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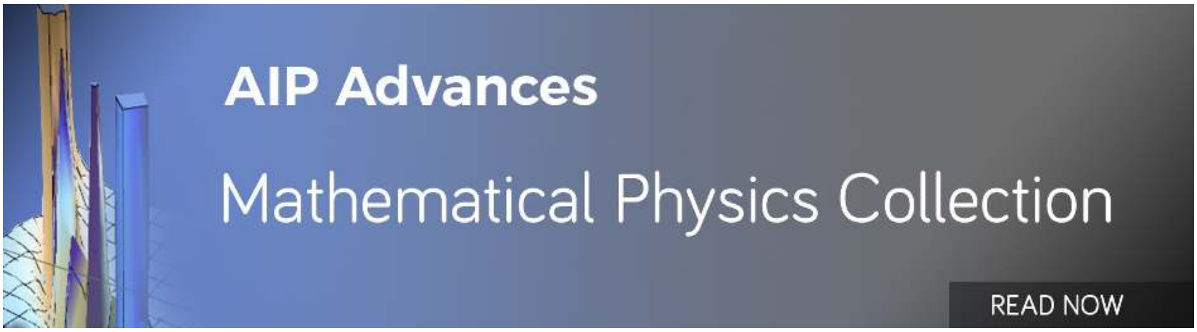

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$(Sm,Zr)(Fe,Co)_{11.0\text{-}11.5}Ti_{1.0\text{-}0.5}$ compounds as new permanent magnet materials

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We investigated $(Sm,Zr)(Fe,Co)_{11.0\text{-}11.5}Ti_{1.0\text{-}0.5}$ compounds as permanent magnet materials. Good magnetic properties were observed in $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$ powder containing a limited amount of the α-(Fe, Co) phase, including saturation polarization (J_s) of 1.63 T, an anisotropic field (H_a) of 5.90 MA/m at room temperature, and a Curie temperature (T_c) of about 880 K. Notably, J_s and H_a remained above 1.5 T and 3.70 MA/m, respectively, even at 473 K. The high-temperature magnetic properties of $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$ were superior to those of $Nd_2Fe_{14}B$. [http://dx.doi.org/10.1063/1.4943051]

Rare earth (R)-Fe-X (X = B, C, N) compounds are the most promising candidates for replacing widely used $Nd_2Fe_{14}B$ magnets.[1] Sakurada et al.[2] reported a high-saturation polarization (J_s) phase, $SmFe_{10}N_x$ (x not determined), with $J_s = 1.70$ T and an anisotropy field (H_a) of 6.2 MA/m at room temperature (RT). The properties of this phase, particularly the mechanism that produces the high J_s value, have not been clarified. Compounds with R_nFe_m compositions and their nitrides ($SmFe_{11}Ti$,[3] $SmFe_9N_x$,[4] $NdFe_{11}TiN_x$[5]) are interesting possibilities for future permanent magnet materials.

We performed preliminary experiments on $NdFe_{11}Ti$-based $ThMn_{12}$ (1-12) compounds and found that $(Nd_{0.7},Zr_{0.3})(Fe_{0.75},Co_{0.25})_{11.5}Ti_{0.5}N_x$ (x = 0.6–1.3) was promising. It had J_s of about 1.67 T, H_a of 4.0–5.25 MA/m at RT, and a Curie temperature (T_c) of more than 840 K.[6,7] We aimed to increase the Fe and Co content and decrease the Ti content in the starting alloy to maintain a high J_s and the 1-12 structure. For the ferromagnetic transition metals, a Co content of 25% and Fe content of 75% were selected based on the Slater-Pauling curve. As in our previous studies,[6,7] the substitution of Zr at Sm sites stabilized the Fe- and Co-rich $ThMn_{12}$-type phase. These ideas were applied to $(Sm,Zr)(Fe,Co)_{11.0\text{-}11.5}Ti_{1.0\text{-}0.5}$ compounds in this study. Nitrogen ($-N_x$) in the Nd-containing 1-12 compounds was not necessary for high anisotropy[8,9] or high coercivity, in the compound in this study, suggesting that they would be suitable as sintered magnet materials.

The strip-cast (SC) method was used to prepare the alloys based on our previous studies.[6,7] As in $SmFe_{11}Ti$, the 1-12 structure was well stabilized and the appearance of the α-(Fe, Co) phase was suppressed by the optimum annealing conditions of 1373 K for 4 h when the Ti content was about 8 atom %. Based on this procedure, the alloys $SmFe_{11}Ti$ (alloy A), $Sm(Fe_{0.75}Co_{0.25})_{11}Ti$ (alloy B), $Sm(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$ (alloy C), and $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$ (alloy D) were prepared. After optimum annealing at 1373 K for 4 h, the Sm, Zr, Fe, Co, and Ti distribution in alloy D, which was the most difficult alloy to prepare, were homogeneous except for limited precipitation of an Fe-rich phase (Fig. 1).

The XRD patterns of the four alloys are shown in Fig. 2. Alloys A and B with $-Ti_{1.0}$ compositions exhibited the 1-12 structure with almost no α-Fe or α-(Fe, Co) phases. In contrast, alloy C with

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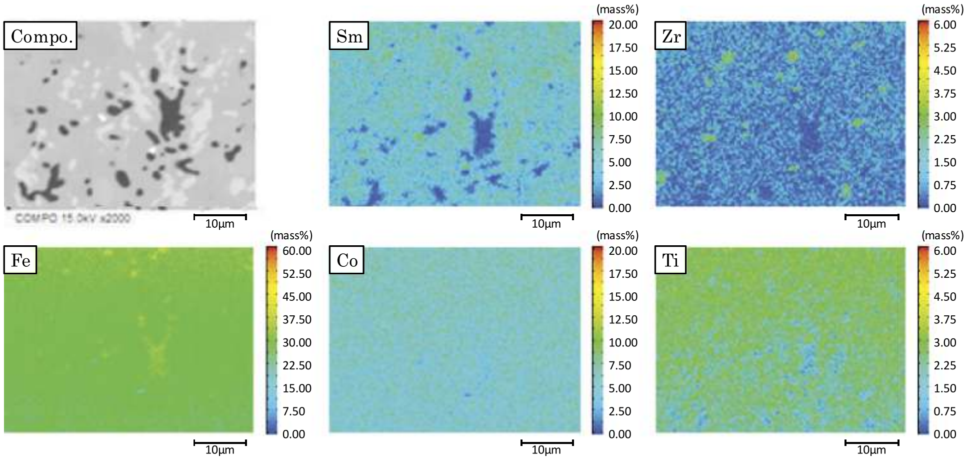

FIG. 1. Microstructure and Sm, Zr, Fe, Co, and Ti elemental distributions in alloy D, $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$, observed by electron probe micro-analyzer.

-$Ti_{0.5}$ showed a clear XRD peak for the α-(Fe, Co) phase at around $2\theta = 44.6°$ (Cu-kα). Alloy D, which contained -$Zr_{0.2}$, showed a smaller α-(Fe, Co) peak compared with the 1-12 phase, indicating that the 1-12 phase was stabilized by Zr substitution at the Sm sites.[7,11]

The a- and c-lattice constants obtained from the XRD patterns of the alloys are shown in Table I. Both constants monotonically decreased in the order of alloy A > alloy B > alloy C > alloy D, and thus a = 0.856 (alloy A) → 0.851 (alloy D) nm and c = 0.480 (alloy A) → 0.477 (alloy D) nm. We interpret the lattice shrinkage as follows: alloy A > alloy B was due to Co substitution at Fe sites; alloy B > alloy C was caused by a decrease in Ti content at the Fe sites[7] (metallic radius

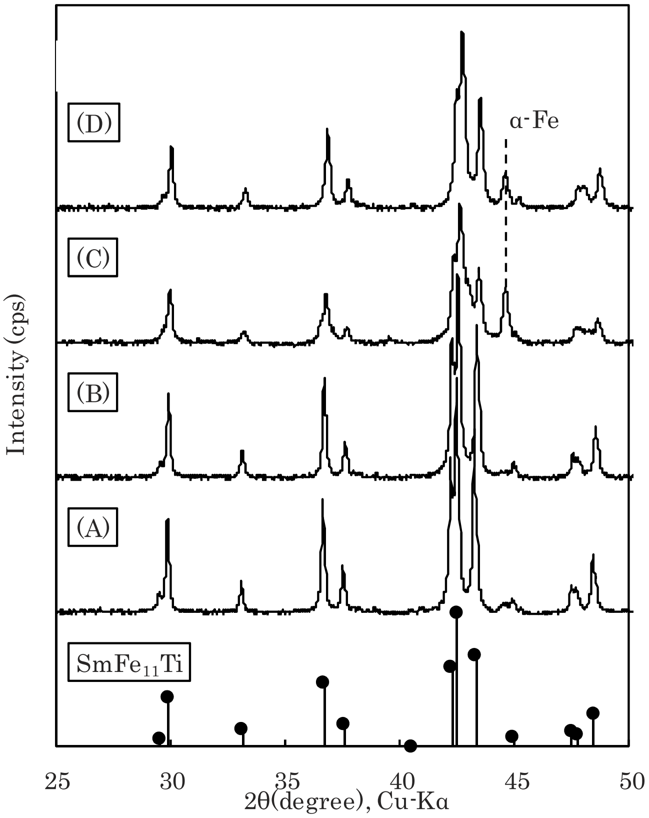

FIG. 2. XRD patterns of alloys A–D, and the standard peaks for $SmFe_{11}Ti$.

TABLE I. Lattice constants, unit cell volumes, and c/a ratios for alloys A–D.

Alloy	a / nm	c / nm	V / nm^3	(c/a) / %
(A) $SmFe_{11}Ti$	0.856	0.480	0.352	56.0
(B) $Sm(Fe_{0.75}Co_{0.25})_{11}Ti$	0.855	0.478	0.350	55.9
(C) $Sm(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$	0.854	0.477	0.348	55.9
(D) $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$	0.851	0.477	0.346	56.0

of Ti (0.147nm)[10] > Fe (0.126 nm)[10]); and alloy C > alloy D arose from Zr substitution at Sm (2a) sites[7,11] (metallic radius of Zr (0.160 nm)[10] < Sm (0.180 nm)[10]).

For magnetic measurements up to 9 T, we used a physical property measurement system-vibrating sample magnetometer (PPMS-VSM; EverCool II, QuantumDesign Inc.). Fig. 3 shows the

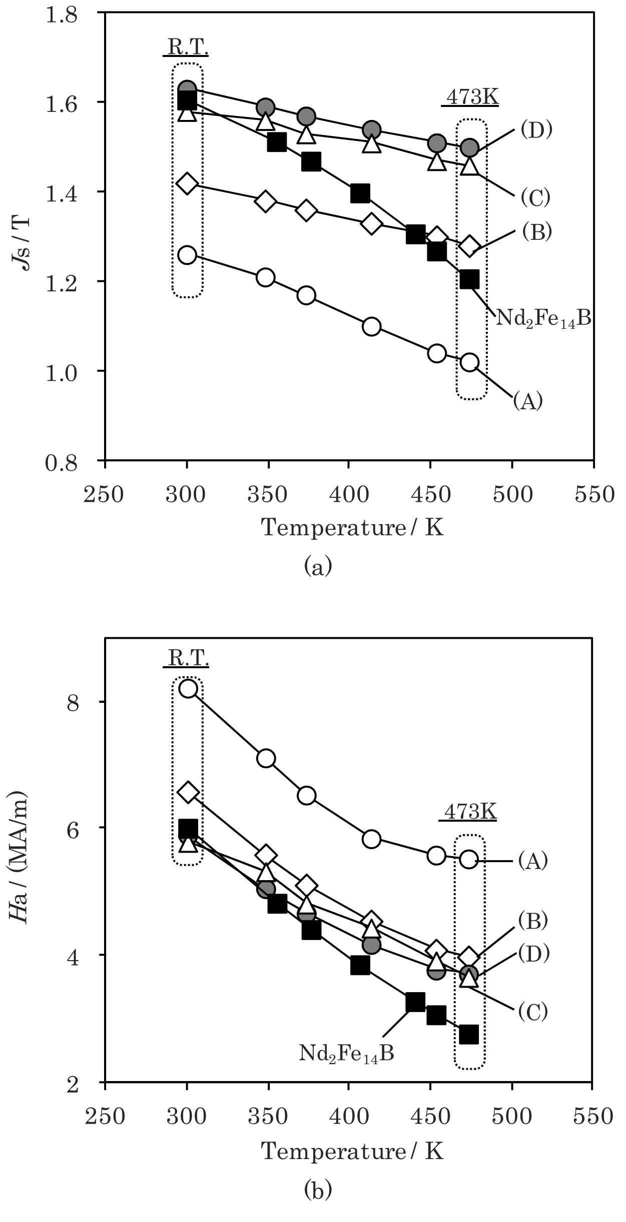

FIG. 3. (a) J_s values and (b) H_a values at 300–473 K for alloys A–D, with those of $Nd_2Fe_{14}B$. Dashed lines in the values at RT and 473 K.

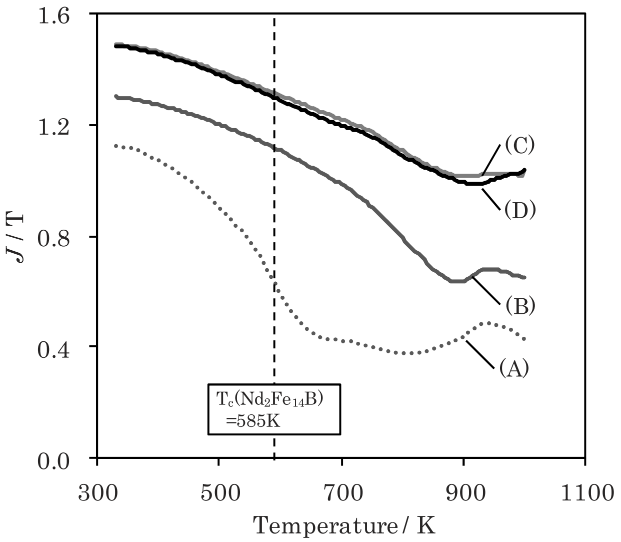

FIG. 4. Temperature dependence of polarization in alloys A–D.

temperature dependence of J_s and H_a. The incremental increase in J_s (alloy A < alloy D at RT (Fig. 3(a)) can be explained as follows. The variation from 1.26 T for alloy A to 1.42 T for alloy B at RT should arise the Co substitution at Fe sites, as explained by the Slater-Pauling curve.[7] The J_s value of alloy B (1.42 T) increased because of the higher Fe and Co transition metal content in alloy C (1.58 T), $Sm(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$, arising from the decrease in Ti content (1.0 → 0.5). Finally, Zr substitution at Sm sites stabilized the $ThMn_{12}$ structure and achieved a higher J_s in alloy D (1.63 T). Although the contribution of the α-(Fe, Co) phase to J_s was eliminated, the values were still 1.50 T for alloy C (-0.08 T) and 1.58 T for alloy D (-0.05 T) at RT.

To determine the anisotropy field, H_a, the law of approaching saturation was used[12–14]; the measured polarization under an applied field, $J(H_{\text{appl}})$ versus $1/H^2$ was plotted, where H is the applied magnetic field. To calculate H_a, we used the magnetization curves of alloy powders A–D isotropically distributed in ceramic cement (5.3 vol.% (14wt.%)), where

$$J(H_{\text{appl}}) = J_s(1 - \alpha/H^2),\ \alpha = \text{constant} \times K_1{}^2/J_s{}^2 \tag{1}$$

H_a was calculated by using the measured K_1/J_s values based on equation (1). When a constant value of 4/15[14] was used in equation (1), the anisotropy fields at RT were 8.21 MA/m for alloy A, 6.58 MA/m for alloy B, 5.78 MA/m for alloy C, and 5.90 MA/m for alloy D (Fig. 3(b)). We also calculated the H_a values by using the dJ/dH vs $1/H^3$ relationship.[15] The results showed unexpected fluctuation in susceptibility (χ_0) values (see, e.g., Ref. 15), which are thought to be caused by the maximum applied field of <9 T = 7.2 MA/m. Therefore, we used equation (1).

The Curie temperature (T_c) of the alloys was measured by using the PPMS-VSM with an applied field of about 9 T.[16] The results are shown in Fig. 4 with a temperature increase rate of 5 K/min. Tc of alloy A was about 620 K, which is slightly higher than the reported value.[17] Those of alloys B, C, and D were estimated to be 830, 880, and 880 K, respectively. Tc of alloy D was notably higher than the value of 586 K for Nd-Fe-B,[18] as shown in Fig. 4.

The temperature dependences of J_s (Fig. 3(a)) and H_a (Fig. 3(b)) showed that the J_s and H_a values at 473 K of alloys B–D were higher than those of Nd-Fe-B.[19,20] Alloy D, $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$, was found to be a promising permanent magnet material for high-temperature applications.

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