

$(\text{Nd}_{0.9}\text{Dy}_{0.1})_{16}\text{Co}_5\text{Fe}_{70}\text{Nb}_2\text{B}_7$ PERMANENT MAGNETIC ALLOY AND BEHAVIOUR OF Nb^①

Pan Shuming

General Research Institute of Non-ferrous Metals, Beijing 100088

Pan Feng

Beijing Tape Recorder Factory, Beijing 100080

Ma Ruzhang

University of Science and Technology Beijing, Beijing 100083

ABSTRACT The magnetic properties of $(\text{Nd}_{0.9}\text{Dy}_{0.1})_{16}\text{Co}_5\text{Fe}_{70}\text{Nb}_2\text{B}_7$ permanent magnetic alloy prepared by powder metallurgy are: $B_r = 1.08\text{ T}$, $H_c = 1620\text{ kA/m}$, $(BH)_{\max} = 208\text{ kJ/m}^3$. The behaviour of Nb in this alloy was studied by joint methods of dynamic observation by high voltage electron microscope (HVEM) and Mössbauer effects. With Nb and Co substituting parts of Fe and adding a little Dy, practical magnetic alloy with excellent properties can be obtained. The thermal stability of it is 80°C higher than that of ternary Nd-Fe-B magnet. The study shows that adding Nb into Nd-Fe-B can make the intrinsic coercivity appear peak value at about Nb = 2% (in mole fraction). Nb mainly enters into Nd-rich and B-rich phases, a little into $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.

Key words $(\text{Nd}_{0.9}\text{Dy}_{0.1})_{16}\text{Co}_5\text{Fe}_{70}\text{Nb}_2\text{B}_7$ permanent magnetic alloy magnetic properties

1 INTRODUCTION

Nd-Fe-B permanent magnetic alloy has excellent magnetic properties, but its Curie temperature of only 312°C means bad thermal stability. So to improve its thermal stability is very important.

Curie temperature and thermal stability are all very sensitive to material structure and the only way to change material structure is alloying. We have had Si, Ta, Nb, V, Ga, Zn, Ti and Al to substitute Fe in Nd-Fe-B respectively. This paper mainly reports the effect of Nb substituting parts of Fe.

Xiao Y *et al* point out that with Nb, Ti, Zr respectively substituting parts of Fe, the coercivity attains peak value when x in $(\text{Nd}_{0.88}\text{Dy}_{0.12})(\text{Fe}_{0.88-x}\text{Co}_{0.12}\text{B}_{0.08}\text{M}_x)_{5.5}$ is 0.036 or Nb is 3% (in mole fraction). The addition of Nb improves H_c and H_k , therefore makes the demagnetizing curve remain good square

degree. However, at Nb = 10% (in mole fraction), 2-14-1 phase disappears. Tokunaga M *et al* point out that when the addition of Nb gets to minimum non-reversible losses, it does not alter T_c ^[1].

How the addition of Nb raises the coercivity is still unknown. We know that the microstructure is related with the coercivity H_c . To make clear the crystal defects, phase changes and microstructure characteristics are the base of studying the coercivity mechanism of Nd-Fe-B alloy.

Mössbauer spectra instrument and X-ray diffraction apparatus were utilized for studying the effect of Nb on the alloy structure and magnetic properties.

2 SAMPLE PREPARATION AND EXPERIMENT

By conventional powder metallurgical

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ways, the following samples were prepared: $\text{Nd}_{16}(\text{Fe}_{1-x}\text{Nd}_x)_{77}\text{B}_7$ ($x=0, 0.01, 0.02, 0.04, 0.08, 0.15$) and $(\text{Nd}_{0.9}\text{Dy}_{0.1})_{16}\text{Fe}_{72}\text{Co}_5\text{Nb}_x\text{B}_7$ ($x=0, 2$). 99.9% purity Nd, Fe and Co, 99.98% purity Nb and B-Fe alloy with B 18.4% are mixed and melted in a vacuum non-self consumed arc furnace. For prevention from oxidization, air was first pumped to vacuum and then Ar was filled in^[2]. The melt procedure was repeated for three times and casting alloy was obtained. Under organic medium, the casting alloy was grounded to 3 ~ 4 μm , shaped in 1.5 T magnetic field, sintered at 1100 °C for 1 h, aged at 630 °C, quenched to room temperature and the sintered samples were formed.

The preparation of samples for TEM observation was that the above-mentioned samples were cut perpendicular to c direction to 0.25 mm thick films, grounded and polished, then thinned and washed for observation^[3].

The observation of film samples were carried on a JEM-1000 HVEM. Operation voltage was 1000 kV, vacuum was 2.5×10^{-4} Pa and after N_2 added in was 0.7×10^{-5} Pa. Ion beam was 10 μA .

Mössbauer spectra were measured on an Oxford Ms-500 apparatus with $^{50}\text{Co}/\text{Rh}$ as radiation source and with $\alpha\text{-Fe}$ to define velocity.

The measurement for remanent magnetic induction and coercivity was performed on a C26-1 magnetic parameter measurer. Curie temperature was measured on a magnetic intensity meter.

3 RESULTS AND DISCUSSION

3.1 Magnetic Measurement

The samples were measured by using a magnetic parameter measurer under a 4 T magnetic field and the results are shown in Table 1. It can be drawn out that for $\text{Nd}_{16}(\text{Fe}_{1-x}\text{Nb}_x)_{77}\text{B}_7$ ($x=0, 0.01, 0.02, 0.04, 0.08, 0.15$), the intrinsic coercivity increases by 45% at $x=0.02$, 20% at $x=0.01$ and monotonously drops at $x=0.04, 0.08$ and 0.15, the remanent magnetic induction and

the maximum magnetic energy product $(BH)_{\text{max}}$ both decline monotonously. Table 2 shows that the coercivity has increment after a little Nb is added in.

Table 1 The magnetic properties of $\text{Nd}_{16}(\text{Fe}_{1-x}\text{Nb}_x)_{77}\text{B}_7$

x	B_r /T	H_c /kA \cdot m $^{-1}$	$(BH)_{\text{max}}$ /kJ \cdot m $^{-3}$
0	1.24	670	292
0.01	1.22	886	270
0.02	1.20	1026	260
0.04	1.17	620	235
0.08	1.10	510	205
0.15	1.08	440	170

Table 2 The magnetic properties of samples with and without Nb

Sample	B_r /T	H_c /kA \cdot m $^{-1}$	$(BH)_{\text{max}}$ /kJ \cdot m $^{-3}$
$(\text{Nd}_{0.9}\text{Dy}_{0.1})_{16}\text{Co}_5\text{Fe}_{72}\text{B}_7$	1.10	1360	216
$(\text{Nd}_{0.9}\text{Dy}_{0.1})_{16}\text{Co}_5\text{Fe}_{70}\text{Nb}_2\text{B}_7$	1.08	1620	208

3.2 Curie Temperature

Curie temperatures of $\text{Nd}_{16}(\text{Fe}_{1-x}\text{Nb}_x)_{77}\text{B}_7$ ($x=0.01, 0.02, 0.04, 0.08, 0.15$) are given out in Table 3. The addition of Nb can not raise the Curie temperature. At $x=0.08$, there appear two iron magnetic phases, T_c of which are respectively 305 °C and 110 °C. These two phases have been proved from thermomagnetic curves. The σ - T curves cross the horizontal axis at 110 °C and 305 °C.

Table 3 The Curie temperatures of $\text{Nd}_{16}(\text{Fe}_{1-x}\text{Nb}_x)_{77}\text{B}_7$

x	0	0.01	0.02	0.04	0.08	0.15
T_c /°C	336	326	330	327	305	126

3.3 Microstructure at Room Temperature

TEM observation for Nd-Fe-B alloy (see Fig. 1) shows that the ternary alloy $\text{Nd}_{16}\text{Fe}_{77}\text{B}_7$ without Nd, Co and Dy has three phases of matrix phase $\text{Nd}_2\text{Fe}_{14}\text{B}$, Nd-rich phase and B-

rich phase ($\text{Nd}_{1+x}\text{Fe}_4\text{B}_4$), sometimes with a little $\alpha\text{-Fe}$ (Fe 99%, Nd 1%)^[4].

After Nb is added, except foresaid matrix phase, Nd-rich phase and B-rich phase which have existed, there appear new phases in Nd-Fe-B. One of them is MgMn_2 -type Fe_2Nb phase, lattice constant $a = 0.482 \text{ nm}$, $c = 0.787 \text{ nm}$. As Fig. 2 shows, it exists in $\text{Nd}_2\text{Fe}_{14}\text{B}$. Its size is very small, with diameter

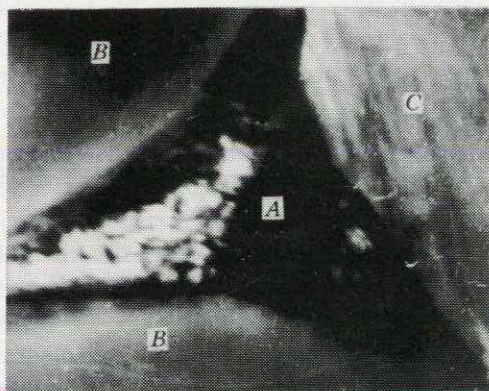


Fig. 1 Microstructure of $\text{Nd}_{16}\text{Fe}_{77}\text{B}_7$ at room temperature, $\times 80\,000$

A — Nd-rich phase;
B — $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix phase;
C — B-rich phase

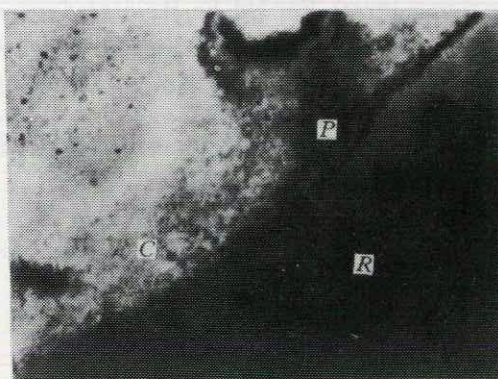


Fig. 2 Electron microstructure of $(\text{Nd}_{0.9}\text{Dy}_{0.1})_{16}\text{Fe}_{70}\text{Co}_5\text{Nb}_2\text{B}_7$ at room temperature, $\times 20\,000$

R — 2-14-1 phase;
P — crystal boundary;
C — Fe_2Nb phase

$2 \sim 4 \mu\text{m}$, the Nb content is 20% ~ 45% in mole fraction. Another kind is Nb-rich phase with size $30 \sim 50 \text{ nm}$ which is coherent with matrix phase and spreads in $\text{Nd}_2\text{Fe}_{14}\text{B}$. However, Nb mainly concentrates at crystal boundaries (see Fig. 2), thus the microstructure shape of Nd-Fe-B changes and so does the case of which Nd-rich phase is mainly at triangle crystal boundaries. From TEM observation, there exist a little precipitations called Nb-rich phase except Fe_2Nb . Its Nb content is 89% ~ 97%, Co and Fe are little. This shows that Nb which precipitates before ageing spreads into Nd-rich phase neighbouring to 2-14-1 phase while ageing and forms new particles containing Nb. This spread makes crystal very regular and smooth.

3.4 Microstructure at High Temperature

The sample was put onto a side-inserted heating platform in a 1000 kV HVEM, heated and held under desired vacuum. The microstructure change was recorded and relevant diffraction was obtained.

For studying the effect of Nb in Nd-Fe-B, comparison experiment was carried out and the result is as follows.

The microstructure of $\text{Nd}_{16}\text{Fe}_{77}\text{B}_7$ at high temperature is $\text{Nd}_2\text{Fe}_{14}\text{B}$ (matrix phase). Highly-spread precipitations fill in field of vision at 280°C , after growing up, they are demarcated *bcc* structure from electron diffraction with lattice constant $a = 10.86 \text{ \AA}$ and finally defined as Nd_2O_3 from card index. B-rich phase $\text{Nd}_{1+x}\text{Fe}_4\text{B}$ begins to change at 140°C . Lattice distortion appears at 320°C and follows the alternation of microstructure, Nd-rich phase films may broaden regularly at high temperature.

For $(\text{Nd}_{0.9}\text{Dy}_{0.1})_{16}\text{Co}_5\text{Fe}_{70}\text{Nb}_2\text{B}_7$ which contains Nb, dynamic observation was carried out while heating. Below 400°C , the microstructure does not change, at above 400°C some fine precipitations appear on the 2-14-1 matrix phase and are defined as Nd_2O_3 by electron diffraction. There is no change on the crystal boundary, the change occurs 100°C

lower than that of 2-14-1 matrix phase, as shown in Fig. 3.

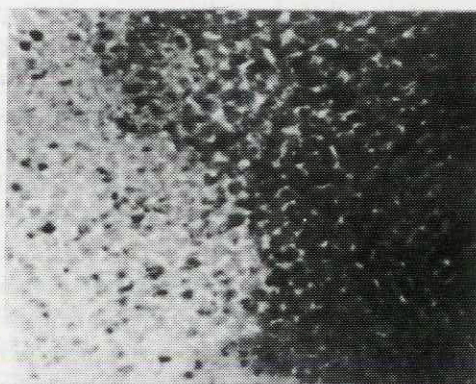


Fig. 3 Electron Microstructure of
 $(\text{Nd}_{0.9}\text{Dy}_{0.1})_{16}\text{Fe}_{70}\text{Co}_5\text{Nb}_2\text{B}_7$
 at 500 °C, $\times 20\,000$

3.5 Mössbauer Spectrum for $\text{Nd}_{16}(\text{Fe}_{1-x}\text{Nb}_x)_{77}\text{B}_7$

Table 4 shows the occupation probability of each crystal position of Fe and Nb in cubic phase. Obviously, in the whole range of cubic phase, Nb atoms first occupy *e* and *c* positions.

Among neighbouring atoms of each crystal position, atoms of *e* and *c* positions are very few, so in case a few Nb elements enter in, they will not cause great change of hyperfine field of each crystal position, *c* crystal position has face anisotropy, the addition of Nb can weaken it and meanwhile is beneficial for increasing uni-axial anisotropy, therefore make

the coercivity improved.

Nb does not enter into cubic phase and alter exchange actions, so the Curie temperature has no great change, which is certified by the test result (Table 3). Nb has little effect on saturated magnetization intensity of 2-14-1 matrix phase, therefore the remanent magnetic drop is small (Table 1). However, when there is much Nb, the stability of 2-14-1 matrix phase is ruined, the cubic phase no longer exists and other two magnetic phases substitute it, i. e. two phases at $T_{c1} = 110\text{ °C}$ and $T_{c2} = 305\text{ °C}$ (the structure of them is remained for study).

3.6 Relation Between Addition of Nd and Coercivity

The addition of Nb makes the coercivity of the alloy appear peak value. For the $\text{Nd}_{16}(\text{Fe}_{1-x}\text{Nb}_x)_{77}\text{B}_7$, at $x=0.02$, the coercivity has peak value (Table 1). Nb elements do not enter into 2-14-1 phase at large amount, then where are they? Nb elements mainly concentrate in Nd-rich phase on the crystal boundary, which makes the smoothing between Nd-rich phase and 2-14-1 phase improved and is beneficial for curbing growing up of 2-14-1 matrix phase and removing defects which may become demagnetization nucleation centres. For Nd-Fe-B sintered magnet of which coercivity is controlled by nucleating field, demagnetization nucleation centers are less, coercivity is higher.

We have proved that for sintered Nd-Fe-

Table 4 The occupation probability of each crystal position of Fe and Nb in $\text{Nd}_{16}(\text{Fe}_{1-x}\text{Nb}_x)_{77}\text{B}_7$

<i>x</i>	Occupation probability	<i>j</i> ₂	<i>k</i> ₂	<i>k</i> ₁	<i>j</i> ₁	<i>e</i>	<i>c</i>
0.01	<i>P</i> (Fe)	1.006	1.007	0.999	0.985	0.948	0.934
	<i>P</i> (Nb)	— 0.006	— 0.007	0.001	0.015	0.052	0.066
0.02	<i>P</i> (Fe)	0.982	0.993	0.986	0.958	0.972	0.958
	<i>P</i> (Nb)	0.018	0.007	0.014	0.042	0.028	0.042
0.04	<i>P</i> (Fe)	0.951	0.968	0.965	0.958	0.951	0.923
	<i>P</i> (Nb)	0.149	0.032	0.035	0.042	0.049	0.077

B, ageing at 550~630 °C may double the coercivity, however, after ageing changes do not occur in grains but at crystal boundaries. We think for sintered Nd-Fe-B alloy, microstructure of boundary has much effects on coercivity. Because of the addition of Nb, except Nd-rich and B-rich phases at crystal boundary, there still exists Laves phase, i. e. Fe_2Nb phase, which can raise the pinning strength to domain walls so increase the coercivity.

3.7 Practical Nd-Fe-B Alloy Containing Nb

From Table 2, it can be seen the six-elemented $(\text{Nd}_{0.9}\text{Dy}_{0.1})_{16}\text{Co}_5\text{Fe}_{70}\text{Nb}_2\text{B}_7$ permanent alloy which contains Nb and Co has excellent magnetic properties. Because of the high coercivity, the service temperature of Nd-Fe-B rises 80 to 150 °C. With Nb and Co joint substituting parts of Fe and a little Dy substituting parts of Nd, this kind of practical magnets owns wonderful thermal stability and high magnetic properties and has got successful application in devices such as micromotors, magnetic controllers and wax-proof device for oil recovery^[5, 6].

4 CONCLUSIONS

(1) $(\text{Nd}_{0.9}\text{Dy}_{0.1})_{16}\text{Fe}_{70}\text{Co}_5\text{Nb}_2\text{B}_7$ with high coercivity, which is a kind of Nd-Fe-B alloy with Nb added in, is obtained by powder metallurgy and may be used up to 150 °C. Its properties are as follows: magnetic property $B_r = 1.08 \text{ T}$, intrinsic coercivity $H_c = 1620 \text{ kA/m}$, maximum magnetic energy product $(BH)_{\max} = 208 \text{ kJ/m}^3$.

(2) At the room temperature, in the

$(\text{Nd}_{0.9}\text{Dy}_{0.1})_{16}\text{Fe}_{70}\text{Co}_5\text{Nb}_2\text{B}_7$, except matrix phase, B-rich phase and Nd-rich phase, there still exists Fe_2Nb phase, whose lattice constants $a = 0.482 \text{ nm}$, $c = 0.787 \text{ nm}$. Nb is mainly at crystal boundary. From microstructure observation at high temperature, the shape of alloy does not change below 400 °C, there are no any precipitations on matrix phase, only at 100 °C higher than that of ternary Nd-Fe-B alloy appear precipitations.

(3) For $\text{Nd}_{16}(\text{Fe}_{1-x}\text{Nb}_x)_{77}\text{B}_7$ permanent magnetic alloy, at $x = 0.04$, it can be drawn out that only a little of Nb enter into e and c crystal positions, most of Nb enter into the Nd-rich and B-rich phases at crystal boundary.

(4) The addition of Nb in Nd-Fe-B can not make the Curie temperature raised.

(5) The addition of Nb in Nd-Fe-B may increase the intrinsic coercivity, and makes it appear peak value at $\text{Nb} = 2\%$.

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