

Phase Monitoring during Nd(Fe,M)₁₂ (M=Mo or Ti) Compound Nitrogenation by Chemical Reaction with Sodium Azide (NaN₃)

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Abstract: NdFe_{10.75}Mo_{1.25} and NdFe₁₁Ti alloys have been successfully nitrogenated by heating a mixture of powdered alloys with sodium azide (NaN₃) at temperatures between 330 and 450 °C. Among the characterization techniques used to evaluate the final product, Mössbauer spectroscopy was invaluable for quantitative determination of 1-12 and α -Fe phases, after and before nitrogenation. The α -Fe phase increased indicated that a competition between the interstitially modified compound formation (alloy + N) and alloy dissociation occurred. This effect was more pronounced in Ti alloys nitrogenated at 450 °C.

Introduction

Interest in NdFe_{12-x}M_x compounds (M = Ti and Mo, 1 ≤ x ≤ 2) as potential candidates for permanent magnet materials has gained impetus after the discovery that their magnetic properties are profoundly modified upon nitrogen absorption [1-5]. Interstitial N strongly enhances the Curie temperature and the saturation magnetization, in a similar way to R₂Fe₁₇ [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 Sm₂Fe₁₇Ny.

In this work, we investigated an alternative method for nitrogenation NdFe₁₁Ti and NdFe_{10.75}Mo_{1.25} powder alloys, based on chemical reaction with sodium azide (NaN₃) as an oxygen-free nitrogen source [6]. The high nitrogenation power of NaN₃ 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 [7,8,9]. 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. 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 $\text{NdFe}_{11}\text{Ti}$ and $\text{NdFe}_{10.75}\text{Mo}_{1.25}$ samples were milled for 1 hour in a high energy planetary ball mill before nitrogenation.

$\text{NdFe}_{11}\text{Ti}$ and $\text{NdFe}_{10.75}\text{Mo}_{1.25}$ alloys, either as-prepared or ball-milled, were mixed into homogeneous powders with slightly overstoichiometric NaN_3 to ensure a maximum N uptake [10].

The powder mixtures were annealed at 330 and 450 °C for 6, 12 and 20 hours. The residual Na was removed by washing with deionized water and $\text{NdFe}_{11}\text{TiN}_y$ and $\text{NdFe}_{10.75}\text{Mo}_{1.25}\text{N}_y$ samples were dried under vacuum. Mössbauer spectroscopy was taken with ^{57}Fe radiation at 293 K. X-ray diffraction (XRD) patterns were taken with $\text{Cu-K}\alpha$ radiation. Thermomagnetic analysis (TMA) was performed with a vibrating-sample magnetometer in fixed fields of 100 or 200 Oe.

Results and Discussion

A. $\text{NdFe}_{11}\text{Ti}$

Fig. 1 shows $\text{CuK}\alpha$ x-ray diffraction patterns of $\text{NdFe}_{11}\text{Ti}$ and $\text{NdFe}_{11}\text{TiN}_y$. The magnetic characteristics of samples are summarized in table 1. The as-prepared powder contained mostly the 1:12 phase, with a small amount of α -Fe. XRD lines are shifted toward smaller angles for all reacted samples, a characteristic signature of cell expansion due to N absorption. The amount of α -Fe, on the other hand, increases upon nitrogenation, though not dramatically.

Table 1. Nitrogenation temperature, nitrogenation time, milling time, magnetic and structure properties of $\text{NdFe}_{11}\text{Ti}$ and $\text{NdFe}_{11}\text{TiN}_y$.

Compound	T_{nit} (°C)	t_{nit} (hr)	t_{mill} (hr)	T_{C} (°C)	ΔT_{C} (°C)	a (Å)	c (Å)	dV/V (%)
$\text{NdFe}_{11}\text{Ti}$	-	-	-	151	-	8.58	4.77	
$\text{NdFe}_{11}\text{TiN}_y$ (203m)	330	20	1	442	291	8.75	4.88	6.4
$\text{NdFe}_{11}\text{TiN}_y$ (204)	450	20	-	452	301	8.76	4.87	6.4
$\text{NdFe}_{11}\text{TiN}_y$ (204m)	450	20	1	454	303	8.79	4.88	7.4

The Mössbauer spectra at room temperature for $\text{NdFe}_{11}\text{Ti}$ and $\text{NdFe}_{11}\text{TiN}_y$ alloys are shown in fig. 2. The transition elements are distributed over the three sites, 8f, 8i and 8j. Iron is found to occupy 8f and 8j sites fully, while the 8i sites is populated by a mixture of Fe and Ti. The spectrum of tetragonal 1-12 phase was fitted with six subspectra. We used

two subspectra to account for each of three crystallographic sites available to Fe and Ti atoms. In addition, an α -Fe spectrum was introduced [11].

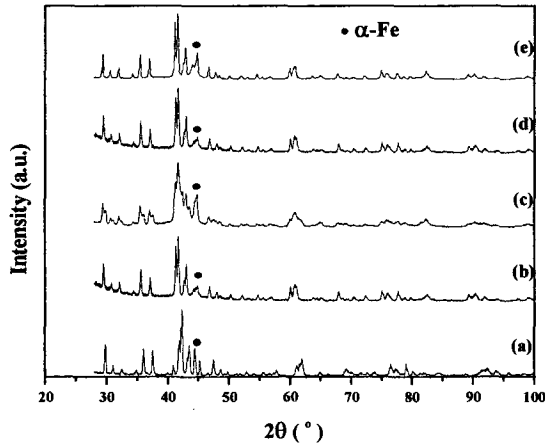


Fig. 1. X-ray diffraction patterns for $\text{NdFe}_{11}\text{Ti}$: (a) as-prepared, (b) nitrogenated at 330°C for 20 hr, (c) crushed and nitrogenated at 330°C for 20 hr, (d) nitrogenated at 450°C for 20 hr, (e) crushed and nitrogenated at 450°C for 20 hr.

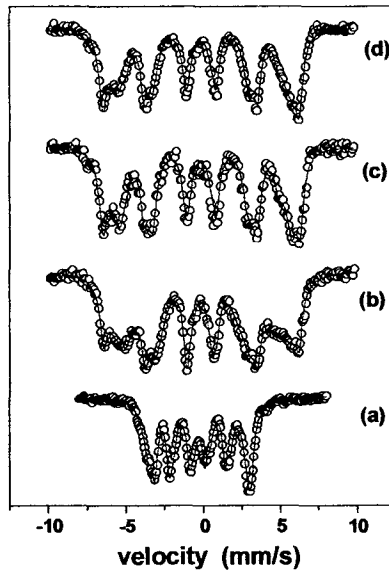


Fig. 2. ^{57}Fe Mössbauer spectra, at room temperature, for $\text{NdFe}_{11}\text{Ti}$ alloy: (a) as-prepared, (b) crushed and nitrogenated at 330°C for 20 hr, (c) nitrogenated at 450°C for 20 hr, (d) crushed and nitrogenated at 450°C for 20 hr.

The quantitative data of phases, mean hyperfine field (B_{HF}) and nitrogen content for $NdFe_{11}Ti$ and $NdFe_{11}TiN_y$ are listed in table 2. The 1:12 magnetic phase as-prepared $NdFe_{11}Ti$ was majority (92.7 %). Milling of mother alloy before nitrogeneration at 330 °C is preferred because reaction kinetics is enhanced. Nevertheless, at 450 °C, a competition occurred between the interstitial compound formation (alloy + N) and alloy dissociation, resulting in an α -Fe phase increase.

Table 2. The quantitative data of phases, 1:12 average hyperfine fields and nitrogen content for $NdFe_{11}Ti$ as-prepared and nitrated 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. $NdFe_{10.75}Mo_{1.25}$

Fig. 3 shows CuK_{α} x-ray diffraction patterns of $NdFe_{10.75}Mo_{1.25}$ and $NdFe_{10.75}Mo_{1.25}N_y$. Similar to the previously discussed materials, a small amount of α -Fe is present in all samples in addition to the main phase. An increase in the amount of α -Fe is observed after nitrogeneration for milling powder. The magnetic characteristics of samples are summarized in table 3.

Table 3. Nitrogeneration temperature, nitrogeneration time, milling time, magnetic and structure properties of $NdFe_{10.75}Mo_{1.25}$ and $NdFe_{10.75}Mo_{1.25}N_y$ compounds.

Compound	T_{nit} (°C)	t_{nit} (h)	t_{mill} (h)	T_C (°C)	ΔT_C (°C)	a (Å)	c (Å)	dV/V (%)
$NdFe_{10.75}Mo_{1.25}$	-	-	-	169	-	8.60	4.78	
$NdFe_{10.75}Mo_{1.25}N_y$ (203m)	330	20	1	430	282	8.70	4.89	4.7
$NdFe_{10.75}Mo_{1.25}N_y$ (204)	450	20	-	452	283	8.70	4.90	4.9
$NdFe_{10.75}Mo_{1.25}N_y$ (204m)	450	20	1	456	287	8.71	4.90	5.2

The Mössbauer spectra at room temperature for $NdFe_{10.75}Mo_{1.25}$ and $NdFe_{10.75}Mo_{1.25}N_y$ alloys are shown in fig. 4. The distribution of Mo causes a distribution of Fe nearest neighbors for each Fe site, which results in quite broad outer lines in the Mössbauer spectrum due to a distribution of hyperfine fields. The spectrum of tetragonal 1-12 phase was fitted with six subspectra, corresponding to $8f:8j_1:8j_2:8i_1:8i_2$. We used three

subspectra for $\text{NdFe}_{10.75}\text{Mo}_{1.25}\text{N}_y$ compounds. In addition, an α -Fe sextet was introduced, as well as a doublet to account for a paramagnetic impurity phase [12].

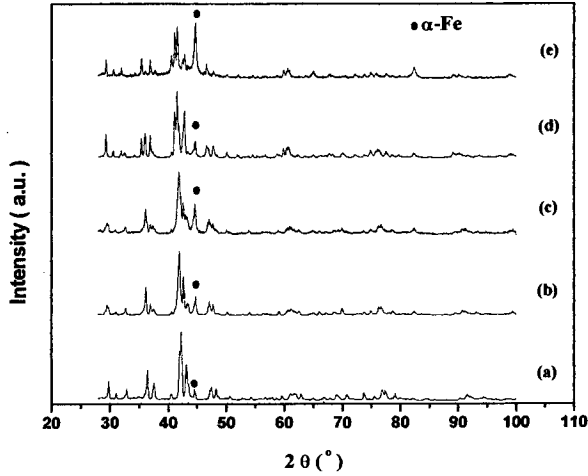


Fig. 3. X-ray diffraction patterns for $\text{NdFe}_{10.75}\text{Mo}_{1.25}$: (a) as-prepared, (b) nitrogenated at 330 °C for 20 hr, (c) crushed and nitrogenated at 330 °C for 20 hr, (d) nitrogenated at 450 °C for 20 hr, (e) crushed and nitrogenated at 450 °C for 20 hr.

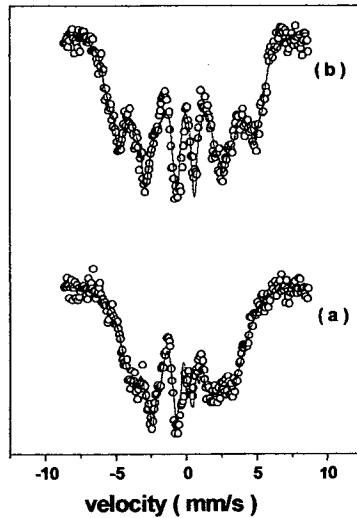


Fig. 4. ^{57}Fe Mössbauer spectra, at room temperature, for $\text{NdFe}_{10.75}\text{Mo}_{1.25}$ alloy: (a) as-prepared and (b) nitrogenated at 450 °C for 20 hr.

The N absorption efficiency seems to be improved by increase of the temperature reaction in the 1.25Mo alloys (see table 4). This effect is particularly noticeable in the as-prepared alloy, making α -Fe segregation less probable. On the other hand, at 330 °C a competition between the interstitial compound formation (alloy + N) and alloy dissociation occurred, resulting in α -Fe phase increase. The Mössbauer spectroscopy showed that the hard magnetic phase (1:12) was 100 % after nitrogenation at 450 °C.

Table 4. The quantitative data of phases, 1:12 average hyperfine fields and nitrogen content for NdFe_{10.75}Mo_{1.25} as-prepared and nitrated at different conditions.

ALLOY	1:12 Phase (%)	α -Fe (%)	B _{HF} (T)	N (wt. %)
1.25Mo (s/N ₂)	100	-	22.7	0.03
1.25Mo (203m)	97.3	2.7	26.1	1.52
1.25Mo (204)	100	-	29.6	1.73

Conclusions

In this work it was shown that the NdFe₁₁Ti and NdFe_{10.75}Mo_{1.25} alloys can be nitrogenated by chemical reaction using sodium azide (NaN₃). The rise in T_C could be as high as 300 °C for both alloy systems. Milling of Ti alloys before nitrogenation at 330 °C enhances the reaction. At 450 °C, competition between the nitrogen-rich compound formation and alloy dissociation gave rise to α -Fe phase increase. On the other hand, 1.25Mo alloys we observed the opposite. At 450 °C, without milling, 1-12 phase was 100 %. Finally, Mössbauer spectroscopy turned out to be invaluable for phases monitoring after and before nitrogenation.

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