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ABSTRACT
We investigated the structural influence of Nd$_2$Fe$_{14}$B phase magnetostriction on the Nd-rich secondary phases of hcp-Nd$_2$O$_3$, fcc-NdO$_x$, dhcp-Nd, and fcc-Nd, in Nd-Fe-B bulk-sintered magnets. The temperature dependence of the secondary phase lattice constants was evaluated by synchrotron X-ray diffraction using rod-shaped isotropic (randomly oriented) and anisotropic (c-axis oriented) Nd-Fe-B-Cu sintered magnets. The lattice constants of each secondary phase in the rod-shaped isotropic and anisotropic samples exhibited an invar-type expansion below the Nd$_2$Fe$_{14}$B phase Curie temperature ($T_C$), despite the phases not showing ferromagnetic ordering at $T_C$. Since such volume expansion has not been seen in powdered sintered magnets, we viewed it as a phenomenon particular to rod-shaped sintered magnets. These results indicated that the Nd$_2$Fe$_{14}$B phase spontaneous volume expansion induced the volume expansion observed in all the constituent phases of the bulk sintered magnets.

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I. INTRODUCTION
Nd-Fe-B sintered magnets have been extensively investigated to improve their magnetic properties, especially coercivity. It has been reported that coercivity is closely related to the microstructure of Nd-Fe-B sintered magnets, which are composed of Nd$_2$Fe$_{14}$B crystal grains and Nd-rich secondary phases, such as hcp-Nd$_2$O$_3$, fcc-NdO$_x$, dhcp-Nd, and fcc-Nd, on the grain boundaries and at the grain boundary triple junctions. For this reason, clarification of the constituent phases and their structural properties has been seen as critical to the further understanding of Nd-Fe-B sintered magnet magnetic properties. It was expected that secondary phase crystallographic properties would be affected by large spontaneous Nd$_2$Fe$_{14}$B magnetostriction. Some reports have mentioned that the structural mismatch between Nd$_2$Fe$_{14}$B and its secondary phases can cause local strain near the interface. Recently, we clarified that, for rod-shaped isotropic (randomly oriented) and anisotropic (c-axis oriented) bulk-sintered magnets, their powdered samples, and fine single crystals, the lattice constants of the Nd$_2$Fe$_{14}$B phase were different below the Curie temperature ($T_C$: approximately 580 K), depending on sample texture. This difference probably originates from the internal stress generated in bulk-sintered magnets, with such internal stresses likely to affect secondary phase crystallographic properties. The crystallographic properties of constituent phases have been experimentally investigated, by focusing on crystal orientation,
chemical stoichiometry, and lattice defects, using transmission electron microscopy, three-dimensional atom probe, electron back scattered diffraction, and synchrotron X-ray diffraction (XRD) techniques. Among them, synchrotron XRD measurements have the advantage of detecting crystallographic properties of small constituent phase amounts in bulk samples, owing to the high resolution and penetrating power of the high-energy synchrotron X-rays. We previously performed in-situ synchrotron XRD measurements using rod-shaped Nd-Fe-B isotropic and anisotropic bulk sintered magnets, and clarified the temperature dependence of the secondary phases up to approximately 1300 K. We clarified that the phase change from dhcp-Nd to fcc-Nd, whose phases likely played an important role in coercivity enhancement, started from approximately 500 K. It was also noted that dhcp-Nd lattice constants in the rod-shaped anisotropic sintered magnets were significantly greater than those of pristine Nd metal, at room temperature. This crystallographic change probably originates from the presence of interstitial oxygen atoms in its structure, although further studies are needed to clarify the origin of the lattice constant change.

In the study described here, we investigated the temperature dependence of synchrotron XRD patterns, using rod-shaped isotropic and anisotropic Nd-Fe-B bulk-sintered magnets and their powdered samples. We have been able to show that crystallographic parameters, such as the lattice constants and the full width at half maximum (FWHM) diffraction peaks for each secondary phase, depend on sample texture.

II. EXPERIMENTS

Preparation methods for the isotropic and anisotropic Nd-Fe-B-Cu sintered magnets, as well as the composition of Nd14Fe9.9B0.8Cu0.1, have been explained in our previous reports. Synchrotron XRD measurements for the Nd-Fe-B-Cu sintered magnets were conducted using rectangular rod-shaped samples (0.2 × 0.2 × 5 mm³), cut from a large sintered block. Anisotropic sintered magnet rods were prepared so that the longitudinal direction was perpendicular to the Nd₃Fe₁₄B c-axis. Powdered samples were prepared by crushing isotropic and anisotropic sintered magnets in an Ar glove box, which was used to prevent oxidation of the constituent phases. The rod-shaped and powdered samples were sealed under Ar atmosphere, in quartz capillary tubes with 0.3 mm internal diameters.

Synchrotron XRD profiles were recorded using a high-resolution one-dimensional solid-state detector (MYTHEN) at the BL02B2 beamline of SPring-8 (λ = 0.4962 or 0.4970 Å). High- and low-temperature measurements were performed using an N₂ gas flow system. Lattice constants were determined by whole-pattern fitting using Le Bail analysis, which was preferred due to the difficulty caused in Rietveld analysis by the rod-shaped anisotropic sintered magnets’ strongly preferred orientation.

III. RESULTS

Figure 1 shows the synchrotron XRD profiles for the rod-shaped isotropic and anisotropic Nd-Fe-B-Cu sintered magnets and their powdered samples at 300 K. As previously reported, XRD profiles for both rod-shaped sintered magnet types were well-indexed to the Nd₃Fe₁₄B (P42/mmm), dhcp-Nd₃O₅ (P5₃m1), fcc-NdO₂ (Fm3m), dhcp-Nd (P6₃/mmc), and Nd₃Fe₂B₁₈ (Pccn) phases. The volume fraction temperature dependence of each rod-shaped sintered magnet secondary phase has been reported previously.

Although the synchrotron XRD profiles for powdered samples looked similar to those of the rod-shaped sintered magnets at first glance, there were significant differences in the XRD profiles of their secondary phases. To begin with, several diffraction peaks from the fcc-Nd phase were observed in the powdered samples, while they were absent for the rod-shaped sintered magnets, at 300 K. Taking account of previous experimental results, the fcc-Nd phase in the powdered samples was most likely generated by a structural change and/or oxidation of the dhcp-Nd phase. In another difference, the peak positions of each secondary phase in the powdered samples were located higher than those of the rod-shaped samples, indicating that powdering had caused a decrease in the lattice constants. The lattice constants for the secondary phases in each sample, at 300 K, have been summarized in Table I, where it can be seen that the lattice constants for each secondary phase decreased in the following order: the rod-shaped isotropic sintered magnet, then the anisotropic magnet, followed by their powdered samples. The lattice constants for the powdered samples were the closest to those previously reported for pristine metals and compounds [Table I]. Note that XRD profiles for the powdered isotropic and anisotropic sintered magnets were almost identical— and so, in this paper, we have referred to both samples as powdered samples.

In order to clarify the origin of the difference in the lattice constants of the secondary phases caused by sample texture,
we investigated lattice constant temperature dependence. Figure 2 shows the temperature dependence for the hcp-Nd$_3$O$_5$, fcc-NdO$_3$, dhcp-Nd, and fcc-Nd lattice constants in the rod-shaped isotropic and anisotropic Nd-Fe-B-Cu sintered magnets, and their powdered samples. The lattice constants for the dhcp-Nd phase in the powdered samples were not well determined, owing to its weak and broad diffraction peaks. Note that temperature dependence of the Nd$_3$Fe$_{14}$B phase lattice constants has been reported elsewhere.\[^{14,15}\]

The unit cell volumes, $V$, for the hcp-Nd$_3$O$_5$, fcc-NdO$_3$, and dhcp-Nd phases in the rod-shaped sintered magnets exhibited similar temperature dependence. Above approximately 580 K, which is the $T_C$ of the Nd$_3$Fe$_{14}$B phase,\[^{16}\] $V$ increased monotonically as the temperature increased. Below $T_C$, the thermal expansion coefficients decreased. In other words, $V$ exhibited invar-like expansion below $T_C$, despite the secondary phases not showing magnetic ordering at $T_C$. Note that the $V$ temperature dependence for hcp-Nd$_3$O$_5$ and fcc-NdO$_3$ in the heating process was quite similar to that for the cooling process (not shown in the graph), indicating that the change with temperature was reversible. This result suggested that the anomaly in the $V$ temperature dependence did not originate from either a compositional change or oxidation. A similar invar-like volume expansion was observed for the fcc-Nd phase in the rod-shaped sintered magnets, over the cooling process. In contrast, fcc-Nd phase $V$ rapidly increased when heated through the temperature range of 500 K – 700 K, and then, had almost the same values as those when cooling above 700 K. We believe this rapid increase was due to slight structural and/or compositional change in the fcc-Nd phase, and that such crystallographic change was completed above 700 K.

In contrast, the secondary phases in the powdered samples exhibited monotonic thermal expansion. One important point is that the $V$ values of the secondary phases in the powdered samples were almost the same as those for the rod-shaped sintered magnets, above $T_C$, but were different at 300 K. These results indicated that some of the interactions that changed lattice constants were generated below $T_C$ in the rod-shaped sintered magnets, but not in the powdered samples. These interactions are probably related to the magnetic ordering of the Nd$_3$Fe$_{14}$B phase at $T_C$. Such interactions in the rod-shaped isotropic sintered magnets were stronger than those of the anisotropic sintered magnets, as secondary phases in former showed clearer anomalies in their $V$ temperature dependence, and exhibited larger $V$ below $T_C$, in comparison to the anisotropic sintered magnets.

Figure 3 shows the temperature dependence of the normalized FWHMs for the secondary phase diffraction peaks. Below $T_C$, the FWHMs for each secondary phase in the rod-shaped sintered magnets increased rapidly with decreasing temperature, whereas above $T_C$, the FWHMs were almost constant. For powdered samples, FWHMs increased slightly, below $T_C$, although the changes were much smaller than those of the rod-shaped sintered magnets.
Each secondary phase had oxygen non-stoichiometry. Phases contained interstitial oxygen within their structures, and that in mind that it has been reported that the dhcp-Nd and fcc-Nd provided one possible reason for this difference; we have borne the invar-like volume expansion of secondary phases in the rod-shaped sintered magnets. These results indicated that peak broadening was closely related for the difference in the lattice constants at 300 K, however, as each secondary phase had almost the same chemical composition. We are of the opinion that the invar-like volume expansion of each secondary phase was attributable to the spontaneous magnetostriction of each secondary phase. The tensile strain applied to each secondary phase in the rod-shaped isotropic sintered magnets was higher than that in the anisotropic sintered magnets, as indicated by the greater lattice constants of each secondary phase in the isotropic samples. Tensile stress was almost absent from the powdered samples, as their internal stress would have been virtually all released.

Tensile stress in bulk magnets can cause their thermal stability to differ to that exhibited in the atmosphere, making it important to investigate secondary phases within bulk magnets, in order to clarify their phase stability. It has also been reported that microstructural strain gave rise to decreased coercivity, although it is difficult to observe actual strain in the bulk magnets. High-energy synchrotron XRD techniques, with high penetrating power, would be advantageous when it comes to investigating strain and phase equilibriums, in bulk magnets.

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