Preparation of NdFe$_{10.5}$V$_{1.5}$N$_x$ powders with potential as high-performance permanent magnets

Jinbo Yang†, Bo Cui†, Benpei Cheng†, Weihua Mao†, Ying-Chang Yang† and Senlin Ge‡

† Department of Physics, Peking University, Beijing 100871,
People's Republic of China
‡ Beijing University of Posts and Telecommunications, Beijing, 100088,
People's Republic of China

Abstract. Fine anisotropic powders of NdFe$_{10.5}$V$_{1.5}$N$_x$ with $(BH)_{max}$ = 17 MG Oe, B_r = 10.6 kG, and H_{cJ} = 4.2 kOe were prepared by optimizing the nitrogenation process and grinding time. The magnetic properties of the powders are very sensitive to the nitrogenation temperature and time and also to the particle size. The temperature stability of NdFe$_{10.5}$V$_{1.5}$N$_x$ is better than that of Nd-Fe-B magnets. It was found that NdFe$_{10.5}$V$_{1.5}$N$_x$ was a promising candidate for permanent magnet applications.

1. Introduction

Findings concerning the effect of nitrogenation on the magnetic properties of rare-earth (R) intermetallic compounds, R$_2$Fe$_{17}$N$_x$ and R(Fe, M)$_{12}$N$_x$ (M = Ti, V, Mo, W and so on) [1, 2], have recently led to great progress in the field of hard magnetic materials. Many studies have been concentrated on the 2:17 and 1:12 nitrides. Among 2:17 compounds, Sm$_2$Fe$_{17}$N$_x$ possesses attractive magnetic properties which are comparable to those of Nd–Fe–B and is expected to have potential applications for bonded magnets [3]. Nd(Fe, M)$_{12}$N$_x$ (M = Mo, V) are also very good candidates for permanent magnet applications.

In contrast to Sm$_2$Fe$_{17}$N$_x$ nitrides, Nd(Fe, M)$_{12}$N$_x$ materials have two advantages: (i) the price of Nd is much lower than that of Sm and (ii) the 1:12 nitrides have a lower ratio of rare earth to transition metal than that of 2:17 nitrides. Compared with Nd(Fe, Mo)$_{12}$N$_x$, Nd(Fe, V)$_{12}$N$_x$ presents a higher Curie temperature and a larger saturation magnetization and it seems easier to create a large remanence. Accordingly, it is worth studying V-stabilized 1:12 nitrides concerning the formation conditions of a good single phase, improvement of the intrinsic magnetic properties and creation of high coercivity.

In this paper, the NdFe$_{10.5}$V$_{1.5}$N$_x$ powders with favourable magnetic properties were obtained by optimizing the homogenizing treatment of parent alloys, nitrogenation temperature and time and particle size before and after nitrogenation. The key problems in dealing with the manufacture of magnets and the prospect of the 1:12 nitrides being of use in the development of permanent magnets are discussed.

2. Experimental methods

Parent alloys were prepared by arc melting of 99.5% pure metals in an argon atmosphere, followed by a heat treatment at 900 °C for 1 week. The nitrides were formed by passing high-purity nitrogen gas at atmospheric pressure over fine powder samples (5–10 μm) at 480–600 °C for 4–12 h. The nitrogen content was estimated by determining the weight difference of the sample before and after nitrogenation. The nitrided powders were then further pulverized into the fine powders and fixed in epoxy resin to form aligned samples of cylindrical shape in a magnetic field of 10 kOe. The hysteresis loops were measured on aligned samples by using a vibrating sample magnetometer (VSM) with a field of up to 20 kOe at room temperature. At 1.5 K and room temperature, the magnetic measurements were also made by using an extracting sample magnetometer with a field of up to 70 kOe. The anisotropy constants K_i were deduced from the fitting of magnetization curves perpendicular to the alignment direction using the Sucksmith–Thompson method. The Curie temperatures were determined from σ–T curves which were measured by using a VSM in the temperature range 300–1000 K. The particle size and topography of the powders were determined by scanning electron microscopy and transmission electron microscopy. The crystal phase was identified by x-ray diffraction analysis with Cu Kα radiation.
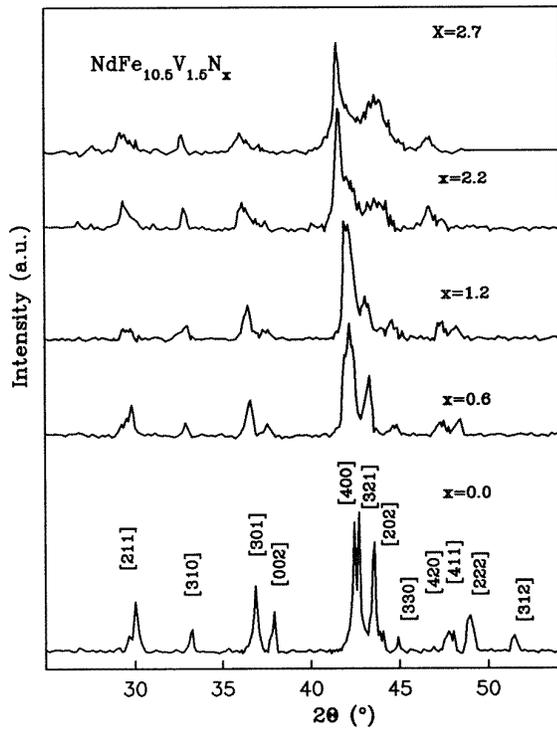
Figure 1. The x-ray diffraction patterns of NdFe$_{10.5}$V$_{1.5}$ and NdFe$_{10.5}$V$_{1.5}$N$_x$.

3. Results and discussion

Figure 1 shows the x-ray diffraction patterns of the NdFe$_{10.5}$V$_{1.5}$ and NdFe$_{10.5}$V$_{1.5}$N$_x$ samples. The x-ray patterns show that the alloy before nitrogenation is of 1:12 single phase, which also can be verified from the theromagnetic curve. It is evident that the diffraction peaks of NdFe$_{10.5}$V$_{1.5}$N$_x$ shift to a lower angle, which means that the nitrides remain of 1:12 structure and the nitrogen atoms mainly occupy interstitial sites. There is a little precipitation of α-Fe after nitrogenation and the α-Fe content increases with increasing N content. This is due to the excess strain caused by the insertion of N, and it has been confirmed to occur in Y$_2$Fe$_{17}$N$_x$ nitrides [4]. The intrinsic magnetic properties of the NdFe$_{10.5}$V$_{1.5}$N$_x$ powders are listed in table 1. The intrinsic magnetic properties of NdFe$_{10.5}$V$_{1.5}$N$_x$ show a significant dependence on the nitrogen content.

The effect of the nitrogenation temperature on the nitrogen content of NdFe$_{10}$V$_{1.5}$ powders is shown in figure 2. The nitrogenation time is 4 h and the particle size is about 5 μm. Compared to RFe$_{11}$Ti, RFe$_{10.5}$V$_{1.5}$ alloy possesses a stronger ability to absorb nitrogen atoms. The x in the NdFe$_{10.5}$V$_{1.5}$N$_x$ ranges from 0 to 2.5, which is much more than the theoretical value of one N per formula unit. Similar results have also been observed for R$_2$Fe$_{17}$N$_x$, with x as high as 6 [5], or even 8 [6]. One point to understand concerning this is that the measurements include everything gained during nitrogenation such as N in Nd–N precipitates, N on the particle's surface (physical absorption) or in the bulk and the formation of Fe–N compound as well. In the nitrogenation process, it is inevitable that small amounts
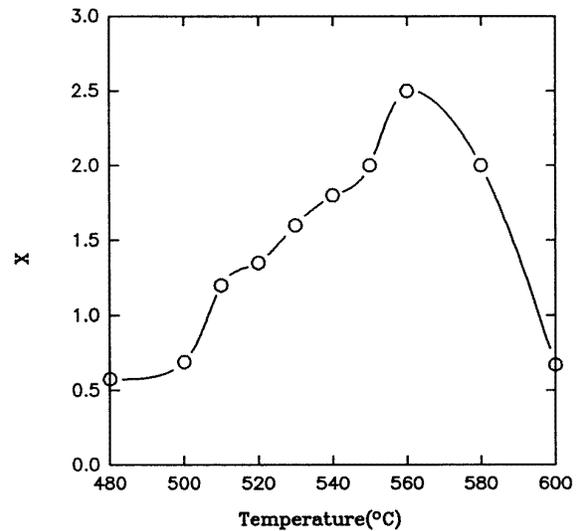
Figure 2. The effect of the nitrogenation temperature on the nitrogen content of NdFe$_{10.5}$V$_{1.5}$ powders.

of impurity phases such as iron and rare-earth nitrides are formed [7]. Thus the actual N content in 1:12 phase may be significantly less than the value measured gravimetrically. It is found that the nitrogen content first increases with temperature, reaching a maximum value at about 560 °C, and then begins to decrease, which mainly results from the decomposition of nitrides.

The magnetic properties of the powders are very sensitive to the nitrogenation temperature, for example, the dependences of the coercive force H_{cj} and remannent magnetization (M_r) of the alloy powders on the nitro-genation temperature are shown in figure 3. The nitrogenation time is 4 h. The maximum values of $H_{cj} = 2.7$ kOe and $M_r = 101$ emu g^{-1} were obtained when the nitrogenation temperature is about 530 °C. The values of H_{cJ} and M_r will decrease with a lower or higher temperature. This is due to the fact that the alloy cannot be fully nitrogenated at a lower temperature; whereas, at a higher temperature, more impurity phases are formed, which is detrimental to the magnetic properties of the nitrides. The nitrogenation time also has essential effects on the magnetic properties of the final nitrides. Figure 4 shows the coercive forces and remanences of powders with various nitrogenation times at $T = 510$ °C. The largest $H_{cJ} = 3.4$ kOe and $M_r = 108.6$ emu g^{-1} are obtained at $t = 8$ h and $t = 10$ h, respectively. Our investigations show that the nitrogenation time will affect the phase composition and the homogeneity of the nitrides. So, in order to obtain high-quality nitrides, the nitrogenation temperature and time must be properly selected.

The dependence of the coercivity on the particle size of the NdFe$_{10.5}$V$_{1.5}$N$_x$ powders is illustrated in figure 5. The coercivity first increases as the particle size decreases and reaches a maximum value at the size of about 1 μm. When the particle size decreases further, the coercivity begins to decrease. The initial increase in coercivity can be explained in terms of the single-domain theory and nucleation model. The remanent magnetization has the same trend with respect

Table 1. The intrinsic magnetic properties of the $NdFe_{10.5}V_{1.5}N_x$ powders.

x	M_s (emu g^{-1})	K_1 (10^7 erg cm^{-3})	K_2 (10^6 erg cm^{-3})	H_a (kOe)
0.0	114.1	0.13	0.47	0.5
0.7	120.6	3.34	5.80	7.3
1.4	126.0	3.52	6.24	9.9
2.0	131.5	3.80	7.07	10.4
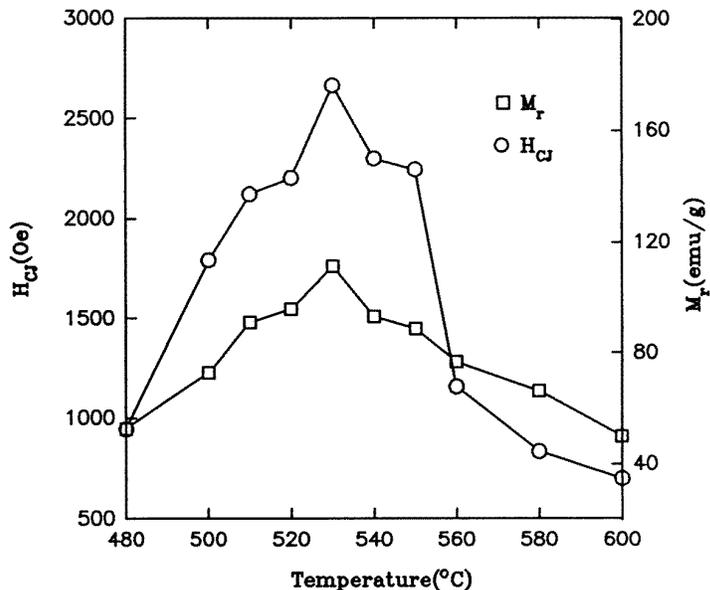
Figure 3. The dependences of the coercive force H_{cj} and remanent magnetization (M_r) of the alloy powders on the nitrogenation temperature.
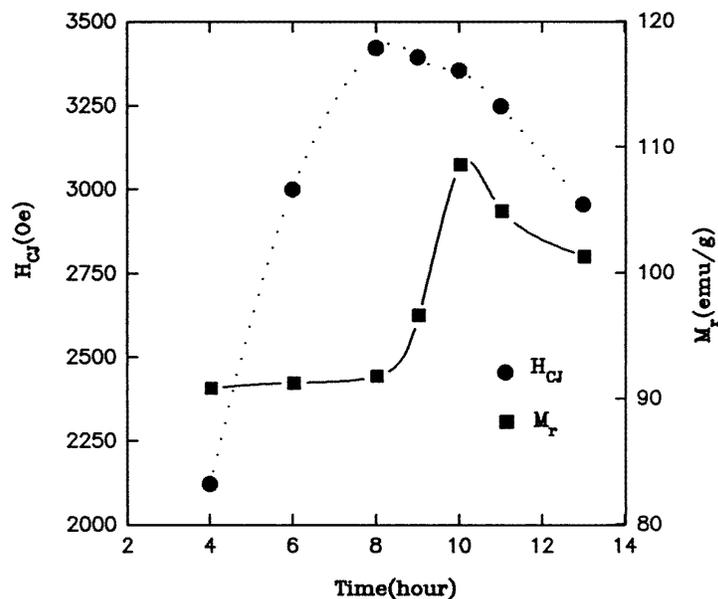
Figure 4. The magnetic properties of $NdFe_{10.5}V_{1.5}$ nitrogenated at various times at $T = 510\,°C$.

to the particle size, but reaches the maximum value at the size of about 3 μm. In order to get more insight into the mechanism of the coercivity and remanent magnetization, transmission electron microscopy was used to investigate the crystal structure of the particles produced with various grinding times. The results indicate that the crystal structure of the powders was damaged after prolonged grinding, which will drastically affect the coercivity and remanent
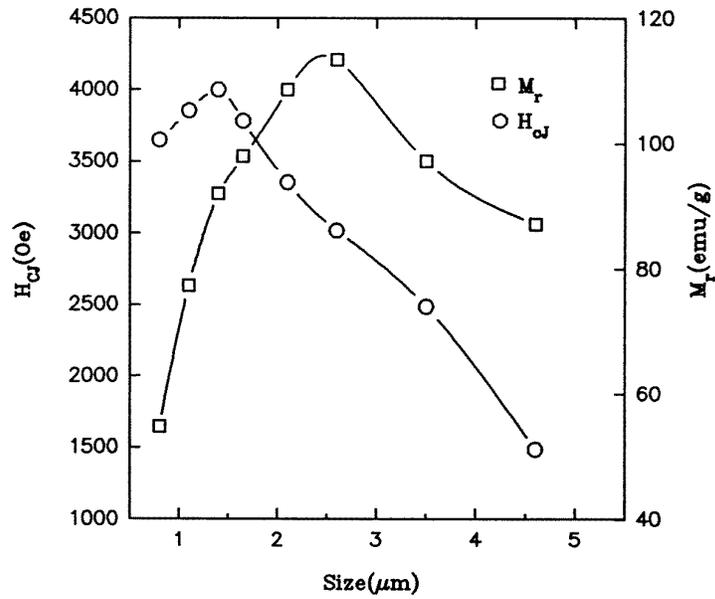
Figure 5. The dependences of the coercivity and remanence on the particle sizes of NdFe$_{10.5}$V$_{1.5}$N$_x$ powders.
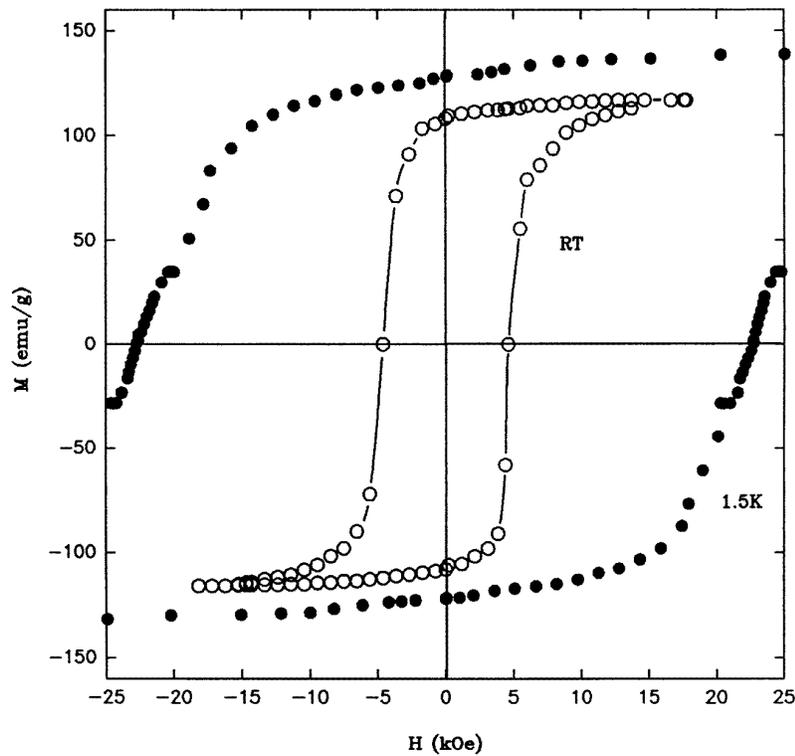
Figure 6. The hysteresis loops of NdFe$_{10.5}$V$_{1.5}$N$_x$ at room temperature and 1.5 K.

magnetization of the nitrides. A similar result has been observed for Nd(Fe, Mo)$_{12}$N$_x$ compounds [8].

Figure 6 is the hysteresis loop of the epoxy-resin-bonded powders after correction for demagnetization (demagnetization factor $N = 0.15$). The density of the sample is obtained from the lattice parameters and is taken to be 7.6 g cm^{-3}. The optimum permanent magnetic properties of NdFe$_{10.5}$V$_{1.5}$N$_x$ are $(BH)_{max} = 17$ MG Oe, $B_r = 10.6$ kG, and $H_{cJ} = 4.2$ kOe. The intrinsic coercivity can be enhanced to 4.5 kOe at the cost of the remanence and energy product (the corresponding values are $B_r = 10.5$ kG and $(BH)_{max} = 16.1$ MG Oe). The intrinsic coercivity H_{cJ} of the powder exhibits a large dependence on the magnitude of the magnetic field applied

285

during measurements. For example, coercivities of 4.0 and 4.6 kOe were obtained under magnetizing fields of 20 and 30 kOe, respectively. A similar effect was also observed in $Nd(Fe, Mo)_{12}N_x$ [9]. This is characteristic of domain nucleation. The demagnetization curve also indicates that the coercivity mechanism is likely to be of a nucleation type.

The temperature dependences of the coercivity and remanent magnetization of the $NdFe_{10.5}V_{1.5}N_x$ powders are determined from the hysteresis loops from room temperature to $150\,°C$. The temperature coefficients of coercivity and remanent magnetization are -0.5 and $-0.09\%\,°C^{-1}$, respectively. The temperature coefficient of coercivity is smaller than that of $Nd_2Fe_{14}B$ magnets and close to that of $Sm_2Fe_{17}N_x$ magnets [3].

4. Conclusions

A magnetic powder of composition $NdFe_{10.5}V_{1.5}N_x$ with $(BH)_{max} = 17$ MG Oe was obtained by using an optimized nitrogenation process and grinding time. The magnetic properties of the nitrides are sensitive to the nitrogenation temperature and time and also to the particle size. The intrinsic coercivity H_{cJ} varies with the particle size, indicating that the coercivity is characteristic of nucleation. The temperature stability of $NdFe_{10.5}V_{1.5}N_x$ is better than that of Nd–Fe–B magnets. These results demonstrate that $NdFe_{10.5}V_{1.5}N_x$ has the potential to become used in permanent magnets with high performance in a field in which cost is of primary importance and only a

medium coercivity is required. Further improvement can be acquired by carefully controlling the particle size after nitrogenation. Reducing the nonmagnetic vanadium content while ensuring retention of the 1:12 single phase is another feasible way to achieve better magnetic properties.

References

[1] Coey J M D and Sun H 1990 *J. Magn. Magn. Mater.* **87** L251
[2] Yang Y C, Zhang X D, Kong L S, Pan Q and Ge S L 1991 *Appl. Phys. Lett.* **58** 2042
[3] Suzuki S, Miura T and Kawasaki M 1993 *IEEE Trans. Magn.* **29** 2815
[4] Zhang Y D, Budnick J I, Yang D P, Fernando G W, Hines W A, Xiao T D and Manzur T 1995 *Phys. Rev.* B **51** 12 091
[5] Takahashi K, Ujihira Y, Kobayashi K, Iriyama T and Konishi T 1991 *Hyperfine Interactions* **68** 413
[6] Wei Y N, Sun K, Fen Y B, Zhang Y X, Hun B P, Rao X L and Liu G C 1993 *J. Alloys Compounds* **194** 9
[7] Hong Sun, Morij Y, Fujii H, Akayama M and Funahashi S 1993 *Phys. Rev.* B **48** 13 333
[8] Yang Y C, Liu Z X, Zhang X D, Chen B P and Ge S L 1994 *J. Appl. Phys.* **76** 1745
[9] Yang Y C, Pan Q, Cheng B P, Zhang X D, Liu Z X, Sun Y X and Ge S L 1994 *J. Appl. Phys.* **76** 6725