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Synthesis and Magnetic Properties of Nd(Fe,M)$_{12}$ (M=Mo,Ti) and their Compounds Nitrided by Chemical Reaction with Sodium Azide (NaN$_3$)

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Abstract: $NdFe_{11}Ti$, $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.75}Mo_{1.25}$ compounds have been successfully nitrogenated by heating a mixture of powdered alloys with sodium azide (NaN_3) at temperatures between 330 and 450 °C. Structural and magnetic characterization yielded the following results: (1) The $ThMn_{12}$ structure of the original compounds is retained with the addition of nitrogen by chemical reaction with NaN_3. (2) The Curie temperature is enhanced by about 300 °C. (3) The volume expansion was 4 % (4) Particle size is found to be an important parameter for efficient nitrogenation at 330 °C.

Introduction

Ternary $NdFe_{12-x}M_x$ compounds (M = Ti and Mo, $1 \leq x \leq 2$) have the tetragonal $ThMn_{12}$-type structure [1]. These compounds can absorb large amounts of nitrogen, resulting in drastic changes in magnetic properties [2-5]. Interstitial N strongly enhances the Curie temperature and the saturation magnetization, in a similar way to R_2Fe_{17} [2]. In addition, the magnetocrystalline anisotropy at the Nd site in these compounds reverses its sign due to the particular location of neighboring N atoms. The nitrided 1-12 compounds present much interest for commercial applications because their raw materials are less costly than for $Sm_2Fe_{17}N_y$. Due to these effects, $Nd(Fe,M)_{12}N_y$ compounds became promising candidates for permanent magnetic applications.

The conventional method for nitrogen insertion into intermetallic compounds involves exposure to a flow of nitrogen, ammonia, or a hydrogen-ammonia mixture at 300-600 °C to ensure a satisfactory nitrogen transfer and diffusion kinetics [6,7]. In this work, we investigated an alternative method for nitrogenating $NdFe_{11}Ti$, $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.75}Mo_{1.25}$ powder alloys, based on chemical reaction with sodium azide (NaN_3) as an oxygen-free nitrogen source [8]. The high nitrogenation power of NaN_3 comes from its low decomposition temperature (90 °C) and an improved nitrogen diffusion rate at the particle surfaces cleaned by sodium.

The mother alloys used in this work were obtained by the reduction-diffusion calciothermic (RDC) process [9,10,11]. By this method it is possible to skip the subsequent homogenization treatment for eliminating the magnetically soft α-Fe phase; in addition, the alloy remains in powder form, which is advantageous for subsequent nitrogenation.

Experimental procedure

The raw materials (99.9% pure $NdCl_3$, 99.99% pure Fe, Ti and Mo) were mixed into homogeneous powder and 99% granular Ca was added in alternating layers in a stainless steel vessel. Excess amounts of $NdCl_3$ (20%) and Ca (50%), relative to reaction balance, were added in order to ensure complete Fe consumption. The temperature was slowly raised to 400 °C under pumping, then the reduction-diffusion took place in an ultrapure Ar atmosphere at 950 °C for 5 hours. The reacted compacts were washed in deionized water to remove the soluble $CaCl_2$, acid-bleached for other metallic residues, and dried under vacuum. Some $NdFe_{11}Ti$ and $NdFe_{10.75}Mo_{1.25}$ samples were milled for 1 hour in a high energy planetary ball mill before nitrogenation.

$NdFe_{11}Ti$, $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.75}Mo_{1.25}$ alloys, either as-prepared or ball-milled, were mixed into homogeneous powders with slightly overstoichiometric NaN_3 to ensure a maximum N uptake according to the following ideal reactions:

$$NdFe_{11}Ti + NaN_3 \rightarrow NdFe_{11}TiN_3 + Na \quad (1)$$

$$NdFe_{12-x}Mo_x + NaN_3 \rightarrow NdFe_{12-x}Mo_xN_3 + Na \quad (2)$$

The powder mixtures were wrapped in a tantalum foil and sealed into evacuated silica tubes to resist pressure increase, then annealed at 330 and 450 °C for 6, 12 and 20 hours. After natural cooling, residual Na was removed by washing with deionized water and $NdFe_{11}TiN_y$, $NdFe_{10.5}Mo_{1.5}N_y$ and $NdFe_{10.75}Mo_{1.25}N_y$ samples were dried under vacuum. X-ray diffraction (XRD) patterns were taken with Cu-K_α radiation. Particle size distribution was determined with a laser scattering apparatus. Thermomagnetic analysis (TMA) was performed with a vibrating-sample magnetometer in fixed fields of 100 or 200 Oe. Mössbauer spectroscopy was taken with ^{57}Fe radiation at 293 K.

Results and Discussion

With the chemical reaction process used in this work, absorbed nitrogen contents could not be reliably evaluated by mass increase measurements due to the possible presence of residual products. Instead, the Curie temperature rise and volumetric expansion were taken as sensible indicators of N uptake. Results for both investigated compounds are separately discussed in the following.

A. $NdFe_{11}Ti$

Processing parameters (i.e. nitrogenation reaction temperatures, reaction times, and pre-reaction milling times), Curie temperatures and volumetric expansions, are summarized in table 1. The average particle diameters of as-prepared and 1-hour ball-milled $NdFe_{11}Ti$ powders were 56.9 and 21.3 μm, respectively, as determined by laser-scattering granulometric analysis. The content oxygen of as-prepared and 1-hour ball-milled $NdFe_{11}Ti$ powders were 0,4 and 0,7 wt %, respectively.

The XRD patterns of $NdFe_{11}Ti$ alloy before and after nitrogenation are shown in Fig. 1. The as-prepared powder contained mostly the 1:12 phase, with a small amount of α-Fe ($2\theta = 44.5^\circ$). XRD lines are shifted toward smaller angles for all reacted samples, a characteristic signature of cell expansion due to N absorption. The latter is confirmed by the substantially enhanced Curie temperatures given in Table 1. The amount of α-Fe, on the other hand, increases upon nitrogenation, though not dramatically. It is apparent from Fig. 1 that the Fe increase is larger for crushed than for non-milled powders, when nitrogenated at 450 °C.

Fig. 2 shows TMA data for $NdFe_{11}Ti$ before and after nitrogenation. The Curie temperature is indicated by an inflection in the σ vs. T curves. The tail above T_C is due to the α-Fe contribution, which is amplified relative to its actual proportion in the samples because of its much larger permeability as compared to the magnetically hard $NdFe_{11}TiN_y$ phase. A large T_C increase upon nitrogenation is evident. The maximum T_C increase, ~300 °C, is much larger than what has been obtained (<200 °C) for $RFe_{11}Ti$ alloys nitrogenated by the conventional gas absorption process [12,13].

The quantitative data of phases, hyperfine field (B_{HF}) and content of nitrogen for $NdFe_{11}Ti$ mother alloy, crushed and nitrogenated at 330 °C for 20 hr, nitrogenated at 450 °C for 20 hr and crushed and nitrogenated at 450 °C for 20 hr nitrided are listed in table 2. The 1:12 magnetic phase as-prepared $NdFe_{11}Ti$ was majority (92,6 %). Milling of mother alloy before nitrogenation at 330 °C is preferred because reaction kinetics is enhanced. Nevertheless, at 450 °C, a competition between the interstitially compound formation (alloy + N) and alloy dissociation was occurred, resulting in a α-Fe phase increase.

Table 1. Nitrogenation temperature, nitrogenation time, milling time, Curie temperature and volumetric expansion of $NdFe_{11}Ti$ and $NdFe_{11}TiN_y$ compounds.

Compound	**T_{nit} (°C)**	**t_{nit} (hr)**	**t_{mill} (hr)**	**T_C (°C)**	**ΔTc (°C)**	**a (Å)**	**c (Å)**	**dV/V(%)**
$NdFe_{11}Ti$	-	-	-	151	-	8.58	4.77	
$NdFe_{11}TiN_y$	330	12	-	206	55	8.69	4.85	4.3
$NdFe_{11}TiN_y$	330	12	1	221	70	8.71	4.86	5.0
$NdFe_{11}TiN_y$	330	20	-	439	288	8.75	4.87	6.2
$NdFe_{11}TiN_y$	330	20	1	442	291	8.75	4.88	6.4
$NdFe_{11}TiN_y$	450	12	-	450	299	8.75	4,87	6.2
$NdFe_{11}TiN_y$	450	12	1	452	301	8.77	4.88	6.9
$NdFe_{11}TiN_y$	450	20	-	452	301	8.76	4.87	6.4
$NdFe_{11}TiN_y$	450	20	1	454	303	8.79	4.88	7.4

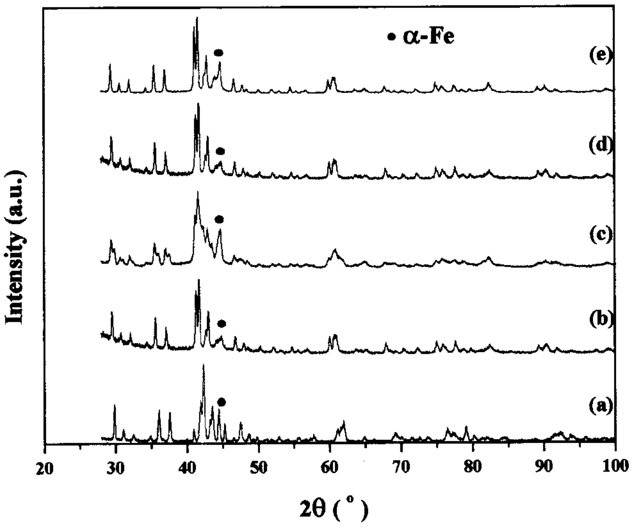

Figure 1. X-ray diffraction patterns for $NdFe_{11}Ti$: (a) as-prepared, (b) nitrogenated at 330 °C for 20 hr, (c) crushed and nitrogenated at 330 °C for 20 hr, (d) nitrogenated at 450 °C for 20 hr, (e) crushed and nitrogenated at 450 °C for 20 hr.

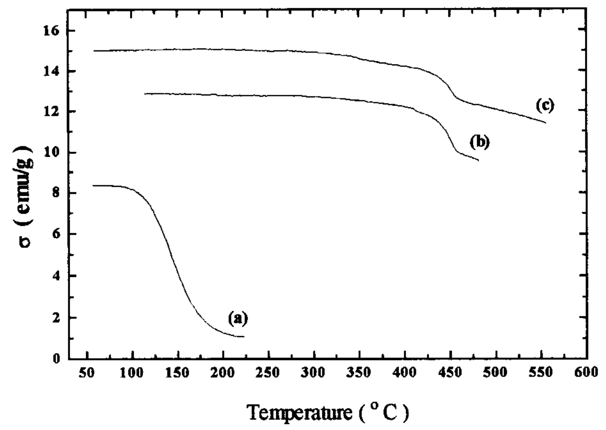

Figure 2. Thermomagnetic data for (a) as-prepared $NdFe_{11}Ti$, (b) $NdFe_{11}Ti$ nitrogenated at 450 °C for 20 hours and (c) $NdFe_{11}Ti$ crushed and nitrogenated at 450 °C for 20 hours.

Table 2. The quantitative data of phases, 1:12 average hyperfine fields and content of nitrogen for $NdFe_{11}Ti$ as-prepared and nitrided at different conditions.

ALLOY	1:12 Phase (%)	α-Fe (%)	B_{HF} (T)	N (wt. %)
$NdFe_{11}Ti$	92,7	2,2	21,7	0,02
$NdFe_{11}TiN_y$ (203m)	90,3	9,7	27,7	1,34
$NdFe_{11}TiN_y$ (204)	63,7	36,3	29,6	1,54
$NdFe_{11}TiN_y$ (204m)	60,5	39,5	29,5	1,81

B. $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.75}Mo_{1.25}$

Processing parameters (i.e. nitrogenation reaction temperatures, reaction times, and pre-reaction milling times), Curie temperatures and volumetric expansions, are summarized in table 3. The average particle diameters of as-prepared and 1-hour ball-milled $NdFe_{10.5}Mo_{1.5}$ powders were 81.9 and 21.7 μm, respectively. For $NdFe_{10.75}Mo_{1.25}$ mother alloy, the average particle diameters were 64.4 and 19.2 μm, respectively. The content oxygen of as-prepared and 1-hour ball-milled powders were 0,4 and 0,7 wt. %, respectively. The x-ray diffraction patterns of $NdFe_{10.5}Mo_{1.5}$ alloy before and after nitrogenation are shown in Fig. 3. Similar to the previously discussed materials, a small amount of α-Fe is present in all samples in addition to the main phase. A increase in the amount of α-Fe is observed after nitrogenation for milling powder. Cell expansion is also evident for the nitrogenated samples (see dV/V data in table 3). The x-ray diffraction patterns of $NdFe_{10.75}Mo_{1.25}$ alloy before and after nitrogenation are similar $NdFe_{10.5}Mo_{1.5}$ alloy.

Thermomagnetic curves for the $NdFe_{10.5}Mo_{1.5}$ alloy, and for both non-milled and milled $NdFe_{10.5}Mo_{1.5}$ nitrogenated at 330 and 450 °C for 20 hours, are shown in Fig. 5. It is noteworthy that the highest T_C obtained for this alloy nitrogenated at 450 °C for 20 hr (378 °C) significantly exceeds that for an alloy of similar composition nitrogenated by conventional means (T_C=311 °C) [14].

The N absorption efficiency seems to be improved by particle size reduction in the Ti and Mo alloys at 330 °C.(see T_C data in tables 1 and 3). This effect is particularly noticeable at the lower reaction times or temperatures, i.e. for the processing conditions that make α-Fe segregation less probable. On the other hand, at 450 °C a competition between the interstitially compound formation (alloy + N) and alloy dissociation was occurred, resulting in a α-Fe phase increase. The content of nitrogen for $NdFe_{10.5}Mo_{1.5}$ mother alloy and crushed and nitrogenated at 330 °C for 20 hr were 0.05 and 1.45 wt. %, respectively. The Mössbauer spectroscopy showed that hard magnetic phase (1:12) decrease of 100 % for 96.1 % after nitrogenation.

Table 3. Nitrogenation temperature, nitrogenation time, milling time, Curie temperature and volumetric expansion of $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.5}Mo_{1.5}N_y$ compounds.

Compound	**T_{nit} (°C)**	**t_{nit} (hr)**	**t_{mill} (hr)**	**T_C (°C)**	**ΔTc (°C)**	**a (Å)**	**c (Å)**	**dV/V(%)**
$NdFe_{10.5}Mo_{1.5}$	-	-	-	163	-	8.62	4.81	
$NdFe_{10.5}Mo_{1.5}N_y$	330	12	-	287	124	8.70	4.86	2.9
$NdFe_{10.5}Mo_{1.5}N_y$	330	12	1	327	164	8.70	4.87	3.1
$NdFe_{10.5}Mo_{1.5}N_y$	330	20	-	357	194	8.70	4.88	3.4
$NdFe_{10.5}Mo_{1.5}N_y$	330	20	1	363	200	8.71	4.90	4.0
$NdFe_{10.5}Mo_{1.5}N_y$	450	12	-	334	171	8.68	4,90	3.3
$NdFe_{10.5}Mo_{1.5}N_y$	450	12	1	368	205	8.69	4.90	3.5
$NdFe_{10.5}Mo_{1.5}N_y$	450	20	-	378	215	8.72	4.91	4.5
$NdFe_{10.5}Mo_{1.5}N_y$	450	20	1	380	217	8.72	4.92	4.7

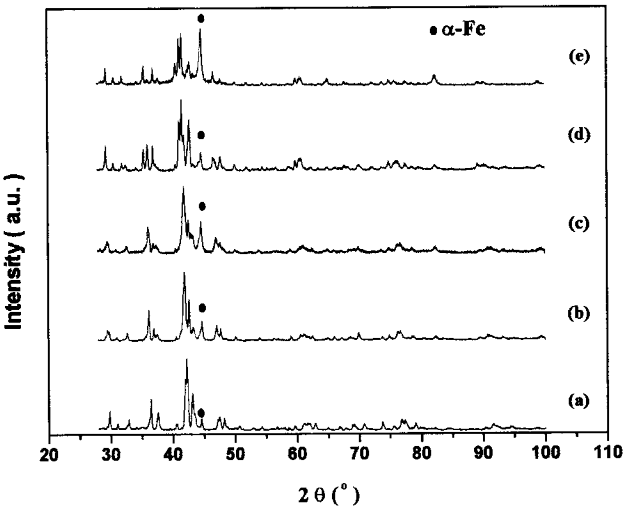

Figure 3. X-ray diffraction patterns for $NdFe_{10.5}Mo_{1.5}$: (a) as-prepared, (b) nitrogenated at 330 °C for 20 hr, (c) crushed and nitrogenated at 330 °C for 20 hr, (d) nitrogenated at 450 °C for 20 hr, (e) crushed and nitrogenated at 450 °C for 20 hr.

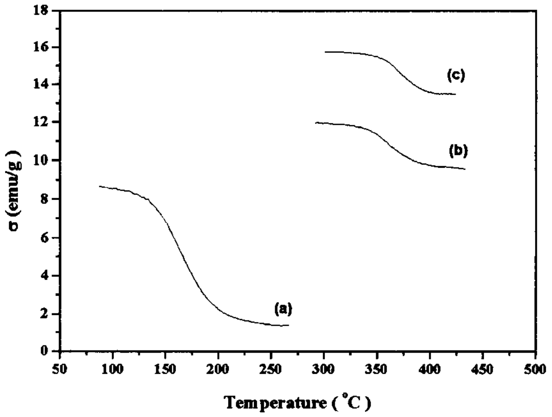

Figure 4. Thermomagnetic data for $NdFe_{10.5}Mo_{1.5}$: (a) as-prepared, (b) crushed and nitrogenated at 330 °C for 20 hr, (c) nitrogenated at 450 °C for 20 hr.

Conclusions

In this work it was shown that the $NdFe_{11}Ti$ $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.75}Mo_{1.25}$ alloys can be nitrogenated by chemical reaction using sodium azide (NaN_3). The absorbed N amount, volumetric expansions and the Curie temperature increase it were found that N uptake by this method is larger than for the conventional solid-gas process. The rise in T_C could be as high as 300 °C for both alloy systems. Milling of Ti and Mo alloys before nitrogenation at 330 °C is preferred because reaction kinetics is enhanced. Nevertheless, at 450 °C, a competition between the interstitially compound formation (alloy + N) and alloy dissociation was occurred, resulting in a α-Fe phase increase.

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