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

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1. INTRODUCTION

The discovery of giant magnetic moment of the Fe₆₀N₂ sample and hard magnetic characteristics of the Sm₂Fe₁₇N₂ has roused the interest in the magnetic properties and the preparation of ferromagnetic nitrides. Kim et al. reported, for the first time, that the ordered bct iron–nitrides of Fe₆₀N₂ exhibit the highest magnetization of 2.8 T at room temperature. Recently, Komura et al. have succeeded in producing the single crystalline Fe₆₀N₂ films by vacuum deposition and confirmed its large magnetic moment. Nakajima et al. 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 concentration. They also found that the magnetization of the disordered bct nitrides is almost same as that of the Fe₆₀N₂. Neither disordered bct iron–nitrides nor the ordered Fe₆₀N₂ 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 phases. 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 deformation. 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. We consider that one of the most interesting solid-gas reaction occurs...
in the iron-nitrogen system as mentioned above. The MA technique might have a potentiality to produce metastable iron-nitrides such as bet martensite phase, which eventually decomposes into stable $\alpha$-Fe and $\gamma'$-Fe$_3$N at 200°C$^{11}$.

In this paper, we show that mechanical alloying technique under a controlled gas atmosphere makes it possible to nitride 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 $\mu$m in size) in NH$_3$ 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 NH$_3$ gas, filled in the vial at 1.3 atm, can nitride Fe powders of 20g up to 1.3 at.%N, provided that all gas is absorbed by Fe powders. NH$_3$ 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\(\alpha\) radiation (RIGAKU, RAD-HC). The magnetization at room temperature was measured with a vibrating sample magnetometer (TOEI VSM-5) calibrated using a pure Ni disk (99.90%).

The N concentration absorbed into the sample was determined with a nitrogen-oxygen analyzer (HORIBA EMGA 630). The sample was heated up to 200°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 the rate of about 1.2 at.% per 50h-milling. Hence, most of NH$_3$ gas in the vial has been consumed during ball milling process. The MA process most likely gives rise to the following reaction: 2xFe + 2NH$_3$ $\rightarrow$ 2Fe$_3$N + 3H$_2$. In the present experiment, Cr impurity from vial is less than 0.01% for 300h-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 NH$_3$ gas. In this process, H$_2$ 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 NH$_3$ and H$_2$. 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 H₂ gas would promote the nitrification in the similar manner to the conventional high temperature process.

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.%. Diffraction lines associated with neither the γ'-Fe₃N nor ε-phase are observed. Hence, we conclude that a supersaturated 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 supersaturated 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'-Fe₃N. The lattice parameters are determined as a=2.71 Å and c=4.37 Å 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 Å and c=4.344 Å. Two faint peaks associated with the ε-phase can be seen at 2θ=70° 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<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-martensite, γ'-Fe₃N and ε-phase nitrides. Rochequade et al. reported that the atomic volume of iron-nitride, whose chemical formula is expressed in the form of FeₙNₓ, is given by the following equation: \( V_n (\text{Å}^3) = 12.01 + 5.5x \). 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 axis, 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 as 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-martensite\(^{11}\) (▲), \(\gamma'\)-FeN\(^{15}\) (□) and \(\varepsilon\)–phase nitride\(^{13}\) (■). 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 implantation\(^{9}\) 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 243emu/g and axial ratio of 1.1 are obtained at a composition of 11 at.\%N\(^{15}\). 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 calculation\(^{19}\). 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 NH\(_3\) atmosphere can nitritify 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


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