



Hard magnetic properties of $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$ powders with high performance

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Abstract

High-performance powders of $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$ with $B_r = 10.8$ kG, $H_{cJ} = 4.3$ kOe, $(BH)_{\text{max}} = 17.2$ MGOe, and $T_c > 800$ K were successfully prepared by using conventional milling process. The relationship of the crystallographic structure and the intrinsic magnetic properties to the nitrogen content is investigated. It is found that the nitrogen content is vital to obtain high-performance magnetic powders based on $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$. In comparison with quenching Nd–Fe–B powders, $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$ powders are characterized by a larger maximum-energy product and a lower cost. Obviously, it is of significance in permanent magnet applications. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since 1990, interstitial atoms such as H, C and N have been introduced into $\text{R}(\text{Fe}, \text{M})_{12}$ ($\text{M} = \text{Ti}, \text{V}, \text{Mo}, \text{W}$, etc.) compounds [1, 2], and world-wide efforts have been made to investigate new hard magnetic materials based on rare-earth iron nitrides. The interstitial nitrogen atoms not only increase Curie temperature and saturation mag-

netization, but also give rise to a profound change in magnetocrystalline anisotropy. Due to these effects, $\text{Nd}(\text{Fe}, \text{M})_{12}\text{N}_x$ ($\text{M} = \text{Ti}, \text{Mo}, \text{V}$) become well-known candidates for permanent magnet applications. By comparison, $\text{Nd}(\text{Fe}, \text{V})_{12}\text{N}_x$ presents a higher Curie temperature and a larger saturation magnetization than $\text{Nd}(\text{Fe}, \text{Mo})_{12}\text{N}_x$, and it seems easier to create a higher coercivity than that of $\text{NdFe}_{11}\text{TiN}_x$. A large coercive force of up to 6–10 kOe was obtained by using mechanical alloying technique [3]. However, the powders prepared by using mechanical alloying are isotropic, then the remanence and the maximum-energy

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product are low. So, it is worth developing a new procedure to prepare the V-stabilized 1 : 12 nitrides pertaining to the formation conditions of good single phase, improvement on intrinsic magnetic properties, and the creation of a high coercivity.

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

2. Experimental methods

Parent alloys were prepared by arc melting of 99.5% pure metals in an argon atmosphere, followed by heat treatment at 900°C for one week. The nitrides were formed by passing purified nitrogen gas at 1 atm over fine powder samples (5–10 μm) at 480–600°C for 4–12 h, followed by rapidly cooling to room temperature. Then the powders were further ground under the protection of ethanol for 0.5–15 h. The nitrogen content was determined by chemical analysis and X-ray diffraction. The hysteresis loops of the samples were measured by a vibrating-sample magnetometer (VSM) with a field of up to 30 kOe at room temperature. The particle size of powders was determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The samples of cylindrical shape ($\varnothing 3 \times 4$ mm) were aligned in a magnetic field of 10 kOe and fixed in epoxy resin. Thermomagnetic curves were measured by a vibrating sample magnetometer in the temperature range from 300 to 1000 K. The saturation magnetization was deduced from the law of approach to saturation and the magnetocrystalline anisotropy parameters were obtained using the Sucksmith–Thompson method [4].

3. Results and discussion

The typical X-ray diffraction patterns of $\text{NdFe}_{10.5}\text{V}_{1.5}$ and $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$ are given in Fig. 1. The X-ray patterns show that the alloys are

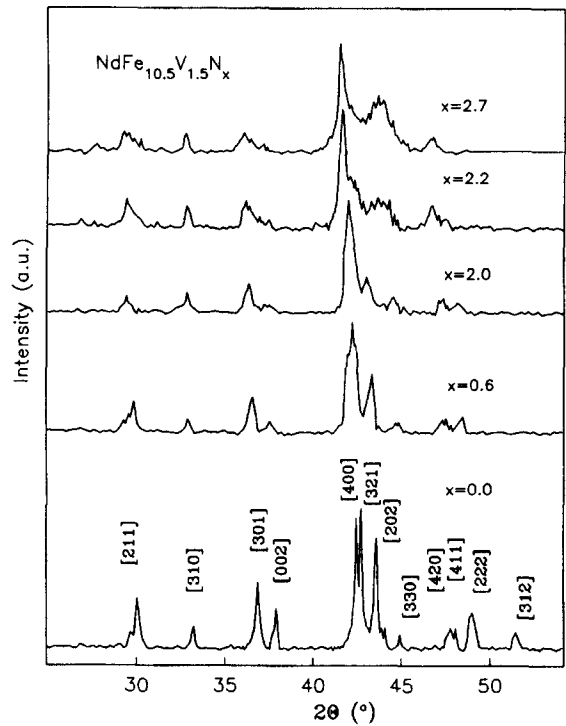


Fig. 1. The X-ray diffraction patterns of $\text{NdFe}_{10.5}\text{V}_{1.5}$ and $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$.

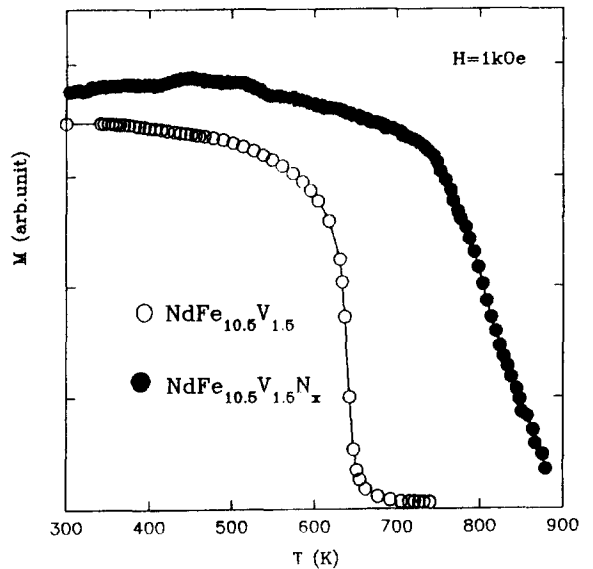


Fig. 2. The thermomagnetic curves of $\text{NdFe}_{10.5}\text{V}_{1.5}$ and $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$.

of 1:12 single phase, which also can be verified from the thermomagnetic curve shown in Fig. 2. There is a little precipitation of α -Fe after nitrogenation and its content increases with increasing nitrogen content. This is due to the excess strain caused by the N insertion, and it has also been confirmed in $Y_2Fe_{17}N_x$ nitride [5]. All the X-ray diffraction peaks of $NdFe_{10.5}V_{1.5}N_x$ shift to lower angles as $x \leq 2.0$, it suggests that the nitrogen enters into interstitial sites and results in lattice expansion. The positions of diffraction peaks are nearly unchanged after $x > 2.0$, indicating that the nitrogen does not enter the interstitial sites any more, and at the same time α -Fe and neodymium nitrides are formed.

So, a proper nitrogen content with impurity phases as little as possible will bring great advantages to the hard magnetic properties of the magnetic powders. In addition, compared to the $RFe_{11}Ti$ alloy, $RFe_{10.5}V_{1.5}$ alloy possesses a stronger ability to absorb nitrogen atoms. The x in $NdFe_{10.5}V_{1.5}N_x$ ranges from 0 to as large as 2.7, which is much more than the theoretical value of one N per formula. One way to understand this is that the measurements included everything gained during nitrogenation such as N in neodymium nitride precipitates, N in the particle surface (physical absorption) or in the bulk, and a formation of the Fe–N compound as well. In fact, during the nitrogenation process, it is inevitable that a small amount of impurity phases such as iron and rare-earth nitrides are formed [6]. Thus, the actual N content in the 1:12 phase may be significantly less than the measured value by weight.

Because the nitrogen content has such a great influence on the crystal structure and the phase composition of the nitrides, it will finally affect the magnetic properties of the magnetic powders. As an illustration, the magnetization curves of the $NdFe_{10.5}V_{1.5}N_x$ with different nitrogen contents at room temperature, parallel and perpendicular to the alignment direction, are plotted in Fig. 3, and the corresponding intrinsic magnetic parameters are listed in Table 1. From Fig. 3 and Table 1, it is seen that the magnetic anisotropy and the saturation magnetization have a remarkable change with different nitrogen content x . H_a and M_s increase steadily with increasing nitrogen content and the

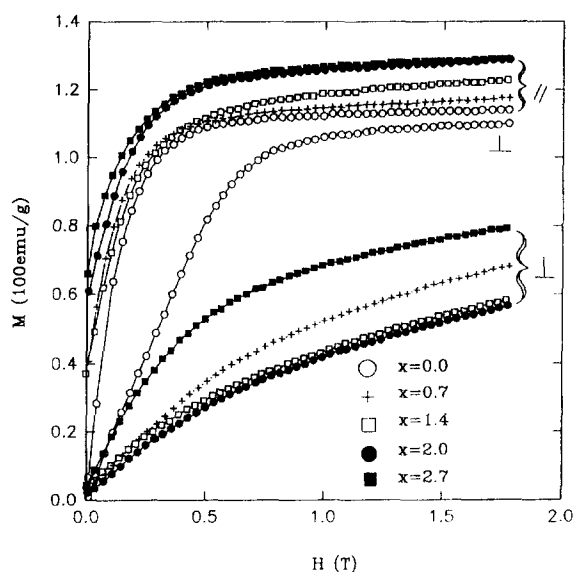


Fig. 3. The room-temperature magnetization curves of the magnetically oriented samples of $NdFe_{10.5}V_{1.5}N_x$.

former reaches a maximum value at $x = 2.0$. Noting the increase in H_a , it can be concluded that $NdFe_{10.5}V_{1.5}$ is not fully nitrogenated until x reaches 2 or so. By further nitrogenation, the magnetocrystalline anisotropy field decreases drastically due to the poor crystal structure. This is consistent with the X-ray pattern of $x = 2.7$, where certain amount of impurity phases are formed. These results suggest that both insufficient nitrogenation and over-nitrogenation are harmful for the intrinsic magnetic properties.

Generally, the nitrogen content is dependent on the nitrogenation process, so the nitrogenation temperature and time play a key role in obtaining good hard magnetic properties. By optimizing the nitrogenation temperature and time, the highest coercivity of $NdFe_{10.5}V_{1.5}N_x$ is obtained with nitrogenation at $T = 510^\circ C$. The hysteresis loops of these powders are presented in Fig. 4. The room-temperature permanent magnetic properties of $NdFe_{10.5}V_{1.5}N_x$ are listed as follows: $(BH)_{max} = 17.2$ MGOe, $B_r = 10.8$ kG, and $H_{cJ} = 4.3$ kOe. The intrinsic coercivity can be enhanced to 4.5 kOe at the cost of remanence and energy product (corresponding values are $B_r = 10.5$ kG, $(BH)_{max} = 16.1$ MGOe). In addition, the intrinsic coercivity

Table 1
The intrinsic magnetic properties of the $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$ powders

x	M_s (emu/g)	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
2.7	132.1	-0.11	33.30	-

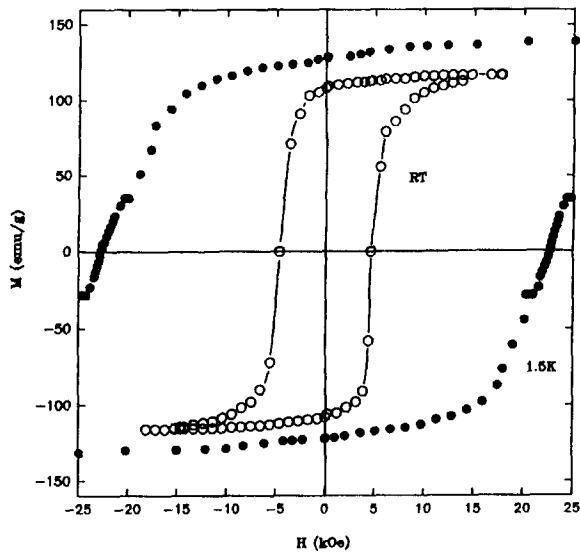


Fig. 4. The hysteresis loop of epoxy-bonded $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$ powders at 1.5 K and room temperature.

H_{cJ} of the powders exhibits a large dependence on the magnetization field. For example, coercivities of 4.0 and 4.6 kOe were obtained under measuring fields of 20 and 30 kOe, respectively.

The coercivity and remanence are extrinsic properties which are strongly dependent on technical process. The dependence of coercivity and remanence on the particle size of the $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$ powders is illustrated in Fig. 5. The coercivity first increases as the particle size decreases, and reaches a maximum value at the size of about 1 μm . As the particle size decreases further, the coercivity begins to decrease. The increase of coercivity at first can be explained by the single-domain theory and nucleation model. The remnant magnetization has the

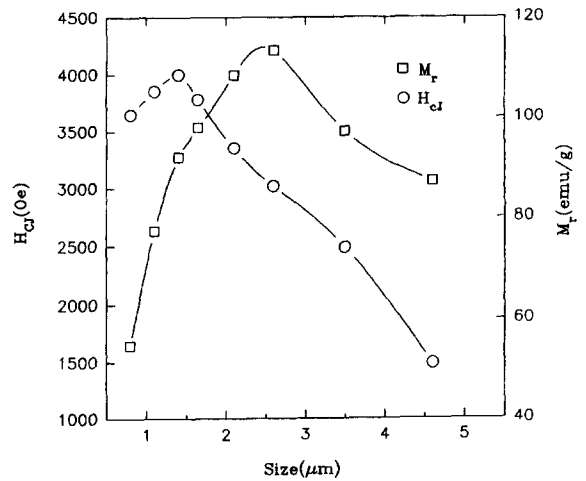


Fig. 5. The dependence of coercivity on the particle size of $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$.

same trend with respect 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 coercivity and remnant magnetization, TEM was used to investigate the crystal structure of the particles with different grinding time. Fig. 6a shows the diffraction pattern of the powders with the maximum coercive force. It is found that the fine powders are single crystals. With prolonged milling, the powders are found to be defective and are transferred into being polycrystal, as shown in Fig. 6b. The results indicate that the crystal structure of the powders was damaged after prolonged grinding, which will drastically degrade the coercivity and remnant magnetization of the nitrides.

Finally, the temperature dependence of coercivity of the $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$ powders was determined by measuring the temperature dependence of the

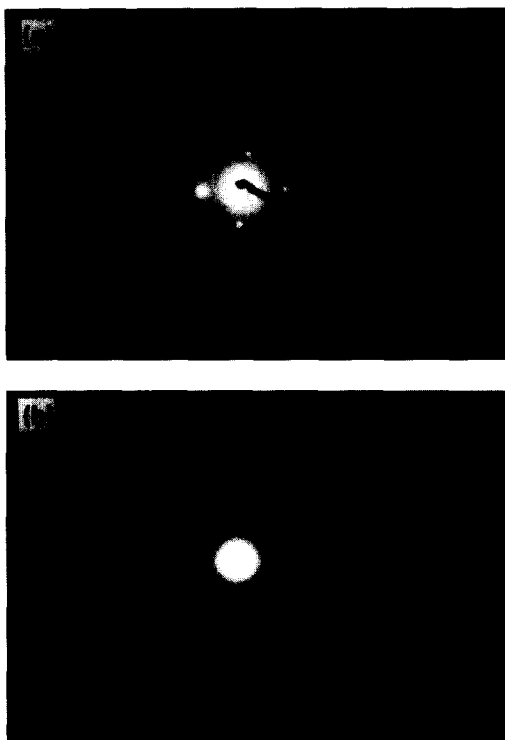


Fig. 6. The TEM diffraction patterns of $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$ with the optimizing milling time (a) and prolonged milling time (b).

hysteresis loops in a temperature range from room temperature to 450 K. The results are shown in Fig. 7. Their temperature coefficient of coercivity is smaller than that of $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets and close to that of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ magnets [7].

4. Conclusions

Fine powders of $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$ with $(BH)_{\text{max}} = 17.2$ MGOe, $B_r = 10.8$ kG, and $H_{cJ} = 4.3$ kOe were prepared by optimized nitrogenation process and grinding time. It is found that the purity of the ThMn_{12} phase and the uniformity of the nitrogenation are two important factors affecting the hard magnetic properties of $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$. The intrinsic magnetic properties are strongly dependent on the nitrogen content. The intrinsic coercivity H_{cJ} and the remnant magnetization vary with particle size, and crystal defects are responsible for the coercive force degradation.

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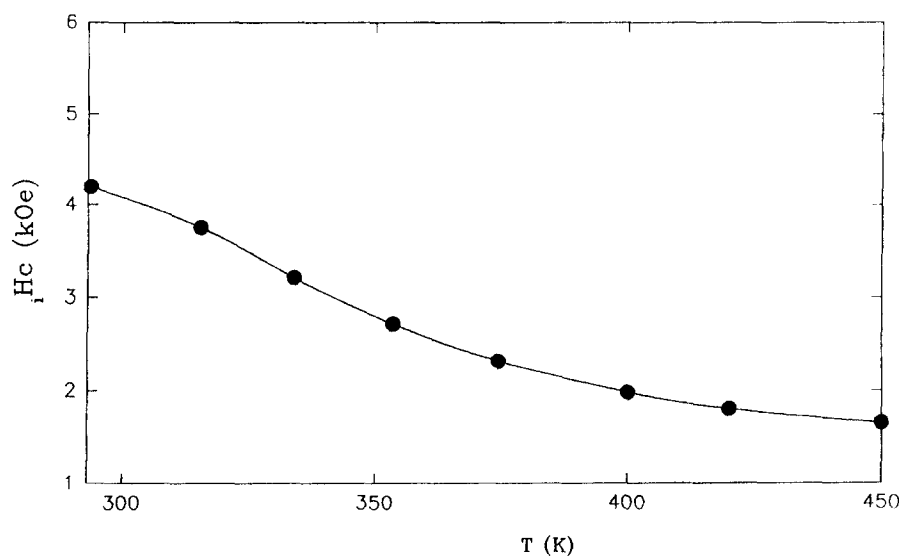


Fig. 7. The dependence of coercivity on the temperature of $\text{NdFe}_{10.5}\text{V}_{1.5}\text{N}_x$.

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