewpoint of magnetic materials, the bct iron nitrides are of great interest, provided that they are produced in a large volume. Mechanical alloying(MA) technique is a new method capable of producing massive powders with metastable phases⁷⁾. The basic idea of MA is to energize an alloy or a mixture consisting some elemental powders, and to assist the mutual diffusion and chemical reaction through the intense mechanical deformation⁸⁾. Using this technique, a number of metastable phases including amorphous phases and nanocrystalline can be obtained at room temperature. The MA is not only applicable to solid-solid reaction, but also solid gas reaction^{9,10)}. We consider that one of the most interesting solid-gas reaction occurs

* : 통상성 공업기술원(일본)

** : 광운대학교 공과대학 전기공학과

접수일자 : 1994년 3월 21일

심사완료 : 1994년 7월 12일

in the iron-nitrogen system as mentioned above. The MA technique might have a potentiality to produce metastable iron-nitrides such as bct martensite phase, which eventually decomposes into stable α -Fe and γ' -Fe₄N at 200°C¹¹⁾.

In this paper, we show that mechanical alloying technique under a controlled gas atmosphere makes it possible to nitrify pure Fe powders even at room temperature. The structural considerations and magnetic properties of the iron-nitrides are also discussed as a function of N concentration.

II. EXPERIMENTAL PROCEDURE

The ball milling was carried out at room temperature for pure iron powders(99.9%, < 150 μ m in size) in NH₃ gas atmosphere. A planetary ball mill (Fritsch Pulverisette 5) was used with its intensity 5, being equivalent to the vial rotation of 430 rpm. The vial and balls are made of the hardened steel(SKD11, containing 11% Cr and 1.8% C). The total mass of powders was about 20g and the ratio of balls to powders was 7:1. Milling was interrupted for 6 min in every 30 min to suppress the excessive temperature rise of the vial and balls. A volume of the vial, after subtracting that of balls and sample, is about 70cc. In the present experiment, the NH₃ gas, filled in the vial at 1.5 atm, can nitrify Fe powders of 20g up to 1.3 at.%N, provided that all gas is absorbed by Fe powders. NH₃ gas was charged every 50h milling after evacuating vial. The ball milling was continued up to 1000h by repeating this process.

The structure of ball-milled powders was studied by X-ray diffraction in continuous and step scanning modes with Cu-K α radiation (RIGAKU, RAD-IIC). The magnetization at room temperature was measured with a vibrating sample magnetometer(TOEI VSM-5) calibrated using a pure Ni disk(99.99%).

The N concentration absorbed into the sample was determined with a nitrogen-oxygen analyzer(HORIBA EMGA 650). The sample was heated up to 2800°C in a carbon crucible and the nitrogen gas desorbed was quantitatively

analyzed. The amount of hydrogen was also measured with a hydrogen gas analyzer.

III. RESULTS AND DISCUSSION

The gas concentrations absorbed during ball milling in the powders are shown in Figure 1. The nitrogen concentration linearly increases at

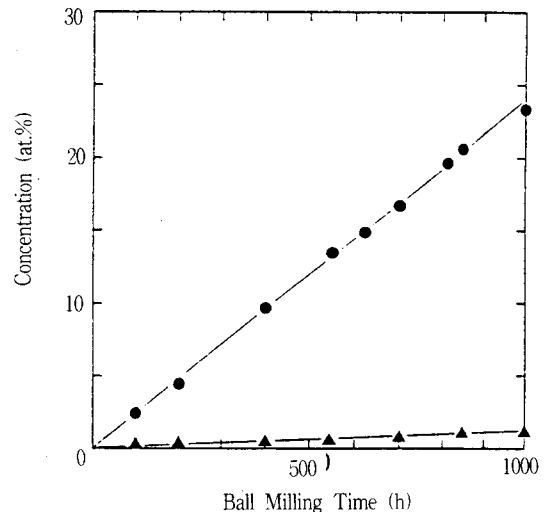


Fig. 1. The concentrations of the absorbed gas elements for the mechanically alloyed Fe-N powders as a function of the ball milling time: nitrogen(●) and hydrogen (▲).

the rate of about 1.2 at.% per 50h-milling. Hence, most of NH₃ gas in the vial has been consumed during ball milling process. The MA process most likely gives rise to the following reaction: $2x\text{Fe} + 2\text{NH}_3 \rightarrow 2\text{Fe}_x\text{N} + 3\text{H}_2$. In the present experiment, Cr impurity from vial is less than 0.01% for 500h-milling sample. Therefore, we can safely believe that the nitrification is not caused by the Cr impurity but the consequence of the solid gas reaction between Fe powders and NH₃ gas. In this process, H₂ gas is also produced as a result of the solid gas reaction. In other words, the iron powders were ball milled in a gas consisting of a mixture of NH₃ and H₂. The concentration of hydrogen impurity was found to be less than 0.9 at.% for all samples. Hence, we tend to believe that the

hydrogen atoms were absorbed on the powder surface and/or dissolved beyond its maximum solubility of 0.017 at.%. Though the effect of hydrogen gas on the reaction was not investigated, we suppose that H_2 gas would promote the nitrification in the similar manner to the conventional high temperature process¹²⁾.

The X-ray diffraction spectra are shown in Figure 2 as a function of the N concentration for the mechanically alloyed Fe-N powders. According to the extinction rule of the diffraction lines, we can deduce its structure to be bcc up to 14.9 at.%N. Diffraction lines associated with neither the γ' -Fe₄N nor ϵ -phase are observed. Hence, we conclude that a super-saturated bcc phase is produced by MA. The diffraction lines become broad with increasing the N content and shift to smaller angles. The

line broadening indicates that substantial lattice defects and strains were introduced in the super-saturated bcc matrix already formed. Admittedly, the line broadening hamper the precise determination of the structure, for example, as to whether the tetragonality exists or not. The structure of the sample containing nitrogen atoms higher than 19.4 at.%N can be identified to hcp. It is found that the high temperature phase, i.e., the ϵ -phase is formed instead of the stable γ' -Fe₄N. The lattice parameters are determined as $a=2.71\text{\AA}$ and $c=4.37\text{\AA}$ for 19.4 at.%N sample. The lattice parameters of the ϵ -phase containing the same amount of N atoms are reported to be $a=2.660\text{\AA}$ and $c=4.344\text{\AA}$ ¹³⁾. Two faint peaks associated with the ϵ -phase can be seen at $2\theta=70^\circ$ and 78° in the diffraction spectrum of 16.7 at.%N sample. Therefore, the bcc phase and ϵ -phase coexist in the composition range of $14.9 < \text{at.\%N} < 19.4$.

The volumes per Fe atom for the bcc and hcp samples are calculated from the lattice parameters, which are deduced from the respective diffraction patterns. The atomic volumes thus obtained are shown in Figure 3 as a function of N concentration together with the values reported for the N-martensite¹⁴⁾, γ' -Fe₄N¹⁵⁾ and ϵ -phase nitrides¹³⁾. Roehgude et al.¹⁶⁾ reported that the atomic volume of iron-nitride, whose chemical formula is expressed in the form of FeN_x, is given by the following equation: $V_{Fe}(\text{\AA}^3)=12.01+5.5x$. This relation is plotted as a dashed line in Figure 3. It can be seen that the equation well explains the composition dependence of atomic volume for the bcc and hcp iron-nitrides. The atomic volume per Fe of the present bcc nitrides increases monotonously with increasing the N concentration though the data points fall below the dashed line up to 17 at.%N. In the case of the N-martensite, N atoms are known to occupy predominantly octahedral interstitial sites only along a given axis¹¹⁾, and as a consequence, the distance between the nearest neighbor Fe atoms along this direction expands slightly. This expansion or the tetragonality is probably responsible for a large volume per Fe atom in the N-martensite than that in the bcc nitrides

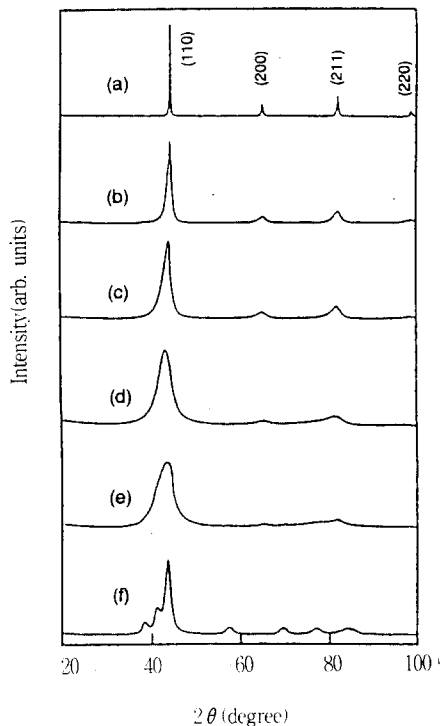


Fig. 2. X-ray diffraction spectra for the mechanically alloyed Fe-N powders as a function of N concentration. (a) pure Fe powders employed by starting sample, (b) N=4.5 at.%, (c) N=9.7 at.%, (d) N=14.9 at.%, (e) N=16.7 at.%, (f) N=20.8 at.%.

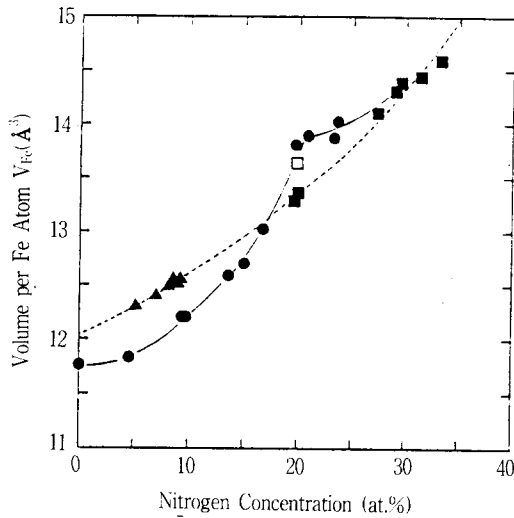


Fig. 3. Volume per Fe atom for the mechanically alloyed Fe-N powders as a function of N concentration. Included are the present data for Fe-N powders (●), N-martensite¹⁴⁾ (▲), γ' -Fe₄N¹⁵⁾ (□) and ϵ -phase nitride¹³⁾ (■). Dashed line indicates the relation between the atomic volume and nitrogen concentration reported by Rochegude et al.¹⁶⁾

we obtained. Further work is needed to clarify the difference in the volume expansion between the bcc and bct structure. Neutron diffraction experiment is in progress with a hope to reveal the local structure of the present samples. In contrast to the bcc phase, the data for the hcp samples locate above the dashed line. Lattice defects accumulated during ball milling might contribute to the large atomic volume.

The saturation magnetization is shown in Figure 4 as a function of the N concentration. The magnetization gradually decreases with increasing the N concentration. This suggests that the magnetic moment of Fe atoms decreases and/or the Curie temperature drops as the nitrification proceeds. The data for the N-martensite produced by nitrogen ion implantation⁶⁾ are incorporated in Figure 4. The magnetization for the N martensite is found to increase with increasing the N concentration, in which the maximum magnetization of 245emu/g and axial ratio of 1.1 are obtained at a composition

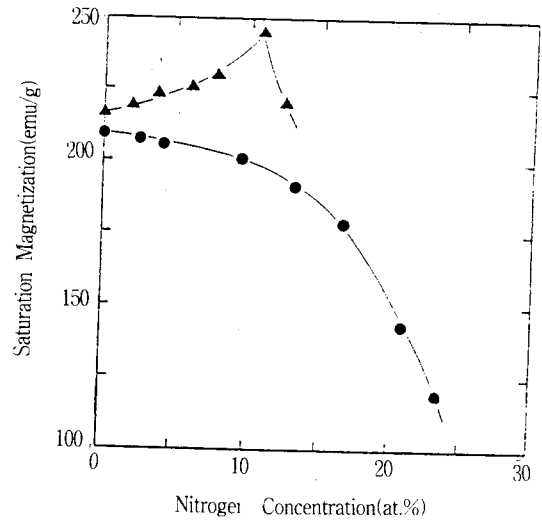


Fig. 4. The composition dependence of the saturation magnetization at room temperature : the present data for Fe-N powders (●) and N martensite⁶⁾ (▲).

of 11 at.%N⁶⁾. Though the present bcc iron-nitride can accommodate N atoms well exceeding 11 at.%N, an increase in the magnetization has not been observed.

Mitsuoka et al.¹⁷⁾ pointed out that volume expansion per Fe atom and the tetragonal deformation contribute to the enhancement in the magnetization. We consider the structure difference between the N-martensite and the present bcc phase to be most likely responsible for the difference in the magnetization behavior. The enhancement in magnetization due to the volume expansion has been discussed in the terms of the energy band calculation for the pure Fe^{18,19)}. As shown in Figure 3, the difference in an atomic volume between the present bcc phase and N-martensite amounts to about 3%, which roughly corresponds to the enhancement of the atomic volume according to the calculation¹⁹⁾. It seems, therefore, probable that the tetragonal distortion is more essential to the enhanced magnetization of the N-martensite.

IV. CONCLUSION

Ball milling in the NH₃ atmosphere can nitrify pure iron powders even at room temperature

and gives rise to the super-saturated bcc iron-nitrides up to 14.9 at.%N. The high temperature ϵ -phase with the hcp structure is obtained for the iron-nitrides containing more than 19.4 at.%N. In the composition range between 14.9 at.%N and 19.4 at.%N, a mixture of the bcc and hcp phases is produced. The volume per Fe atom in the bcc phase is found to be smaller than that in the N-martensite. We also reveal that the magnetization at room temperature gradually decreases with increasing the N concentration.

REFERENCES

- [1] T. K Kim and M. Takahashi, "New magnetic material having ultra magnetic moment" Appl. Phys. Lett. 20, pp.492-494, 1972.
- [2] H. Sun, J. M. D. Coey, Y. Otani and D.P.F. Hurley, "Magnetic properties of a new series of rare-earth iron nitrides: $R_2Fe_{17}N_y$ ($y \sim 2.6$)", J. Phys. Condens. Matter. 2, pp.6465-6470, 1990.
- [3] M. Komuro, Y. Kozono, M. Hanazono and Y. Sugita, "Epitaxial growth and magnetic properties of $Fe_{16}N_2$ films with high saturation magnetic flux density", J. Appl. Phys. 67, pp.5126-5130, 1990.
- [4] K. Nakajima and S. Okamoto, "Formation of ferromagnetic iron nitrides in iron thin films by high-dose nitrogen ion implantation", J. Appl. Phys. 65, pp.4357-4361, 1989.
- [5] K. Nakajima and S. Okamoto, "Nitrogen-implantation-induced transformation of iron to crystalline $Fe_{16}N_2$ in epitaxial iron films", Appl. Phys. Lett. 54, pp.2536-2538, 1989.
- [6] K. Nakajima and S. Okamoto, "Structure and magnetic properties of $Fe_{16}N_2$ films prepared by nitrogen ion implantation", J. Magn. Soc. Jpn. 14, pp.271-274, 1990.
- [7] C. C. Koch, O. B. Cavin, C. G. Makamey and J. O. Scarbrough, "Preparation of amorphous $Ni_{60}Nb_{40}$ by mechanical alloying" Appl. Phys. Lett. 43, pp.1017-1019, 1983.
- [8] C. H. Lee, M. Mori, T. Fukunaga and U. Mizutani, "Effect of ambient temperature on the MA and MG process in Ni-Zr alloy system", Jpn. J. Appl. Phys. 29, pp.540-544, 1990.
- [9] T. Fukunaga, E. Ishikawa, N. Kuroda, C. H. Lee and U. Mizutani, "Nitrogen-induced amorphization due to mechanical alloying", Proc. 4th Japan-Russia Symp. on Mechano-chemistry(Nagoya), pp.69-74, 1992.
- [10] K. Sakurai, C. H. Lee, N. Kuroda, T. Fukunaga and U. Mizutani, "Nitrogen effect in mechanical alloying of immiscible Cu-V: Extended X-ray absorption fine structure study", to be published in J. Appl. Phys., 1994.
- [11] K. H. Jack, "The occurrence and the crystal structure of α' -iron nitride; a new type of interstitial alloy formed during the tempering", Proc. Roy. Soc. A208, pp.216-224, 1951.
- [12] J. D. Fast, "Interaction of Metals and Gases", Academic Press, New York, 1965.
- [13] K. H. Jack, "The iron-nitrogen system: The crystal structure of ϵ -phase iron nitrides", Acta. Cryst. 5, pp.404-411, 1952.
- [14] K. H. Jack, "The iron-nitrogen system: the preparation and the crystal structure of nitrogen-austenite (γ) and nitrogen-martensite (α')", Proc. Roy. Soc. A208, pp.200-215, 1951.
- [15] K. H. Jack, "The iron-nitrogen system: the structures of Fe_4N and Fe_2N ", Proc. Roy. Soc. A 195, pp.34-41, 1948.
- [16] P. Rochegude and J. Foct, "The transformation $\epsilon \rightarrow \alpha'$ in iron-nitrogen solid solutions studied by Mössbauer spectroscopy", Phys. Stat. Sol. A88, pp.137-142, 1985.
- [17] K. Mitsuoka, H. Miyajima, H. Ino and S. Chikazumi, "Induced magnetic moment in ferromagnetic Fe alloys by tetragonally elongated lattice expansion", J. Phys. Soc. Jpn. 53, pp.2381-2390, 1984.
- [18] O. K. Andersen, J. Madsen, U. K. Poulsen and J. Kollar, "Magnetic ground state properties of transition metals", Physica 86-383, pp.249-256, 1977.
- [19] V. L. Moruzzi, P. M. Marcus, K. Schwaltz and P. Mohn, "Ferromagnetic phases of bcc and fcc Fe, Co and Ni", Phys. Rev. B34, pp.1784-1791, 1986.

저자소개



이충효

1960년 4월 2일생. 1982년 2월 한양대학교 공대 금속공학과 졸업. 1990년 3월 나고야대학 대학원 결정재료공학전공(석사). 1993년 3월 나고야대학 대학원 결정재료공학전공(공학). 1993년- 현재 일본 통산성 공업기술원 나고야공업기

술연구소 기능재료연구실.



홍진웅

1955년 2월 23일생. 1982년 2월 한양대학교 공대 전기공학과 졸업. 1984년 2월 광운대 대학원 전기공학과(석사). 1987년 8월 광운대 대학원 전기공학과(공학). 1992년 7월- 1993년 7월 일본 나고야대학 전기학과 객원연구원. 1989

년 3월-현재 광운대학교 공대 전기공학과 부교수.