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Phase transformation and magnetic properties of $Nd_8Fe_{84}Ti_8$ alloy during HDDR process

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Abstract

The effects of the hydrogenation-disproportionation-desorption-recombination (HDDR) process on the structure and the magnetic properties of the $Nd_8Fe_{84}Ti_8$ alloy prepared by mechanical alloying (MA) and its nitride counterpart have been studied in detail. It has been found that $Nd(Fe,Ti)_{12}H_x$ is formed from 300°C to 550°C. The disproportionation starts at 550°C and is completed at 960°C. The desorption and the recombination are almost synchronized. $Nd(Fe,Ti)_7$ is formed at 750°C during the HDDR treatment. With increasing temperature of HDDR process, the metastable structure of $TbCu_7$ type is gradually transformed into the structure of $ThMn_{12}$ type. The intrinsic coercivity increases with increasing the temperature of HDDR process.

Keywords: HDDR; Phase transformation; Permanent magnetic properties

1. Introduction

The comparable intrinsic magnetic properties of $Nd(Fe,Ti)_{12}N_\delta$ with those of $Nd_2Fe_{14}B$ [1] and the possibility of preparing magnets with a high coercivity by using mechanical alloying (MA) in comparison to traditional methods [2–4] have drawn extensive attention in exploring new candidates of rare earth permanent magnets. We have reported our successful preparation of $Nd(Fe,Ti)_{12}N_\delta$ by using mechanical alloying [8,9]. However, its optimum coercivity was only 183.08 kA/m(2.3 kOe). The low coercivity was mainly due to the excessive growth of α-Fe grains. In recent years, HDDR technique has been successfully applied to the preparation of many magnetic systems, such as Nd–Fe–B [5], Sm–Fe–N [6,10] and Nd–Fe–Mo–N [7]. Our previous work indicated that the transformation from $SmFe_7$ to Sm_2Fe_{17} occurred at 800°C in the HDDR process rather than at 1000°C in the MA process [10]. Obviously, the decrease of the transformation temperature should be favourable for the suppression of the growth of α-Fe grains, which makes it possible to prepare nanocomposite magnet with a remanence enhancement. In addition, from the fundamental point of view, it is very interesting to study the formation and transformation of phases in the MA prepared Nd–Fe–Ti–N system undergone a HDDR process. In this paper, some systematic studies concerning HDDR process in the MA prepared Nd–Fe–Ti–N system are reported.

2. Experimental procedures

The nominal $Nd_8Fe_{84}Ti_8$ alloys were prepared by mechanical alloying (MA) powders with purities of 99.6%, 99%, 99.5% for Fe, Ti, Nd respectively, under an argon atmosphere for 5 h. The MA prepared powder was then annealed at 960°C for 30 min in vacuum of $(1–2)\times10^{-3}$ Pa. Subsequently, the annealed powder was heated at 300–960°C for 30 min in 1.3 atm hydrogen atmosphere. Then, the specimen was kept in vacuum of $(1–2)\times10^{-3}$ Pa at the same temperature for 30 min. After cooling to room temperature, the powder was nitrogenated in 1.0 atm nitrogen atmosphere at 400°C for 12 h. X-ray diffraction (XRD) analysis of specimen was performed using Cu Kα radiation with a Rigaku D/Max-rA diffractometer equipped with a graphite crystal monochromater. A.C. initial susceptibility measurement was applied to determine Curie temperature and to estimate preliminarily the possible magnetic phases in the specimens. The magnetic measurements were made by using a pulsed magnetometer

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in fields up to 8 T. The demagnetization correction was made by using the effective demagnetization factor 0.28 determined experimentally [12].

3. Results and discussion

3.1. Reaction mechanism of HDDR in Nd(Fe,Ti)$_{12}$

3.1.1. Hydrogenation

The MA prepared powder of $Nd_8Fe_{84}Ti_8$ followed by annealing at 960°C for 30 min was further heated in 1.3 atm hydrogen atmosphere at 300–550°C for 30 min. The corresponding XRD patterns are shown in Fig. 1 (b)–(e). For comparison, the XRD pattern of the specimen as-annealed at 960°C for 30 min is given in Fig. 1 (a). It reveals that the $ThMn_{12}$ structure of the specimens is perfectly kept during hydrogenation below 550°C except the systematic movement towards relatively low angles of XRD peak positions, which indicates an increase of the lattice constants due to the absorption of hydrogen and the formation of the hydride of $Nd(Fe,Ti)_{12}H_x$. The results of a.c. initial susceptibility measurements showed that the Curie temperature T_c is accordingly increased from 280°C to 331°C.

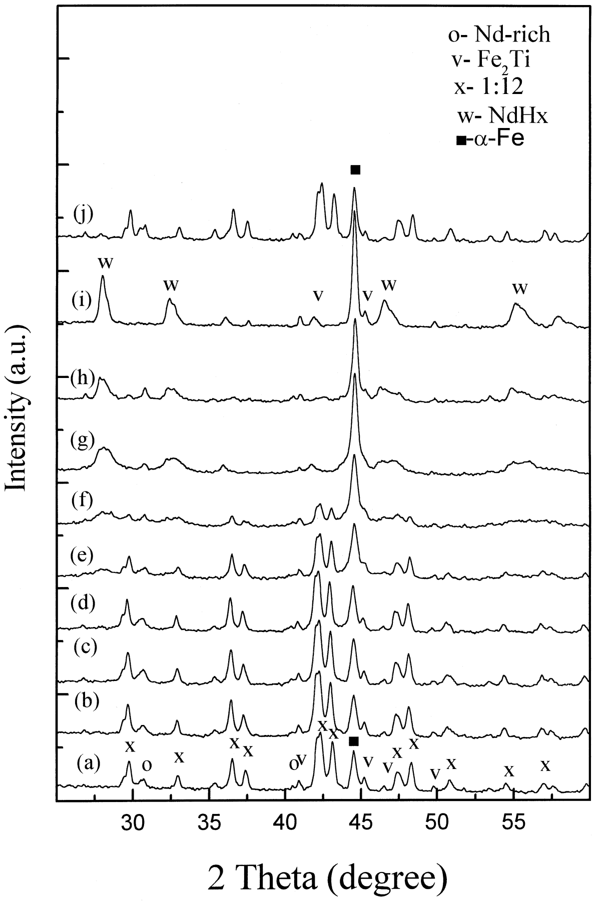

Fig. 1. XRD patterns of $Nd_8Fe_{84}Ti_8$ prepared by the following procedures: (a) annealing the MA powders at 960°C for 30 min; (b)–(i) the specimens with the preparation of (a) heated in hydrogen atmosphere at 300°C, 400°C, 500°C, 550°C, 600°C, 650°C, 800°C and 960°C, respectively, for 30 min; (j) the specimen with the preparations of (i) heated in vacuum at 960°C for 30 min.

3.1.2. Disproportionation

From Fig. 1 (e), it can be seen that the decrease of the content of the main phase of Nd(Fe,Ti)$_{12}$ is accompanied by the increase of the content of α-Fe when the specimen as-annealed at 960°C for 30 min is heated at 550°C for 30 min in the hydrogen atmosphere, as it is confirmed from the notable depression of the characteristic peaks of the main phase and the slight rise of the iron peaks. It implies that the disproportionation is ready to start at 550°C. With the increase of the temperature of hydrogen treatment, the content of Nd(Fe,Ti)$_{12}$ decreases further. The characteristic peaks of the main phase completely disappear at 650°C, instead, a mixture in which α-Fe grains is embedded in a nearly amorphous matrix containing Nd, Ti and Fe is produced (cf. Fig. 1 (g)). Further increasing the temperature leads to beginning of crystallization of the amorphous matrix at about 800°C and the crystallization process is basically completed at 960°C as it can be identified by the formation of the sharp characteristic XRD peaks of NdH_{2+x} and Fe_2Ti (cf. Fig. 1 (i)). The prominent characteristic diffraction peaks of α-Fe remain throughout the disproportionation.

3.1.3. Desorption and recombination

After disproportionation, the resulting mixture of powder was followed by heating at 960°C for 30 min in a constant vacuum of $(1–2)\times10^{-3}$ Pa. Then, it can be observed that the main phase of Nd(Fe, Ti)$_{12}$ are formed again, as it is confirmed from comparing Fig. 1 (j) with Fig. 1 (a). In fact, the two processes, desorption and the recombination are almost synchronized hence it is very hard to distinguish one process from the other. It may be visualized that the hydride of NdH_{2+x} is dissociated into Nd and H, and the Nd atoms immediately react with both α-Fe and Fe_2Ti to produce Nd(Fe,Ti)$_{12}$ possibly according to the following chemical reaction,

$$NdH_{2+x} + 9Fe + Fe_2Ti \rightarrow NdFe_{11}Ti + 2H,$$

due to the extremely high chemical activity of the newborn atoms for the atomic state hydrogen, the rapid diffusion to the surface of powder particles owing to the high concentration gradient caused by the easy evaporation of the hydrogen at the surface of the powder particle in vacuum, besides the originally favourable factors for the high diffusibility including the extremely large Brownian movability of the hydrogen atoms due to the high temperature at which the powder specimen is treated and the low collision probability of hydrogen atoms with the lattice atoms originating from the very small atomic volume of hydrogen atom which may be, to some extent, even considered as a proton, due to the weak association of the electron with the nucleus in metallic lattice. So hydrogen atoms diffuse to the surface of the powder at very rapid speed and results in the synchronization of the desorption and the recombination.

3.2. Phase transformation in $Nd_8Fe_{84}Ti_8$ alloy during HDDR process

Fig. 2 shows XRD patterns of the MA prepared $Nd_8Fe_{84}Ti_8$ annealed at 960°C for 30 min after HDDR process from 750°C to 960°C and Fig. 3 shows the dependence of the Curie temperature on the temperature of HDDR process. From these results, it follows that the phase of $Nd(Fe,Ti)_7$ with the hexagonal $TbCu_7$ structure is formed at 750°C, whose Curie temperature is 190°C in agreement with the previous report [8]. With increasing the temperature, $Nd(FeTi)_7$ is gradually transformed into the $Nd(Fe,Ti)_{12.}$ $Nd(Fe,Ti)_{12}$ begins to occur at 920°C. This transformation is continuous and is basically completed at 960°C. However, the a.c. initial susceptibility measurement indicated that there were two Curie temperatures of $T_{c1} = 190°C$ and $T_{c2} = 275°C$, corresponding to $Nd(Fe,Ti)_7$ and $Nd(Fe,Ti)_{12}$, respectively, for the HDDR process at 920°C. In contrast, only a single magnetic main phase of $Nd(Fe,Ti)_{12}$ existed for the corresponding simple MA prepared specimen annealed at 920°C [8]. The phenomena that the HDDR process leads to an increase of the temperature of the formation of 1:12 phase and a coexistence of 1:7 and 1:12 phases may originate from a possible composition segregation during the disproportionation process in which the hydride of $Nd(Fe,Ti)_{12}H_x$ is further dissociated into NdH_{2+x}, α-(Fe,Ti), and Fe_2Ti. Thus, the 1:7 phase may be easily formed in the Nd-rich regions, as contrasted to the Nd-poor regions where the formation of the 1:12 phase may be easy, during the recombination process at a relatively low temperature, such as at 920°C in the present work. The temperature of 960°C is critical for the complete formation of 1:12 phase in this alloy system during the HDDR process.

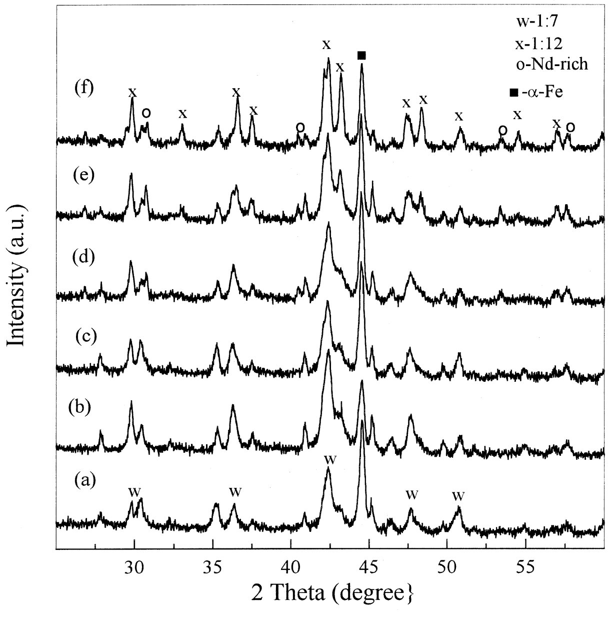

Fig. 2. XRD patterns of the MA prepared $Nd_8Fe_{84}Ti_8$ alloy heated in hydrogen atmosphere for 1 h and then in vacuum for 0.5 h at different temperature: (a) 750°C; (b) 800°C; (c) 850°C; (d) 900°C; (e) 920°C and (f) 960°C.

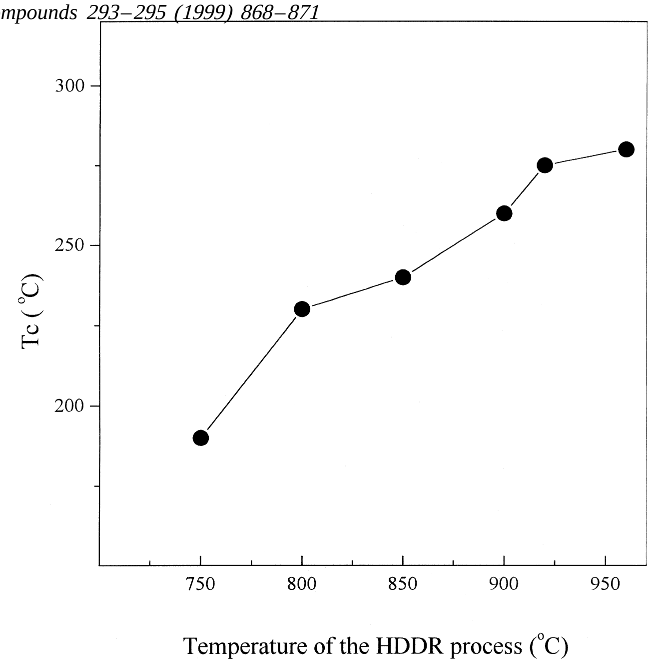

Fig. 3. Dependence of the Curie temperature of the main phase on the HDDR process temperature. (Note: for the process at 920°C, a.c. initial susceptibility measurement gives two Curie temperatures which are 190°C and 275°C, respectively, and only the latter is shown here).

3.3. Effects of temperature of HDDR process on the magnetic properties of $Nd(Fe,Ti)_{12}N_\delta$ compound

The specimens HDDR-treated as shown in Fig. 2 were nitrided at 400°C for 12 h. The nitrided specimens kept the same structure as one before nitrogenation except the expansion of the lattice identified by the movement towards to low angles of XRD peaks. Fig. 4 shows the dependences of the magnetic properties of the nitrides on the temperature of HDDR process. It can be seen that the intrinsic coercivity increase with increasing the temperature and a rapid increase at 920°C is apparent. As above mentioned, the disordered metastable 1:7 phase was resulted from 750–900°C. It is impossible to get a high coercivity of the material with the main phase of $Nd(Fe,Ti)_7N_\delta$ due to the easy in-plane magnetocrystalline anisotropy. Moreover, the relatively excessive inclusion of α-Fe, Fe_2Ti and Nd-containing phase etc. is detrimental to magnetic hardening of the material at the relatively low temperatures. With increasing the temperature, the $TbCu_7$ structure is gradually transformed into $ThMn_{12}$ structure

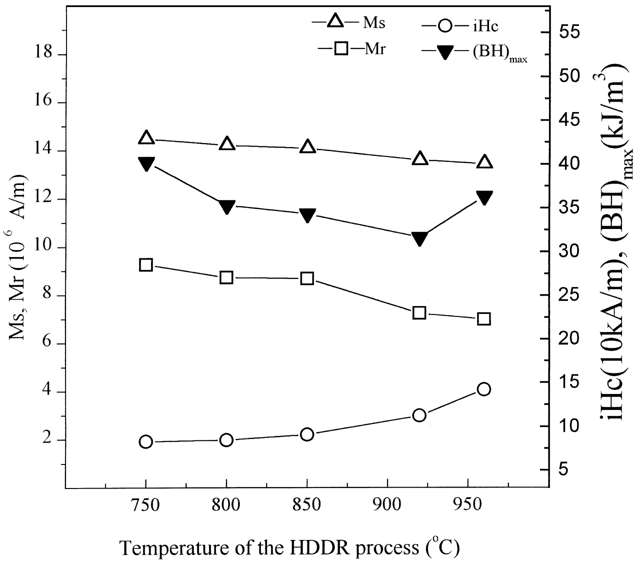

Fig. 4. Dependences of M_s, M_r, ${}_iH_c$ and $(BH)_{max}$ on HDDR process temperature for the MA+HDDR prepared $Nd_8Fe_{84}Ti_8$ alloy nitrided at 400°C for 12 h.

and the magnetocrystalline anisotropy of the corresponding nitrides transits from easy in-plane to easy *c*-axis, accompanied by increasing the coercivity. The rapid increase of the coercivity beginning at 920°C just corresponds to the emergence of the 1:12 and a complete formation of the 1:12 phase at 960°C with disappearing of the 1:7 phase results in an improvement of coercivity. The relatively slow increase of the coercivity from 750°C to 900°C originates from the gradual increase in quantity of the 3d dumbbell substitution, accompanied by gradually reducing amount of α-Fe and Fe_2Ti. The slight decrease of the saturation magnetization with increasing the temperature may originate from the decrease of the free α-Fe during the transformation from the 1:7 to the 1:12 phase. The slight decrease of the remanence results from the slight decrease of the saturation magnetization and the phase transformation(the reduced remanence Mr/Ms is 0.5 or $2/\pi$ for magnetically isotropic powder which has the easy *c*-axis or easy in-plane magnetocrystalline anisotropy respectively [11]). The maximum magnetic energy product decreases from 750°C to 900°C then increases, which is dependent on both the remanence and coercivity.

4. Conclusion

$Nd(Fe,Ti)_{12}H_x$ is formed from 300°C to 550°C. The disproportionation start at 550°C and the main phase of $Nd(Fe,Ti)_{12}$ decomposes into α-Fe and a nearly amorphous matrix containing Nd, Ti and Fe at 650°C. The crystallization of the amorphous matrix begins to appear at about 800°C and is completed at 960°C. The desorption and the recombination are almost synchronized. $Nd(Fe,Ti)_7$ is formed when the HDDR treatment temperature is at 750°C. With increasing the temperature, $Nd(Fe,Ti)_7$ is gradually transformed into $Nd(Fe,Ti)_{12}$. The transformation is continuous and $Nd(Fe,Ti)_{12}$ occurs at 920°C. This transformation is basically completed at 960°C. The intrinsic coercivity increases with increasing the temperature of HDDR process.

Acknowledgements

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