Preparation of Rare-earth-saved hard magnetic materials

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Rare-earth magnets are used in numerous devices and are essential materials. However, rare-earth elements, especially heavy rare-earth elements, are limited natural resources; therefore, it is important to develop rare-earth-free permanent magnets. Recently, developing rare-earth-free hard magnetic materials has been performed by using tins films, nano-powders, and non-equilibrium process. Some research have focused on α "-Fe₁₆N₂^{1,2)}, L1₀-FeNi³⁻⁵⁾, and Mn alloy^{6,7)} showing relatively high magnetic anisotropy. Although Mn-based compounds show low saturation magnetization, some Mn-based compounds show high corecivity because of high crystalline anisotropy. Our group reported that Mn-Sn-N and Mn-Sn-Co-N alloys⁸⁾ exhibit high coercivity more than 800 kAm⁻¹ without rear-earth elements. High performance permanent magnets must have the large coercivity, therefore revelation of cause of high coercivity has possibility of important clue for development of new type magnets.

FeCo alloys are also candidates for rare-earth-free permanent magnets because they exhibit high saturation magnetization. FeCo alloys, which have a stable cubic structure phase, can show high magnetocrystalline anisotropy when the unit cell is distorted tetragonally.^{9,10)} In these days, distorted FeCo film grown on Ir(001), Pd(001) or Rh(001) underlayer have been reported by several researchers¹¹⁻¹³⁾. Our group reported that Rh/FeCo-Ti-N thin film has perpendicular magnetic anisotropy derived from lattice distortion at the interface¹⁴⁾.

Our group have also preparing nano-particles for high coericivity, and shows high coercive Mn-Bi and Fe nano-particles. Then, I introduce our recent research about rare-earth free hard magnetic materials. Topics are shown as follows;

High coercive Mn-Sn-Co-N alloy

 $Mn_{82.5}Sn_{10}Co_{7.5}$ (at%) alloy was annealed at 900 °C (high-temperature annealing) and subsequently annealed at 400-700 °C (low-temperature annealing) under N₂ gas atmosphere. The coercivity strongly depended on the low-temperature annealing and reached a maximum of 1270 kAm⁻¹ for annealing at 500 °C (Fig. 1). The alloy consists of two phases of perovskite-type Mn-N and β -Mn phases, and there are many twins and stacking faults in the perovskite-type phase. In addition, Co and Sn enriched at the twin interfaces. These results indicate that the magnetic anisotropy could change at twins, and the twins could play as a pinning site of domain wall motion for Mn-Sn-Co-N alloy.

FeCo-Ti-N anisotropic films

FeCo-Ti-N thin films with the thickness (*t*) of 23~62 nm deposited on Rh buffer layer. The FeCo-Ti-N film shows relatively high anisotropy constant (K_u) of 0.98 MJm⁻³ for t=23 nm (Fig. 2), and the value is 0.46 MJm⁻³ for t=64 nm. Addition of Ti and N into FeCo layer improves lattice distortion of the lattice and it also improved the K_u .

Mn-Bi and FeCo-based nano-particles with relatively high coercivity

High coercivity Mn-Bi nano-powder are obtained by Hydrogen-Plasma-Metal-Reaction (HPMR) process. The coercivity is 1090 kAm⁻¹, and $(BH)_{max}$ reached to 105 kJm^{-3 15)}. The $(BH)_{max}$ is highest value for Mn-Bi. The HPMR process can prepare Fe-based nano-particles, and FeCo nano-particles shows relatively high coercivity over 90 kAm⁻¹.



Fig. 1 2nd-annealing temperature dependence of coercivity of Mn-Sn-Co nitrided alloy.



Fig. 2 Hysteresis loops measured with the external field perpendicular to the plane (\perp) and in-plane (//) directions for the FeCo-Ti-N films prepared with 5% N₂ gas.

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