Determination of constituent phase changes in Nd-Fe-B-Cu sintered magnets on heating and cooling processes by *in-situ* synchrotron X-ray diffraction

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For the production of Nd-Fe-B sintered magnets with high coercivity, optimized heat treatments to improve the microstructure are essential. Thus, the clarification of the thermodynamic behavior of secondary phases that form microstructure is important to manufacture such magnets effectively. To clarify phase changes in bulk magnets during heating treatments, we have conducted *in-situ* high-temperature synchrotron X-ray diffraction (XRD). The previous measurements for Nd-Fe-B-Cu bulk sintered magnets were successfully conducted only on heating [1,2]; however, it is difficult to distinguish between reversible and irreversible changes with temperature, which is essential for comparing experimental and theoretical results. Therefore, it is desirable to observe phase changes on cooling as well, although it is challenging because of the easy oxidation of rare-earth elements at high temperatures. In this study, we improved the experimental setup in the high-temperature *in-situ* XRD and carried out measurements on both heating and cooling.

A rectangular rod-shaped isotropic as-sintered magnet with the composition of $Nd_{13.74}Fe_{78.35}B_{5.92}Cu_{0.10}O_{1.88}$ in at.% was used. The preparation method has been reported elsewhere [2]. Synchrotron XRD measurements were conducted using a carefully designed sample holder to prevent the oxidization of magnets during heating. Synchrotron XRD profiles were collected using a high-resolution one-dimensional solid-state detector at the BL02B2 beamline of SPring-8. The sample was heated from room temperature to 1100°C using a cylindrical heater. The experimental results were compared to the computational phase diagram of this magnet based on the combined *ab initio*/CALPHAD approach [3].

We have observed similar XRD profiles at the same temperatures on heating and cooling except for slight differences in peak intensities, indicating the successful observation of the almost reversible phase changes. Figure 1 exhibits the temperature dependence of the amounts of secondary phases on cooling. There are two remarkable changes, which are compared to the computational diagram. One is the change in the amount of dhcp-Nd phase between 500°C and 650°C, which is similar to the previous observation except for the slight difference in temperatures [1,2]. This phase change is considered to originate from the eutectic reaction of dhcp-Nd and NdCu phases, as confirmed by the calculation. The NdCu binary phases, which were suggested in previous reports [3,4], were not detected in XRD probably because of the broad XRD peaks resulting from small crystalline sizes on the order of nanometers. The other finding is the change in the amounts of fcc-NdO_x and hcp-Nd_2O_3 above 1000°C. The result is likely explained as follows: fcc-NdO_x ↔ hcp-Nd_2O_3 + Liquid (the rightward and leftward reactions represent a phase change on heating and cooling, respectively). Although the phase change temperature we observed is much higher than that in the calculated phase diagram of this magnet composition (650°C), the temperature is close to that in the calculated NdO binary diagram (1100°C) [4]. This means that the fcc-NdO_x phase does not show the phase equilibrium with the other secondary phases in the Nd-Fe-B-Cu sintered magnet but shows the phase change almost independently.

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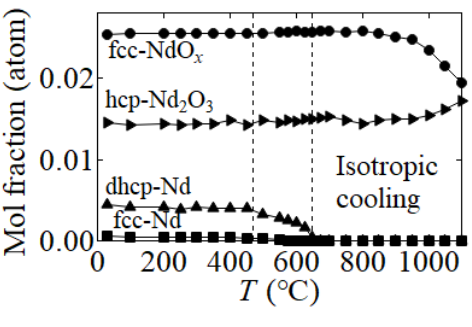

Fig. 1 Temperature dependence of amounts of secondary phases in the Nd-Fe-B-Cu isotropic sintered magnet on cooling.

References

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