In situ observation of phase separation in α”-$Fe_{16}N_2$

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1. Introduction

Although the extreme price hike of rare earths in 2011 has subsided, there is still a strong social demand for inexpensive and stable magnet materials that do not contain rare earths. Iron nitride is an important candidate for such a material. Fig. 1 shows the magnetic properties of α"-$Fe_{16}N_2$. Although the magnetic anisotropy of α"-$Fe_{16}N_2$ is very small, the saturation magnetization is superior to that of the neodymium magnet. Ogawa groupe of Tohoku Univ., who are our collaborators, have succeeded in synthesizing α"-$Fe_{16}N_2$ in bulk (powder), and its application is expanding greatly.

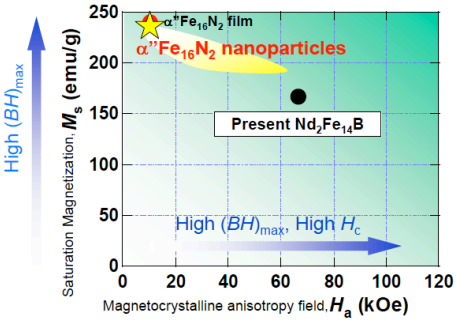


Fig.1 Properties of magnet materials

α"-$Fe_{16}N_2$ has a tetragonal unit cell (space group: I4/mmm), consisting of a stack of body-centered cubic crystals distorted by nitrogen (red) penetration as shown in Fig. 2, with three crystallographic iron sites with different color. Previous band calculations [1] and our polarized neutron diffraction experiments [2] have shown that the magnetic moment of the three iron species is larger for the iron sites farther from the nitrogen (Table I). Therefore, the behavior of nitrogen is a major key to the performance as a hard magnet.

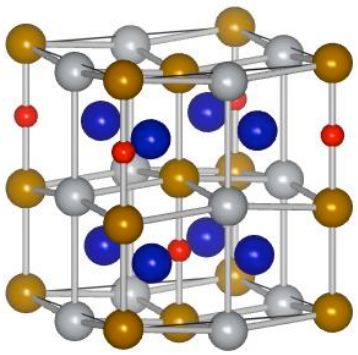


Fig2 Crystal Structure of α”-$Fe_{16}N_2$

Table I Relation of Magnetic moment and Fe-N distance

	Fe-N	Magnetic moment
Fe1-N	1.835(2)Å	1.4(2)μ_B
Fe2-N	1.963(1) Å	1.8(2)μ_B
Fe3-N	3.2636(1) Å	2.6(3)μ_B

For α"-$Fe_{16}N_2$, decompositions to other iron nitrides are reported at higher temperatures above 200°C. Therefore, we aim to measure the nitrogen behavior during the decomposition process from α"-$Fe_{16}N_2$ to γ-Fe_4N or other iron nitrides at high temperatures by high-intensity neutron diffraction experiments. We expect that this will provide a detailed understanding of the stability of nitrogen in each phase, and pave the way for sample preparation and improvement of magnetic properties by nitrogen control.

2. Experiment

The powder sample was prepared by Ogawa Group. To avoid container rupture and sample scattering, the powder sample was sealed in a quartz tube and then sealed in an aluminum cell. The in-situ neutron diffraction experiments were performed on BL20 of MLF using the Vanadium Furnace of BL20. The temperatures is fixed at 200 °C ; it takes 30 hours to decompose to Fe4N. As

confirm the accurate sample temperature, CeO2 powder was mixed in the powder sample to determine sample temperature using the lattice constant of CeO_2.

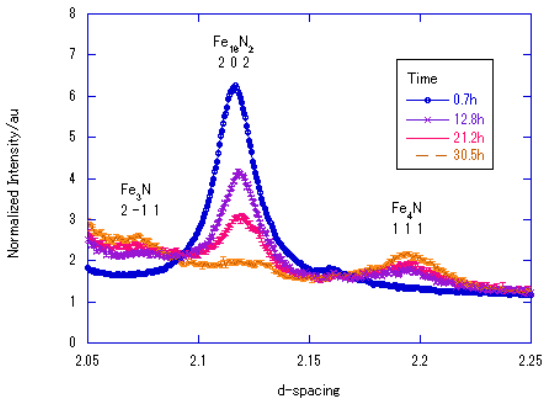
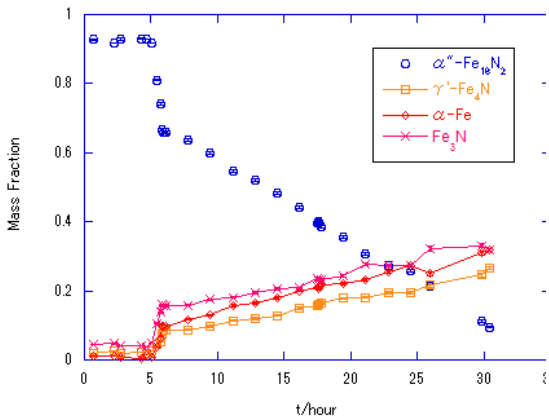


Fig.3 Time dependence of peaks around 202 at about 200°C.



Time

Fig.4 Time dependence of weight ratio of each phase.

3. Results

Fig.3 shows the time dependences of Bragg peaks around 202 at about 200°C. Decrease of $Fe_{16}N_2$ and increase in Fe_4N were successfully observed. By Rietveld Analysis, we determined the mass ratio of each phase: α"-$Fe_{16}N_2$, γ-Fe_4N, α-Fe, Fe_3N. With time, α"-$Fe_{16}N_2$ decreases and the other phases increase, indicating that phase decomposition is progressing. It is expected that nitrogen deficiency occurs in each phase generated the decompositions. However, by Rietveld analysis, we confirmed that no the occupancy of N in each phase is almost 1 without time dependence, meaning that the iron nitride phases are stable without nitrogen deficiency. This implies that α"-$Fe_{16}N_2$ is decomposed to γ-Fe_4N and α-Fe as soon as nitrogen is transferred. Therefore, it can be expected that suppression of nitrogen migration is effective in stabilizing α"-$Fe_{16}N_2$. On the other hand, in the experiments, we observed Fe_3N. Since the structure is hexagonal, Fe_3N is though to be formed by a different process than the other phases, in which the structures can be understood based on the distorted body-centered tetragonal crystal by N migration.

4. Conclusion

We successfully observed the progress of phase decomposition of α"-$Fe_{16}N_2$ to γ-Fe_4N, α-Fe, and Fe_3N by in-situ neutron diffraction experiments on BL20. By Rietveld analysis, we confirmed that the N occupancy is almost 1 in each iron nitride phase, suggesting that each phase decomposed from α"-$Fe_{16}N_2$ exists as a stable state. It is expected that suppression of nitrogen migration is effective in stabilizing α"-$Fe_{16}N_2$.

References

[1] Sakuma, JMMM, 102(1991)127.

[2] Hiraka et al. PRB 90 (2014)134427.