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Magnetic properties of $Nd_{1+\delta}(Fe,M)_{12}N_X$ (M=Ti,V,Mo) non-stoichiometric compositional powders prepared by utilizing HDDR phenomena

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Present works describe the magnetic properties of $Nd_{1+\delta}(Fe,M)_{12}N_X$ powders prepared by utilizing hydrogenation disproportionation desorption recombination (HDDR) phenomena. The stoichiometric powders include α-Fe phase and show low coercivity after nitriding. But the α-Fe phase decreases with increasing Nd content and high coercivity can be obtained with non-stoichiometric compositional powders. The Co addition increases the coercivity and $Nd_{1.6}(Fe_{0.9}Co_{0.1})_{10}V_2N_X$ powders exhibit high coercivity of $664kAm^{-1}$ (8.3kOe).

1. INTRODUCTION

The nitrogen interstitially modified $Nd(Fe,M)_{12}$ (M=transitional metal) compound with $ThMn_{12}$ structure is interested as new class permanent magnets because of their relatively high magnetic properties [1]. Takeshita et al. [2] reported that hydrogen disproportionation desorption recombination (HDDR) phenomena are very useful methods for preparing powders with high coercivities in Nd-Fe-B magnets. Our previous papers show the possibilities of HDDR phenomena in nitrogen contained R-Fe (R=rare earth elements) compounds such as $Sm_2Fe_{17}N_X$ and $Nd(Fe,M)_{12}N_X$ compounds [3]-[5]. High coercivity can not be obtained with stoichiometric compositional $Nd(Fe,M)_{12}N_X$ powders but non-stoichiometric compositional $Nd_{1.3}Fe_{10}VMoN_X$ powders exhibit high coercivity of $464kAm^{-1}$ (5.8kOe) [5]. It is also important to know the reason why high coercivity can be obtained with the non-stoichiometric compositional $Nd_{1+\delta}(Fe,M)_{12}N_X$ powders.

It is reported that the Co addition is very effective for increasing magnetic properties of $Nd(Fe,M)_{12}N_X$ compound [6]. But the magnetic properties of $Nd(Fe,Co,M)_{12}N_X$ powders prepared by utilizing HDDR phenomena have not been investigated.

Then there are two purposes in this investigation. The first one is to investigate the magnetic properties of non-stoichiometric compositional $Nd_{1+\delta}(Fe,M)_{12}N_X$ (δ=0, 0.3, 0.6) powders prepared by utilizing HDDR phenomena in conjunction with the phase changes of their powders. The second one is to study the effect of Co addition on the magnetic properties of $Nd_{1+\delta}(Fe,M)_{12}N_X$ powders.

2. EXPERIMENTAL PROCEDURES

The compositions of studied alloys were $Nd_{1+\delta}(Fe_{1-y}Co_y)_{11}Ti$ and $Nd_{1+\delta}(Fe_{1-y}Co_y)_{10}M_2$ (M=V,Mo) (δ=0, 0.3, 0.6). The alloys were induction-melted and homogenized at 800-1000℃ for 50 h in Ar atmosphere. The ingots were crushed into powders with the size less than 63 μm and the powders were pressed into the compacts at a pressure of 150MPa (1.5 ton/cm^2). The green compacts were heat-treated at 650-1000℃ in hydrogen and subsequently in vacuum (HV treatment). Details of this heat treatment are described elsewhere [3][4].

The compacts after HV treatment were nitrided at 450-550℃ for 4 h and were ground into powders by hand milling. These powders mixed with molten paraffin were solidified in a magnetic field of $960kAm^{-1}$ (12kOe). Magnetic properties were measured by VSM with maximum applied field of $1.2MAm^{-1}$ (15kOe) after applying a pulsed field of 4MAm^{-1} (50kOe) to the samples. The microstructures were studied by X-ray diffraction using Fe-Kα radiation. The characteristics of hydrogen absorption and desorption were investigated by monitoring the quantitative changes of the flowing gas. The samples for investigating these characteristics are the green compacts described above. These equipments and details were described in our previous paper [4].

3. RESULTS AND DISCUSSION

3.1. The Characteristics of Hydrogen Absorption and Desorption of $Nd(Fe,M)_{12}$ and $Nd(Fe,Co,M)_{12}$ Stoichiometric Compositional Alloys

The X-ray diffraction revealed that $Nd(Fe,M)_{12}$ alloys consist of $ThMn_{12}$ phases and small amount of α-Fe after homogenization. These alloys were used for the investigations. Figure 1 shows the characteristics of hydrogen absorption and desorption of $NdFe_{11}Ti$, $NdFe_{10}V_2$ and $NdFe_{10}Mo_2$ alloys heating at a rate of 400°C/h in hydrogen. The X-ray diffraction patterns show that the absorption peaks around 800°C correspond to the disproportionation reaction of $Nd(Fe,M)_{12}$ phases with $ThMn_{12}$ type structure. These phases are called as $ThMn_{12}$ phase hereafter. The shape of these absorption peaks is different among three alloys. The $NdFe_{11}Ti$ alloy shows a sharp absorption peak but the $NdFe_{10}Mo_2$ alloy does a broad one. The absorption temperature of $NdFe_{10}Mo_2$ alloy is higher than that of $NdFe_{11}Ti$ alloy. It can be said that the temperature range of hydrogen absorption corresponding to disproportion reaction is changed by the transition metals which stabilize $ThMn_{12}$ phases.

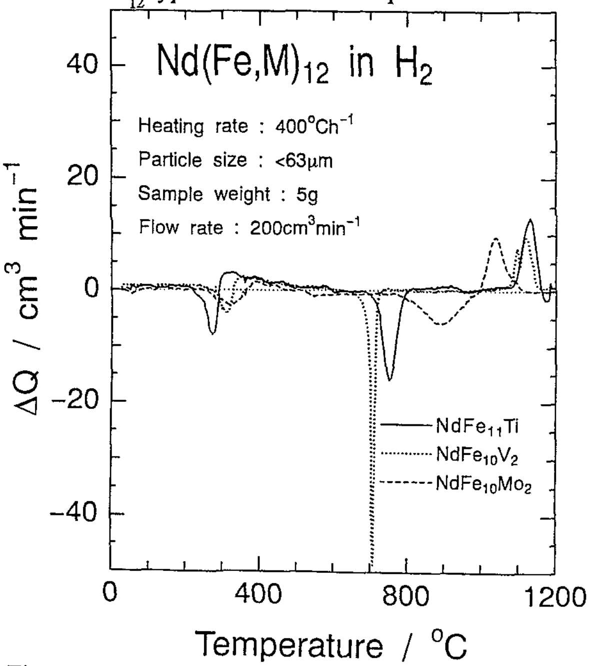

Figure 1. The characteristics of hydrogen absorption and desorption of $NdFe_{11}Ti$, $NdFe_{10}V_2$ and $NdFe_{10}Mo_2$ alloys.

Figure 2 shows the characteristics of hydrogen absorption and desorption of $NdFe_{11}Ti$ and $Nd(Fe_{0.7}Co_{0.3})_{11}Ti$ alloys. The temperatures of disproportionation reaction are almost the same between two alloys. But the recombination temperature of Co added alloy, which corresponds to the desorption peak around 1000 °C in Fig. 2, is lower than that of $NdFe_{11}Ti$ alloy. It can be said that the Co addition has an effect of lowering the temperature of recombination reaction.

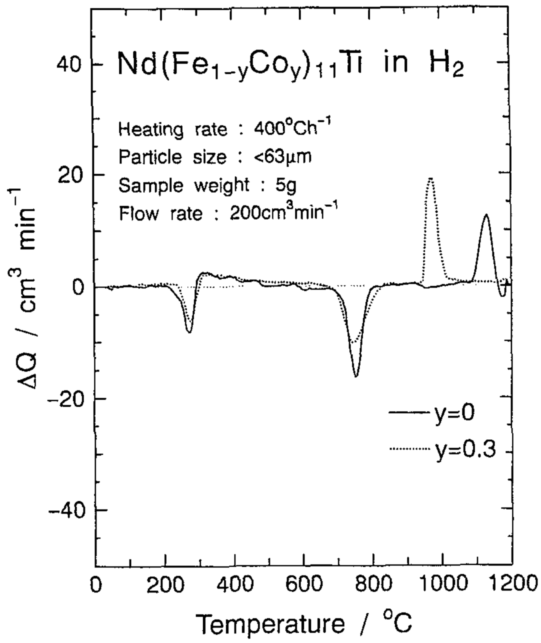

Figure 2. The characteristics of hydrogen absorption and desorption of $NdFe_{11}Ti$ and $Nd(Fe_{0.7}Co_{0.3})_{11}Ti$ alloys.

3.2. HDDR Phenomena of $Nd(Fe,M)_{12}$ and $Nd(Fe,Co,M)_{12}$ Stoichiometric Compositional Alloys

The X-ray diffraction patterns of $Nd(Fe,M)_{12}$ powders (a) after heat treatment in hydrogen at 800 °C for 1 h and (b) those after HV treatment at 800

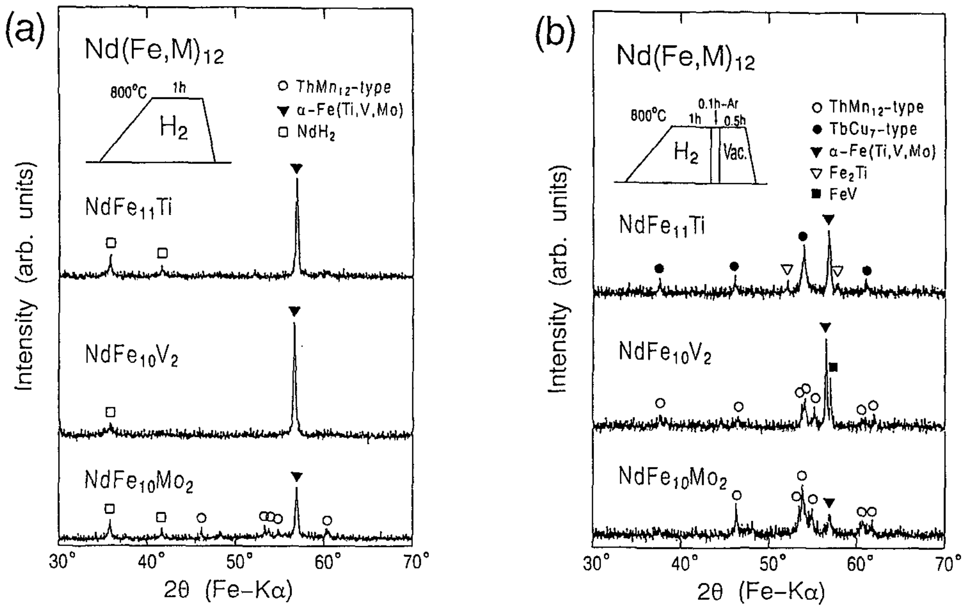

Figure 3. The X-ray diffraction patterns of $Nd(Fe,M)_{12}$ alloys after (a) heat treatment in hydrogen and (b) HV treatment at 800 °C.

°C are shown in Fig. 3. Figure 3(a) reveals that the $NdFe_{11}Ti$ and $NdFe_{10}V_2$ alloys disproportionate to α-Fe and NdH_2 after heat treatment in hydrogen. But the $NdFe_{10}Mo_2$ alloys consist of three phases such as NdH_2, α-Fe and $ThMn_{12}$ phases. Judging from this result, the disproportionation reaction is incomplete in the $NdFe_{10}Mo_2$ alloys at 800°C for 1 h. It can be considered that this tendency depends on the hydrogen absorption and desorption characteristics shown in Fig. 1. Namely, the temperature of disproportionation reaction in $NdFe_{10}Mo_2$ alloys is higher than those of $NdFe_{11}Ti$ and $NdFe_{10}V_2$ alloys.

Figure 3 (b) shows that the X-ray diffraction peaks of NdH_2 phase disappear and HDDR phenomena occur in all of these alloys. The $ThMn_{12}$ phase can be observed in $NdFe_{10}V_2$ and $NdFe_{10}Mo_2$ alloys but the $NdFe_{11}Ti$ alloys show the recombination reaction to the phase with $TbCu_7$ type structure ($TbCu_7$ phase). The recombination reaction to $ThMn_{12}$ phase can be observed in $NdFe_{11}Ti$ alloys when HV treatment temperature increases up to 1000 °C. These three alloys show HDDR phenomena but they involve other phases such as Fe_2Ti, FeV and α-Fe phases after HV treatment.

The tendency of disproportionation reaction of $Nd(Fe,Co,M)_{12}$ alloys is the same as the alloys without Co. The Mo contained alloys show the incompleteness of disproportionation reaction at 800 °C. The HDDR phenomena can be observed in all of alloys but the $Nd(Fe_{0.7}Co_{0.3})_{11}Ti$ alloys show the recombination reaction to $TbCu_7$ phase. These Co contained alloys involve other phases besides $ThMn_{12}$ phase.

From the results described above, the $NdFe_{10}V_2$ and $Nd(Fe,Co)_{10}V_2$ alloys are chosen for the following investigation.

3.3. The Magnetic Properties of $Nd_{1+\delta}Fe_{10}V_2N_X$ and $Nd_{1+\delta}(Fe,Co)_{10}V_2N_X$ Non-stoichiometric Compositional Powders Prepared by Utilizing HDDR Phenomena

The variation of coercivity of stoichiometric compositional $Nd(Fe_{1-y}Co_y)_{10}V_2N_X$ powders after HV treatment and nitriding were investigated. The $NdFe_{10}V_2N_X$ powders exhibit low coercivity and the Co addition tends to increase the coercivity. The $Nd(Fe_{0.9}Co_{0.1})_{10}V_2N_X$ powders HV-treated at 800°C and nitrided at 550 °C have coercivity of $160kAm^{-1}$ (2.0kOe). It is reported that the increment of Nd content increases coercivity and $Nd_{1.3}Fe_{10}VMoN_X$ powders exhibits high coercivity of $464kAm^{-1}$

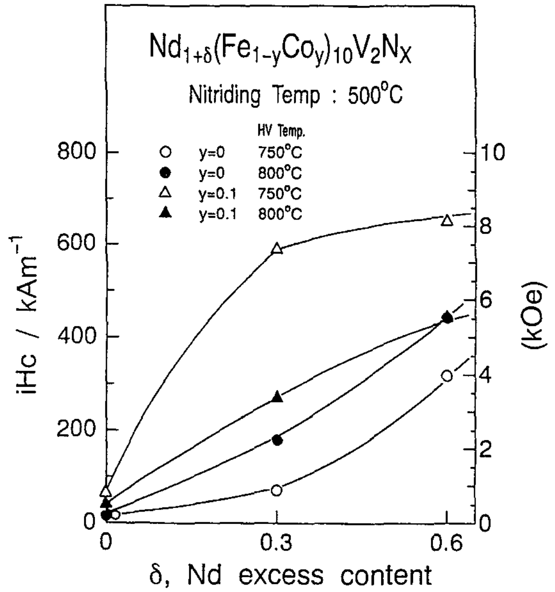

Figure 4. The Variation of coercivities of $Nd_{1+\delta}(Fe_{1-y}Co_y)_{10}V_2N_X$ powders vs. Nd content.

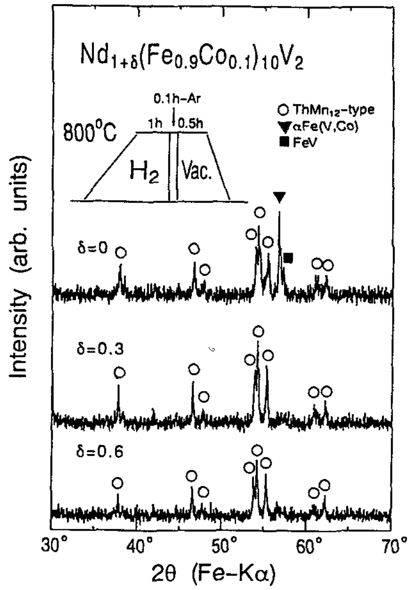

Figure 5. The X-ray diffraction patterns of $Nd_{1+\delta}(Fe_{0.9}Co_{0.1})_{10}V_2$ alloys after HV treatment.

(5.8kOe) [5]. Then the Nd content increases in $Nd(Fe_{1-y}Co_y)_{10}V_2N_X$ powders.

Figure 4 shows the variation in coercivity of $Nd_{1+\delta}(Fe_{1-y}Co_y)_{10}V_2N_X$ powders vs. Nd content. The coercivity increases with increasing Nd content. This tendency is the same as the $Sm_{2+\delta}Fe_{17}N_X$ powders prepared with HDDR phenomena [7]. The Co contained alloys exhibit higher coercivities than the alloys without Co. Especially $Nd_{1.6}(Fe_{0.9}Co_{0.1})_{10}V_2N_X$ powders exhibit the highest coercivity of $664 kAm^{-1}$ (8.3kOe). This is the highest value among the reported values of $Nd(Fe,M)_{12}$ powders prepared by utilizing HDDR phenomena.

Figure 5 shows the X-ray diffraction patterns of $Nd_{1+\delta}(Fe_{0.9}Co_{0.1})_{10}V_2$ alloys after HV treatment. The stoichiometric powders (δ=0) contain a certain amount of α-Fe(V,Co) and FeV phases. But the non-stoichiometric $Nd_{1.6}(Fe_{0.9}Co_{0.1})_{10}V_2$ powders consist of only $ThMn_{12}$ phase. The increment of coercivity with non-stoichiometric powders depends on the disappearance of α-Fe(Co,V) and FeV phases, which will give low coercivity. It can be said that the increment of Nd content is very useful method for decreasing low coercivity phase and it results in obtaining high coercivity.

4. ACKNOWLEDGMENT

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