Reduction-Diffusion Preparation of $Nd_{15}Fe_{77}B_8$, $NdFe_{11}Ti$, $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.75}Mo_{1.25}$ Alloys for Magnets

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Abstract: The calciothermic reduction-diffusion (CRD) process is a alternative preparation route for $Nd_{15}Fe_{77}B_8$, $NdFe_{11}Ti$, $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.75}Mo_{1.25}$ alloys, which eliminates the need for long homogenizing heat treatment; in addition, the resulting alloy is already in powder form. We have examined the effect of various processing variables in the preparation of mother alloys. Compacts made of $NdCl_3$, Fe, Ti, Mo and Fe-B powders and Ca granules were heated under argon for different times and temperatures. The alloys as-prepared contained mostly the hard magnetic phase. The $NdFe_{11}Ti$, $NdFe_{10.75}Mo_{1.25}$ and $NdFe_{10.5}Mo_{1.5}$ alloys have been successfully nitrogenated by heating a mixture of powdered alloys with sodium azide (NaN_3) at temperatures between 330 and 450 ^{o}C.

Introduction

Preparation of the $Nd_{15}Fe_{77}B_8$ and $NdFe_{12-x}M_x$ (M = Mo and Ti, $1 \leq x \leq 2$) mother alloys are the first step for manufacturing high-performance magnets [1,2]. This is usually done by melting pure elements together, homogenizing by heat treating and pulverizing. An alternative route, by which some of these processing steps can be abbreviated or even suppressed, is the calciotermic reduction-diffusion process (CRD) [3,4,5]. In this tecnique, the transition metals and the appropriate rare earth halide are mixed in powder form with metallic Ca (the reducing agent) and heated at temperatures around 1000 ^{o}C. Since reaction heat is small, the resulting alloys remain in powder form, which is adantageous for the subsequent stages of magnet fabrication. $NdCl_3$ was chosen as starting material because its low melting point ensures the reduction reaction to occur in the liquid statempleted in a shoter time or at lower temperature [6].

In this work, we investigated another alternative method for nitrogenation $NdFe_{11}Ti$, $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.75}Mo_{1.25}$ powder alloys, based on chemical reaction with sodium azide (NaN_3) as an oxygen-free nitrogen source [7]. The high nitrogenation power of NaN_3 comes from its low decomposition temperature (90 ^{o}C) and an improved nitrogen diffusion rate at the particle surfaces cleaned by sodium. The mother alloys used in this stage were obtained by the reduction-diffusion calciothermic (RDC) process [8,9,10]. 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, Fe-B alloy, 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 NdCl3 (20%) and Ca (50%), relative to reaction balance were added to ensure complete Fe consumption. The temperature was slowly raised to 400 ^{o}C under pumping, then the reduction-diffusion took place in an ultrapure Ar atmosphere at 950 ^{o}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 $NdFe_{11}Ti$ $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.75}Mo_{1.25}$ samples were milled for 1 hour in a high energy planetary ball mill before nitrogenation.

The $NdFe_{12-x}M_x$ (M = Mo and Ti, $1 \leq x \leq 2$) alloys, either as-prepared or ball-milled, were mixed into homogeneous powders with slightly overstoichiometric NaN_3 to ensure a maximum N uptake [9,10].

The powder mixtures were annealed at 330 and 450 ^{o}C for 6, 12 and 20 hours. The 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. Mössbauer spectroscopy was taken with ^{57}Fe radiation at 293 K. X-ray diffraction (XRD) patterns were taken with 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. Reduction-Diffussion Process (CRD):

A.1. $Nd_{15}Fe_{77}B_8$ alloy

X-ray showed that all samples were mainly constituted by required ϕ phase (i.e. $Nd_2Fe_{14}B$), when were prepared at 950 ^{o}C for 3 hours (with 50% excess Ca and 20 % excess $NdCl_3$).

As is weel known, the as-prepared $Nd_{15}Fe_{77}B_8$ alloy contains, in addition to the ferromagnetic ϕ phase, both a Nd-rich phase and $Nd_{1.1}Fe_4B_4$ (η-phase). Upon appropriate heat treatment, the former gives rise to an intergranular microstructure which is essencial in developing a high coercivity. The latter, in contrast, is stable, nonmagnetic phase generally believed to be detrimental to magnetic properties; a good Nd-Fe-B magnet alloy is thus expected to exibit a low η/ϕ volume ratio. The spectrum of η at room temperature is a doublet with one of its lines well resolved from magnetically split ϕ phase spectrum. This is illustrated in fig. 1. All measured spectra were fitted with a superposition of a doublet. The quantitative data of phases are summarized in table 1. The phase ϕ is majority in the alloy with 50% excess Ca and 20 % excess $NdCl_3$.

Table 1. The quantitative data of phases by Mössbauer spectroscopy.

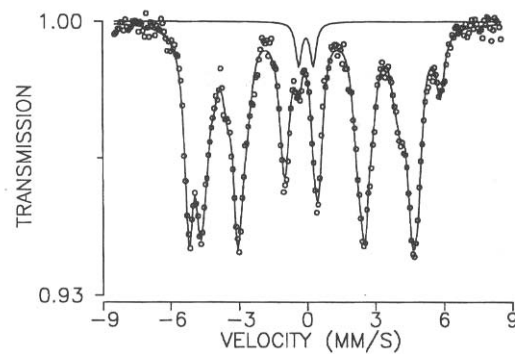| ALLOY	ϕ - Phase (%)	α-Fe (%)	η - phase (%)
$Nd_{15}Fe_{77}B_8$ (20 % excess of $NdCl_3$)	93.2	0.0	6.8
$Nd_{15}Fe_{77}B_8$ (without excess of $NdCl_3$)	54.6	30.6	4.8
$Nd_{15}Fe_{77}B_8$ (commercial alloy)	93.8	0.0	6.2

Fig. 1. Mössbauer spectrum of $Nd_{15}Fe_{77}B_8$ alloy prepared by reduction-diffussion process, fitted as a superposition of $Nd_2Fe_{14}B$ and $Nd_{1.1}Fe_4B_4$ spectra. The latter is sparately drawn.

A.2. NdFe$_{12-x}$M$_x$ (M = Mo and Ti, $1 \leq x \leq 2$) alloys

The temperature of 950 ^{o}C was chosen for CRD treatments after preliminary tests. Fig. 2 show CuK$_\alpha$ x-ray diffraction pattern of of $NdFe_{11}Ti$ obtained after 5 hr treatments (with 40 % excess $NdCl_3$ and 50 % excess Ca). The $NdFe_{11}Ti$ as-prepared powder contained mostly the tetragonal $ThMn_{12}$ strucutre, with a small amount of α-Fe and Fe_2Ti being also present. The $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.75}Mo_{1.25}$ alloys are nearly single-phase 1:12 and small amounts of α-Fe, Nd_2Fe_{17} and Mo.

The quantitative data of phases, mean hyperfine field (B_{HF}) for $NdFe_{11}Ti$, $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.75}Mo_{1.25}$ alloys are listed in table 2. The 1:12 magnetic phase was majority for all mother alloys.
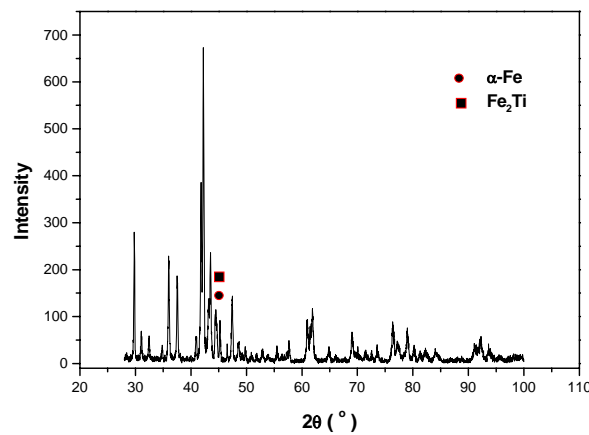

Fig. 2. X-ray diffaction of $NdFe_{11}Ti$ powder obtained after 5-hr treatments at 950 ^{o}C.

Table 2. The quantitative data of phases, 1:12 average hyperfine fields for $NdFe_{11}Ti$, $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.75}Mo_{1.25}$ as-prepared.

ALLOY	1:12 Phase (%)	α-Fe (%)	B_{HF} (T)
$NdFe_{11}Ti$	92.7	2.2	21.7
$NdFe_{10.5}Mo_{1.5}$	100	---	20.7
$NdFe_{10.75}Mo_{1.25}$	100	---	22.7

B. Nitrogenation by Chemical Reaction with Sodium Azide (NaN_3)

B.1. $NdFe_{11}TiN_y$

The processing parameters (i.e. nitrogenation reaction temperatures, reaction times, and pre-reaction milling times), quantitative data of phases, mean hyperfine field (B_{HF}), nitrogen content for $NdFe_{11}Ti$ and $NdFe_{11}TiN_y$ and Curie temperature are listed in table 3. The 1:12 magnetic phase as-prepared $NdFe_{11}Ti$ was majority (92.7 %). Milling of mother alloy before nitrogenation at 330 ^{o}C is preferred because reaction kinetics is enhanced. Nevertheless, at 450 ^{o}C, a competition occurred between the interstitial compound formation (alloy + N) and alloy dissociation, resulting in an α-Fe phase increase.

Table 3. The process variables, quantitative data of phases, 1:12 average hyperfine fields, nitrogen content for $NdFe_{11}Ti$ and Curie temperature as-prepared and nitrided at different conditions.

ALLOY	T_{nit} (^{o}C)	t_{nit} (hr)	t_{mill} (hr)	1:12 Phase (%)	α-Fe (%)	B_{HF} (T)	N (wt. %)	T_C (^{o}C)
$NdFe_{11}Ti$	-	-	-	92.7	2.2	21.7	0.02	151
$NdFe_{11}TiN_y$	330	20	1	90.3	9.7	27.7	1.34	442
$NdFe_{11}TiN_y$	450	20	-	63.7	36.3	29.6	1.54	452
$NdFe_{11}TiN_y$	450	20	1	60.5	39.5	29.5	1.81	454

B.2. $NdFe_{12-x}Mo_x\ Ny(x = 1.25$ and $1.75)$

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 nitrogenation for milling powder. The content oxygen of as-prepared and 1 hour ball-milled powders were 0,4 and 0,7 wt. %, respectively. The processing parameters, quantitative data of phases and magnetic properties of samples are summarized in table 4. The x-ray diffraction patterns of $NdFe_{10.5}Mo_{1.5}$ alloy before and after nitrogenation are similar $NdFe_{10.75}Mo_{1.25}$ alloy.

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 ^{o}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 ^{o}C.

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

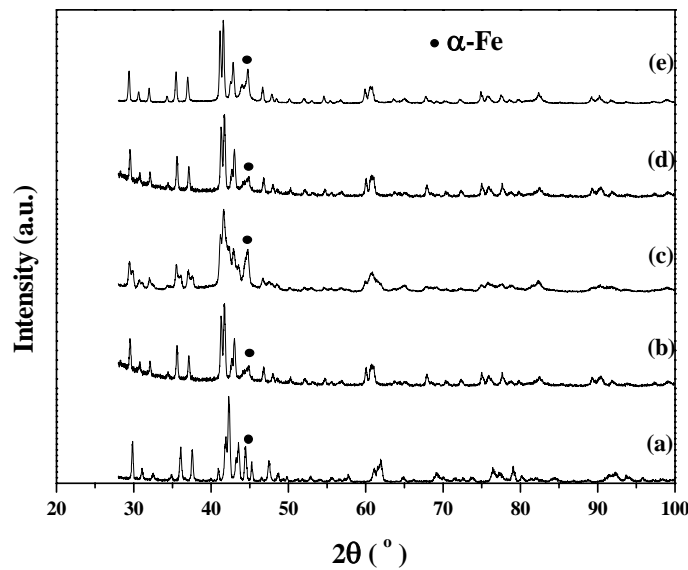| ALLOY	T_{nit} (^{o}C)	t_{nit} (h)	t_{mill} (h)	1:12 Phase (%)	α-Fe (%)	B_{HF} (T)	N (wt. %)	T_C (^{o}C)
1.25Mo (s/N$_2$)	-	-	-	100	-	22.7	0.03	169
1.25Mo	330	20	1	97.3	2.7	26.1	1.52	430
1.25Mo	450	20	-	100	-	29.6	1.73	452

Fig. 3. X-ray diffraction patterns for $NdFe_{10.75}Mo_{1.25}$: (a) as-prepared, (b) nitrogenated at 330 ^{o}C for 20 hr, (c) crushed and nitrogenated at 330 ^{o}C for 20 hr, (d) nitrogenated at 450 ^{o}C for 20 hr, (e) crushed and nitrogenated at 450 ^{o}C for 20 hr.

The processing parameters, quantitative data of phases and magnetic properties of $NdFe_{10.5}Mo_{1.5}$ as-prepared and nitrided at different conditions are summarized in table 5.

Table 5. Processing parameters, quantitative data of phases, 1:12 average hyperfine fields and nitrogen content for $NdFe_{10.5}Mo_{1.5}$ as-prepared and nitrided at different conditions.

ALLOY	T_{nit} (^{o}C)	t_{nit} (h)	t_{mill} (h)	1:12 Phase (%)	α-Fe (%)	B_{HF} (T)	N (wt. %)	T_C (^{o}C)
1.5Mo (s/N$_2$)	-	-	-	100	-	20.7	0.03	163
1.5Mo	330	20	1	96.1	3.9	21.4	1.45	363
1.5Mo	450	20	-	96.9	3.1	25.3	1.62	380

The N absorption efficiency seems to be improved by particle size reduction in the Mo alloys at 330 ^{o}C.(see T_C data in tables 4 and 5). 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 ^{o}C a competition between the interstitially compound formation (alloy + N) and alloy dissociation was occurred, resulting in

a α-Fe phase increase. The Mössbauer spectroscopy showed that hard magnetic phase 1.5 Mo alloy decrease of 100 % for 96.1 % after nitrogenation and. 1.25 Mo alloy the 1:12 was 100 % after nitrogenation at 450 $^{\circ}$C.

Conclusions

In this work we have shown that $Nd_{15}Fe_{77}B_8$, $NdFe_{11}Ti$, $NdFe_{10.5}Mo_{1.5}$ and $NdFe_{10.75}Mo_{1.25}$ alloys can be prepared in powder form by calciothermic reduction-diffusion (CRD) process, using Nd chloride as starting material. The alloys as-prepared contained mostly the hard magnetic phase (ϕ and 1:12) and can be used for manufacturing permanent magnet.

The $NdFe_{11}Ti$ and $NdFe_{12-x}Mo_x$ N_y(x = 1.25 and 1.75) alloys can be nitrogenated by chemical reaction using sodium azide (NaN_3). The rise in T_C could be as high as 300 $^{\circ}$C for both alloy systems. Milling of Ti alloys before nitrogenation at 330 $^{\circ}$C enhances the reaction. At 450 $^{\circ}$C, competition between the nitrogen-rich compound formation and alloy dissociation gave rise to α-Fe phase increase. On the other hand, 1.25Mo and 1.5 Mo alloys we observed the opposite. At 450 $^{\circ}$C, without milling, 1-12 phase was 100 % and 96.9 %, respectively. Finally, Mössbauer spectroscopy turned out to be invaluable for phases monitoring after and before nitrogenation.

References

[1] M. sagawa, S. Fujimura, H. Togawa, H. Yamamoto and Matsauura, J. Appl. Phys. 55, 1984, 2083.

[2] K.H.J. Buschow and D.B. De Mooij, The Concerted European Action on Magnets (Elsevier, Amsterdam, 1989), p. 63

[3] E.G. Guilherme, MSc Dissertion 1992 (unpublished).

[4] E.G. Guilherme, J.O.A. Paschoal and H. R. Rechenberg, Hyperfine Int., 83, (1994), 395.

[5] E.G. Guilherme and H.R. Rechenberg, 13th Int. Workshop on RE Magn and Appl. (1994), p. 871.

[6] G Sun, J Chen, W Dahl, H J Klaar and W G Burchard, J. Appl. Phys. 64 (1988) 5519.

[7] M. Febri, P. Ezekwenna, P. Chaudouët, Ph. l'Héritier and J.C. Joubert, J. Magn. Magn. Mater. 157/158 (1996), p. 103.

[8] C. Herget, Proc. 8th Int. Workshop on Magnetic Anisotropy and Coercivity in RE-TM Alloys, ed. K.J. Strnat (1985), p. 407.

[9] E.G. Guilherme and H.R. Rechenberg, Congress Powder Metallurgy (1998), v.5, p.590.

[10] E.G. Guilherme and H.R. Rechenberg, Key Eng. Mater. 189-191 (2001), p. 655.

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