

Newly developed (R,Zr)(Fe,Co)_{12-x}Ti_x-N_y compounds for permanent magnets (y=1.3 for R=Nd, y=0 for R=Sm)

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(R_{0.7-0.8}Zr_{0.3-0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5} (R = Nd and Sm) alloys for permanent magnet materials were prepared by strip-casting. The homogeneity of the elements detected using electron-probe micro-analysis (EPMA) was fairly good. The occupation sites of the substituted elements, i.e. Zr in R sites, Ti in Fe(8i) sites and Co in Fe(8j) and Fe(8f) sites, were revealed by using spherical aberration-corrected scanning transmission electron microscopy (Cs-STEM). The stabilization of ThMn₁₂ structure at a low Ti content of Ti_{0.5} mainly originated from the substitution of R sites with Zr. The nitrogenated R = Nd alloy, (Nd_{0.7}Zr_{0.3})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}N_{1.30} compound, showed good magnetic properties of $J_s = 1.67$ T and $H_a = 5.25$ MA/m at room temperature (RT). The R = Sm alloy, (Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}, also had $J_s = 1.58$ T and $H_a = 5.90$ MA/m at RT. The values in the R = Sm alloy were still $J_s = 1.50$ T and $H_a = 3.70$ MA/m at 473 K, and were higher than those of Nd₂Fe₁₄B phase at the temperature [1]-[6]. Because the R = Sm alloy is a Dy-free and N-free powder, it is a promising candidate as a material for sintered magnets (4).

For the measurement of magnetic properties of the samples, physical properties measurement system-vibrating sample magnetometer (PPMS-VSM) under a maximum applied field of 9 T was employed. Especially, the J_s and H_a , i.e. K_1 , was calculated from the magnetization curve using the law of approach to saturation (LAS) method. The sample powder consisted of secondary grains composed of isotropic agglomerated primary grains of about $5 \times 5 \sim 20$ μm . The sample powder was mixed in epoxy resin, then the magnetically isotropic sample. The analysis was performed by using the following equation [7], [8].

$$dJ(H)/dH = J_s (8/15) (K_1^2/J_s^2) (1/H^3) + \chi_0 \quad (1)$$

Here, $J(H)$ is the measured polarization under applied field H , J_s is the saturation polarization, and K_1 is the first-order anisotropy constant. Equation (1) was applied to the measured polarization under a high field of 6-9 T, and the plots between $dJ(H)/dH$ and $1/H^3$ are used to calculate J_s and K_1 values. This method was used to obtain the results in our previous studies [1]-[4]. In the study [4], however, we compared the results obtained using above equation (1) with those using $J(H)$ vs $1/H^2$ plots, and employed the latter method for the stability of obtained values. As mentioned above, the comparatively high magnetic properties in R=Nd nitrogenated compound and R=Sm alloy were measured using the LAS method.

Evaluating the α -(Fe,Co) phase concentrations in the samples is important for calculating precise J_s . We determined the volume fractions of the phase using two methods. First, we compared the largest XRD peak height of the α -(Fe,Co) phase around $2\theta=44.5^\circ$ with that of the main ThMn₁₂ phase of around $2\theta=42.4^\circ$. The ratios of peak heights corresponded to the volume fractions of the phases. This method included the error from the crystallinity of each phase in the samples and the local distribution of the phases in the sample particles. Second, we obtained the volume fractions directly, through measuring the surface area fractions of the α -(Fe,Co) phase on the polished surface of electron back-scattering diffraction (EBSD) image of the sample particles. Each phase was clearly distinguished in this method, however, there were errors arising from the difference in the particles observed. Although numerous observations are required for this method, the number of observations was limited for some particles in the experiments.

The above J_s values of samples were corrected using XRD data those for eliminating the contribution from α -(Fe,Co) phases. The obtained values were indicated in Fig.1. The values (a) were shown in our previous papers [1]-[4], and those of (b) were newly obtained in our recent measurements.

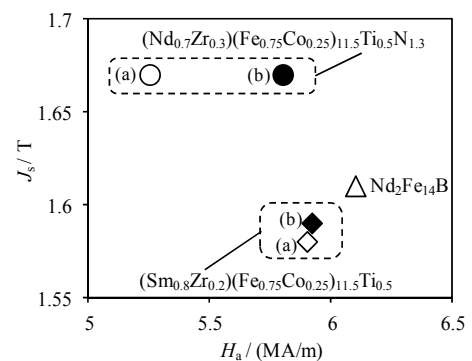


Fig. 1 Results of the LAS method using PPMS-VSM (at RT)

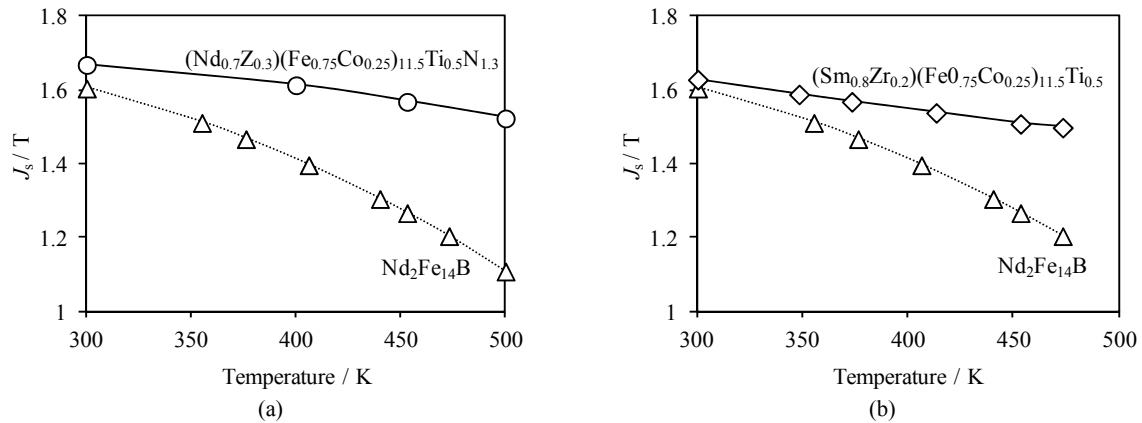


Fig. 2 Temperature dependences of J_s in R=Nd compound (a) and in R=Sm alloy (b) with those in $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase [6].

The Curie temperature (T_c) of the alloys was measured also using the PPMS-VSM with an maximum applied field of about 9 T. T_c of $(\text{Nd}_{0.7}\text{Zr}_{0.3})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.5}\text{Ti}_{0.5}\text{N}_{1.30}$ compound is more than 840K that is sufficiently higher than that of an Nd-Fe-B magnet of about 584 K [5], [6]. The temperature dependences of J_s (Fig. 2) and H_a of the alloys showed that the J_s and H_a values at 473 K of $(\text{Nd}_{0.7}\text{Zr}_{0.3})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.5}\text{Ti}_{0.5}\text{N}_{1.30}$ compound and $(\text{Sm}_{0.8}\text{Zr}_{0.2})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.5}\text{Ti}_{0.5}$ alloy (T_c estimated to be 880K) were higher than those of Nd-Fe-B (the figure for H_a exists in ref.[4]). As mentioned above, $(\text{Sm}_{0.8}\text{Zr}_{0.2})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.5}\text{Ti}_{0.5}$ has still $J_s = 1.50$ T and $H_a = 3.70$ MA/m at 473K, and we would like to insist again that the alloy is Dy-free and N-free, therefore, it is a promising candidate for permanent magnet material for high-temperature applications.

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