8 Elements Strategy Initiative Center for Magnetic Materials (ESICMM)

– in situ analysis using neutrons and X-rays –

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8-1. Introduction

We have performed research on rare earth permanent magnet materials, such as sintered magnets and hot-deformed magnets, and rare-earth-free magnet materials with the comprehensive use of neutrons and synchrotron radiation to investigate the magnetic structure of the main phase of magnetic materials, the structure of crystal grain, grain boundary, grain boundary phase, and magnetic microstructure. We investigated the following themes.

(1) Structure analysis and magnetic structural analysis of materials using neutron and synchrotron radiation

By using neutron diffraction and synchrotron radiation X-ray diffraction, precise structural analysis of magnetic material samples was performed on rare earth · transition metal 1-12 system and rare earth · iron · copper 6-13-1 phase to analyze crystal structure and magnetic structure. Regarding the magnetic material (1-12 series of rare-earth and transition metals), the magnetic structure in the temperature range from low temperature to the Curie temperature should be precisely determined, and the rare-earth and transition metal sites in the rare-earth magnets were measured to clarify the temperature dependence of the magnetic moment per site. We discussed the comparison of the experimental results with the results of the first principles calculation at the finite temperature for feedback to the electronic group.

(2) In situ high-temperature structural analysis of magnetic materials using neutron diffraction

To clarify the structure of the main phase of the magnetic material and the subphase at high temperature, in situ structure analysis at high-temperature was performed using neutron diffraction. Under the high-temperature process condition, the crystal structure of the main phase, as well as the subphases in the grain boundary phase such as metal Nd-rich phase, Nd oxide phase, rare earth - iron phase, etc., are clarified. Also the temperature dependence of the volume fraction of each phase, and their formation mechanism was clarified. The neutron diffraction data elucidates the thermodynamic information on the magnet composed of the main phase and the grain boundary phase. Based on the knowledge obtained from the analysis of experimental data, we propose a guideline for optimizing the magnet production process.

(3) Characterization of fundamental physical properties of magnetic materials

We investigated to establish a method to accurately measure fundamental physical parameters such as magnetocrystalline anisotropy and exchange stiffness constant of the magnetic material. About the magnetic material, we developed a method to determine magnetocrystalline anisotropy and exchange stiffness constant by neutron/synchrotron radiation experiment and optical measurement. Electronic and magnetic states of rare-earth and transition metals of magnetic materials were clarified by the measurement of the magnetic circular dichroism spectra of rare-earth magnet materials using scanning transmission X-ray microscopy (STXM). We also studied the preparation of single crystal samples for the evaluation of fundamental physical properties of magnetic materials and prepared them preliminarily.

(4) Study of magnetization reversal process using neutron small-angle scattering and X-ray microscopy

To elucidate the magnetization reversal process of the magnetic materials, we studied the magnetization reversal process by using small-angle neutron scattering (SANS) and micromagnetics simulation and STXM. We succeeded in observing the magnetization reversal process of the magnet material in detail by performing the first-order-reversal-curve (FORC) measurement using neutron small-angle scattering for the first time in the world. Moreover, by combining with micromagnetic simulation, details of magnetization reversal processes such as domain wall movement and magnetization rotation of hot-deformed magnets were clarified. Besides, we investigated to evaluate the magnetic interaction between grains quantitatively.

8-2. Results

(1) Structure analysis and magnetic structural analysis of materials using neutron and synchrotron radiation

In the magnetic materials, not only the crystal structure but also the magnetic structure is closely related to the magnetic properties. Therefore, it is indispensable to clarify not only the crystal structure but also the magnetic structure to analyze the structure of the magnetic materials. Since conventional X-ray diffraction has no sensitivity to magnetism, it is not possible to determine the magnetic structure, and it is necessary to use neutrons as a probe related to magnetism. From the magnetic structure and its temperature change, it is possible to clarify the quantitative value of the magnetic moment and its temperature dependence at each site of the main phase crystal constituting the magnetic materials. Based on these backgrounds, we have investigated methods to clarify the determination of the crystal structure and magnetic structure of magnetic materials. As a result, we confirmed that it is effective to characterize the crystal structure using synchrotron radiation X-ray diffraction and the magnetic structure should be estimated by neutron diffraction. Based on the established method, neutron and synchrotron experiments were conducted at the neutron experiment facility J-PARC / MLF and synchrotron radiation facility KEK-PF. To clarify the temperature change of the magnetic moment at each site of the rare earth magnet, neutron diffraction was performed in the temperature range from low temperature to the Curie temperature. An example of the results obtained by this experiment is shown in Fig. 1. Neutron diffraction data of Nd (Fe 0.75 Co 0.25) 11 Mo and Nd (Fe 0.75 Co 0.25) 11 MoN of the rare-earth / transition metal 1-12 system. Neutron diffraction is useful for precisely determining the position of nitrogen in nitrides of the rare-earth / transition metal 1-12 system. We find that neutron diffraction is effective for magnetic structure analysis for magnetic materials. By analyzing the diffraction data, the structure of rare-earth / transition metal 1-12 system was clarified as shown in Fig. 2. Experimental results were compared with the result of first principles calculation in cooperation with the electronic structure group of ESICMM. From the magnetic structure analysis and crystal structure analysis of rare-earth / transition metal 1-12 system, the role of each crystal site

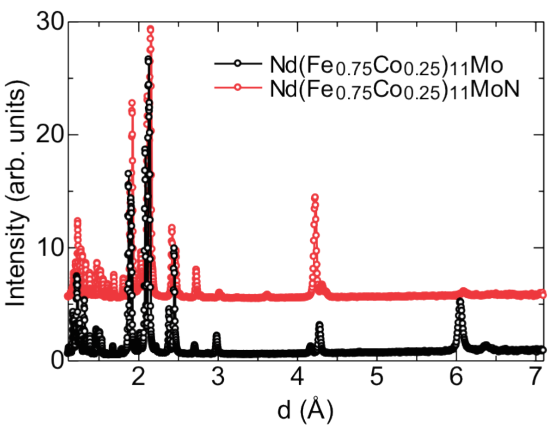

Fig. 1: Neutron diffraction patterns of Nd (Fe $_{0.75}$ Co $_{0.25}$) $_{11}$ and Nd$(Fe_{0.75}Co_{0.25})_{11}$MoN

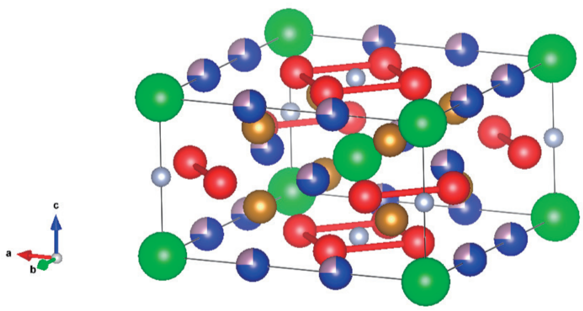

Fig. 2: Crystal structure of Nd$(Fe_{0.75}Co_{0.25})_{11}$MoN

was elucidated.

(2) In situ structural analysis of the high-temperature state of magnetic materials using neutron diffraction

In magnetic materials, not only intrinsic magnetic properties determined by the main phase characterized by (1), but also extrinsic magnetic properties due to the microstructure are essential for the magnetic properties of the magnet. It is essential to observe the formation process of the microstructure, to realize the development of a high-performance magnet. However, to observe the interior of the bulk magnet, a probe is necessary to have a high transmittance of the magnetic material and atomic level structure observation capability. Therefore, we have investigated the methodology for structural analysis of the main phase and subphase under high temperature. As a result, we confirmed that in situ high-temperature structure analysis using neutron diffraction is effective. Neutron diffraction experiments were performed on standard sintered rare-earth permanent magnets under high-temperature process conditions. The results are shown in Fig. 3. From the result, thermodynamic information on the main phase and the grain boundary phase formation was obtained. The results reveal the temperature dependence of the crystal structure and volume fraction of the main phase and the grain boundary phase such as metal Nd-rich phase, Nd oxide phase, rare earth and iron phase, etc. We found that the addition of Cu reduced the formation of $Nd_5Fe_{18}B_{18}$ phase. The findings obtained from this experiment are necessary to clarify the formation mechanism and give a guideline for optimizing the magnet production process.

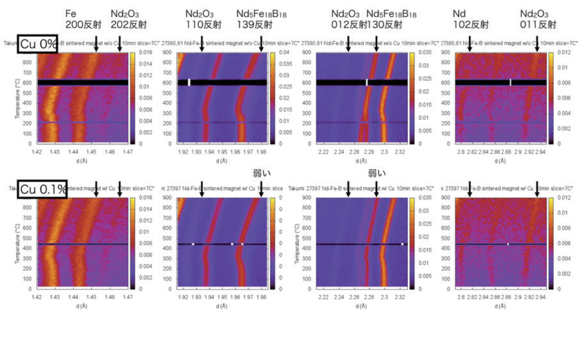

Fig. 3: High temperature neutron diffraction patterns of sintered Nd-Fe-B magnets with Cu addition.

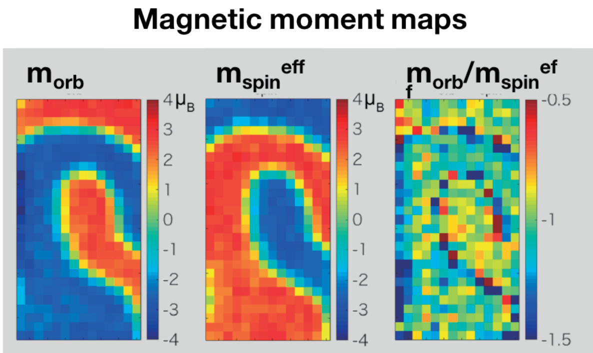

Fig. 4: XMCD images of SmCo5 magnet using scanning x-ray transmission microscopy

(3) Evaluation of fundamental physical properties of magnetic materials

We investigated to establish a method to accurately measure fundamental physical parameters such as magnetocrystalline anisotropy and exchange stiffness constant of the magnetic material. It is possible to determine magnetocrystalline anisotropy and exchange stiffness constants for magnetic materials by neutron/synchrotron radiation experiment and optical measurement method. Electronic and magnetic structure of rare-earth and transition metals of magnetic materials were clarified by the magnetic circular dichroism spectra of the rare-earth permanent magnet using STXM. Fig. 4 shows a spatial map of the rare-earth magnetic moment of the rare-earth permanent magnet using STXM. From this result, it was possible to characterize the fundamental physical properties in the microscopic region, and the physical properties of the realistic permanent magnet samples can be measured without preparing the single crystal sample. Also, preliminary fabrication of single crystal samples for evaluating fundamental physical properties of magnetic materials. As a result, it was found that a single crystal of about 5 mm can be produced by using the flux method.

(4) Study of magnetization reversal process using neutron small-angle scattering and X-ray microscopy

To elucidate the magnetization reversal process of the magnet material, we studied the magnetization reversal process by using small-angle neutron scattering (SANS) and micromagnetics simulation and STXM. We considered that FORC (first-order-reversal-curve) measurement using SANS is essential and conducted the FORC experiment using SANS for the first time. The experimental results are shown in Fig. 5. From this result, we found that the magnetization reversal process of the magnetic materials can be observed in detail by the FORC experiment using SANS. Moreover, by combining FORC-SANS results and micromagnetics simulation, details of the magnetization reversal process such as domain wall movement and magnetization rotation of hot-deformed magnets were clarified. We also conducted the quantitative evaluation of the magnetic interaction between the grains and obtained by a combination of the experiment and micromagnetics simulation.

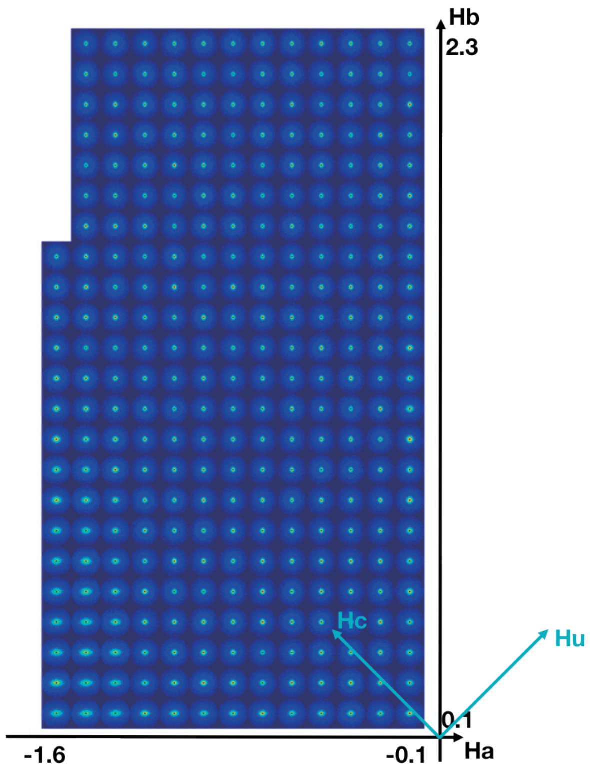

Fig. 5: SANS-FORC diagram of Nd-Fe-B magnet