

## Electrochemical behavior of Nd-(Fe,Co,Ni)-B sintered magnets

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Potentiostatic anode polarization curves were measured on the grain boundary phases and main phases in Nd-(Fe,Co,Ni)-B, Nd-(Fe,Co)-B, Nd-(Fe,Ni)-B and Nd-Fe-B sintered magnets in acid, neutral and alkaline solution containing  $\text{Cl}^{-1}$  ions. Corrosion potential differences among constituent phases in Nd-(Fe,Co,Ni)-B magnet were very small. The excellent corrosion resistance of this magnet is understood in terms of a inhibition of electrochemical corrosion.

### 1. INTRODUCTION

Nd-Fe-B magnets are known to possess the large energy maximum product. However, because of their poor corrosion resistance [1], corrosion-resistant coating is required in long-time service. Epoxy resin [2], Al ion-plating [3] and Ni-plating [4] as protection films have been used for practical use. However, the hygroscopic nature of epoxy resin, non-uniform thickness in Al ion-plating [5], poor adhesion in Ni-plating [6] and trace of pin-holes in all of the protection films raise a questions of reliability in practical use. In addition, the coating steps in technical production lowers the productivity of Nd-Fe-B magnets.

In a previous paper [7], a improvement of corrosion resistance while maintaining their good magnetic properties was reported for a pseudo-ternary system of Nd-( $\text{Fe}_{1-x-y}\text{Co}_x\text{Ni}_y$ )-B sintered magnets ( $0.2 \leq x \leq 0.45$  and  $0.05 \leq y \leq 0.25$ ). Their good corrosion resistance is supposed to depend on the Nd(Ni,Co) grain boundary phase [8] and the good magnetic properties on the ordered iron sub-lattice in  $\text{Nd}_2(\text{Fe,Co,Ni})_{14}\text{B}$  main phase [9].

The objective of this study is to clarify

the mechanism of corrosion resistance of Nd-(Fe,Co,Ni)-B sintered magnet throughout electrochemical measurements.

### 2. EXPERIMENTAL

The alloy specimens were prepared by induction melting under Ar atmosphere. The specimens for sintered magnets were crushed into 32 mesh and then subjected to jet-milling. The fine powders were aligned in a magnetic field of 12 kOe, followed by pressing under a load of 1.5ton/cm<sup>2</sup>. Resulting compact were sintered in a vacuum at temperatures between 1000~1100°C. The single phase specimens which comprise sintered magnets were obtained by homogenization of the cast ingot at 600 ~1000°C for 10 days.

Corrosion tests for sintered magnets were carried out by exposing to a corrosive environment at 70°C in air with relative humidity of 95 %. To quantify the corrosiveness, the rusty surface of specimens was subjected to graphic analysis.

Electrochemical behavior of constituent phases was measured by means of a potentiostatic anode polarization curves. Potentiodynamic scans were carried out with a

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potentiostat using electrolytes as follows : (1) 0.01%NaCl+0.01%H<sub>2</sub>SO<sub>4</sub>, pH=2.7 (2) 0.01%NaCl, pH=5.8 (3) 0.01%NaCl+0.02%NaOH, pH=11.8. A saturated Calomel electrode provided a reference. The initial value of equilibrium corrosion potential was taken after 600s immersing in electrolytes (no applied potential).

### 3. RESULTS AND DISCUSSION

#### 3. 1. SINTERED MAGNETS

Compositions and magnetic properties of sintered magnets are shown in Tables 1 and 2, respectively. Small amount of titanium was added to the magnets to get a fine-grained structure and to enhance coercivity [10]. The nickel substitution in Nd-Fe-B magnet decreased the coercivity drastically. It is important to note that double substitution of Co and Ni atoms for Fe atoms restores the coercivity. This behavior has been attributed to an ordered iron sublattice in Nd<sub>2</sub>(Fe, Co, Ni)<sub>14</sub>B main phase [9].

Table 1 Compositions of specimens

Specimen	Composition
A	Nd <sub>15</sub> (Fe <sub>.585</sub> Co <sub>.3</sub> Ni <sub>.1</sub> Ti <sub>.015</sub> ) <sub>77</sub> B <sub>8</sub>
B	Nd <sub>15</sub> (Fe <sub>.685</sub> Co <sub>.3</sub> Ti <sub>.015</sub> ) <sub>77</sub> B <sub>8</sub>
C	Nd <sub>15</sub> (Fe <sub>.885</sub> Ni <sub>.1</sub> Ti <sub>.015</sub> ) <sub>77</sub> B <sub>8</sub>
D	Nd <sub>15</sub> (Fe <sub>.985</sub> Ti <sub>.015</sub> ) <sub>77</sub> B <sub>8</sub>

Table 2 Magnetic properties of specimens

Specimen	Maximum energy product (MG0e)	Residual magnetization (kG)	Intrinsic coercivity (kOe)
A	34.0	11.9	10.8
B	36.8	12.4	12.8
C	24.0	11.0	4.0
D	40.0	13.3	13.0

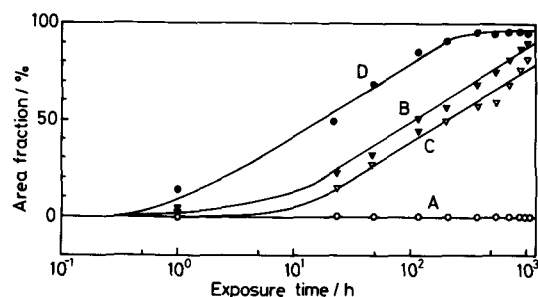


Figure 1. Area fraction of surface of specimens A~D exposed to humid(95%) atmosphere at 70 °C

Results on environmental tests on specimens of A, B, C and D are shown in Fig. 1. Specimen A shows no rust after 1000h. Specimen B and C are covered with rust of 25 and 30% surface area after 48h. Rusty surface area fraction of specimen D exceeds 75% after 48h and the rust proceeds also inside the specimen with the lapse of time. The corrosion product of Nd-Fe-B magnet are reported to be Fe<sub>3</sub>O<sub>4</sub>, Nd<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> [11].

#### 3. 2. CONSTITUENT PHASE MATERIALS

The poor corrosion resistance of Nd-Fe-B sintered magnet is suggested to result from

Table 3 Compositions of specimens

Specimen	Composition
E	Nd(Ni <sub>.85</sub> Co <sub>.15</sub> )
F	Nd(Fe <sub>.4</sub> Co <sub>.4</sub> Ni <sub>.2</sub> ) <sub>4</sub> B
G	Nd <sub>2</sub> (Fe <sub>.6</sub> Co <sub>.3</sub> Ni <sub>.1</sub> ) <sub>14</sub> B
H	Nd <sub>3</sub> Co
I	Nd(Fe <sub>.46</sub> Co <sub>.54</sub> ) <sub>4</sub> B
J	Nd <sub>2</sub> (Fe <sub>.7</sub> Co <sub>.3</sub> ) <sub>14</sub> B
K	Nd(Ni <sub>.95</sub> Fe <sub>.05</sub> )
L	Nd <sub>1.1</sub> (Fe <sub>.97</sub> Ni <sub>.03</sub> ) <sub>4</sub> B <sub>4</sub>
M	Nd <sub>2</sub> (Fe <sub>.9</sub> Ni <sub>.1</sub> ) <sub>14</sub> B
N	Nd
O	Nd <sub>1.1</sub> Fe <sub>4</sub> B <sub>4</sub>
P	Nd <sub>2</sub> Fe <sub>14</sub> B

a formation of local cell at the Nd-rich grain boundary phase [1]. On the other hand, analytical TEM observation of Nd-(Fe,Co,Ni,Ti)-B has showed a presence of Nd(Ni,Co) intermetallic compound phase instead of Nd phase at a grain boundary region [8]. In this section the electrochemical behavior estimated by means of a potentiostatic anode polarization curves taken on the constituent

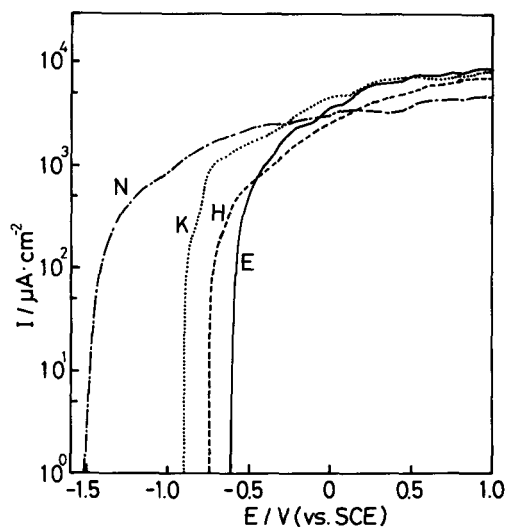


Figure 2 Potentiostatic anode polarization curves of specimen E, H, K and N in a pH 2.7 acid solution containing  $\text{Cl}^-$  ions

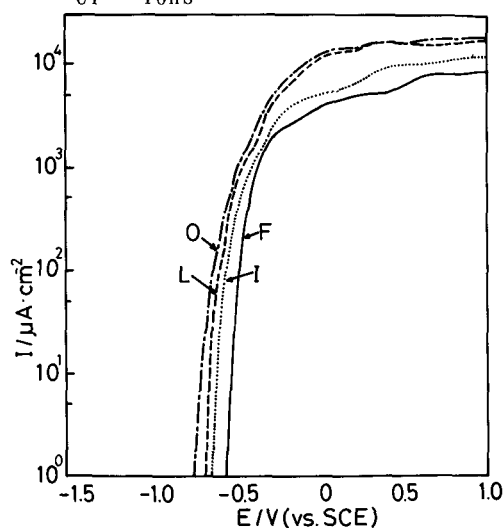


Figure 3 Potentiostatic anode polarization curves of specimen F, I, L and O in a pH 2.7 acid solution containing  $\text{Cl}^-$  ions

phases in sintered magnets is stated and the corrosion resistance mechanism in Nd-(Fe,Co,Ni,Ti)-B magnet is discussed. The compositions of the constituent phase have been determined by analytical TEM [8] and EPMA. They are shown in Table 3. Specimens E-G are comprised in magnet specimen A, H-J in B, K-M in C and N-P in D. Specimens E,H,K and N are Nd-rich grain boundary phases, specimens F,I, L and O are B-rich phases and G, J, M and P are 2-14-1 main phases. Potentiostatic anode polarization curves in a pH 2.7 acid solution are shown in Figs 2-4. Corrosion and pitting potential in acid, neutral and alkaline solutions are shown in Table 4.

Drastic changes occur in Nd-rich phases (Fig.2). Corrosion potential of Nd is very low and becomes nobler in the sequence  $\text{Nd}_3\text{Co} \rightarrow \text{Nd}(\text{Ni,Fe}) \rightarrow \text{Nd}(\text{Ni,Co})$ . The similar tendency are also observed in Figs 3 and 4. It is important to note that the corrosion potential differences among constituent phases of Nd-(Fe,Co,Ni)-B magnet is remarkably smaller than that of Nd-Fe-B magnet. For example, the corrosion potential difference between Nd-rich phase and main-phase of Nd-Fe-B and Nd-(Fe,Co,Ni)-B magnet in acid solution is 0.7V and 0.1V, respectively. In

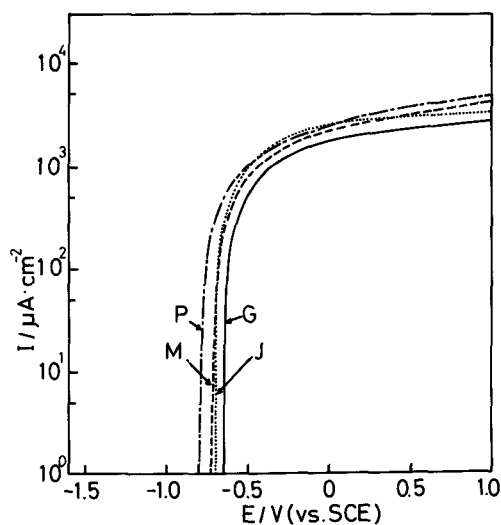


Figure 4 Potentiostatic anode polarization curves of specimen G, J, M and P in a pH 2.7 acid solution containing  $\text{Cl}^-$  ions

neutral and alkaline solutions, a passive state appear and the pitting potentials of constituent phases of Nd-(Fe,Co,Ni)-B magnet (E,F,G) are remarkably improved.

Based on the above results it is possible to make a following argument about the mechanism of the corrosion resistance of Nd-(Fe,Co,Ni)-B magnet : In Nd-(Fe,Co,Ni)-B

Table 4 Corrosion and pitting potentials of specimens E-P

Specimen	pH 2.7	pH 5.8	
	Corrosion potential (V)	Corrosion potential (V)	Pitting potential (V)
E	-0.7	-0.7	0
F	-0.6	-0.5	-0.2
G	-0.6	-0.5	-0.1
H	-0.9	-0.9	-0.4
I	-0.7	-0.6	-0.3
J	-0.7	-0.6	-0.5
K	-0.8	-0.8	-0.4
L	-0.7	-0.7	-0.3
M	-0.7	-0.6	-0.5
N	-1.5	-1.5	-1.4
O	-0.8	-0.8	-0.7
P	-0.8	-0.8	-0.7

Specimen	pH 11.8	
	Corrosion potential (V)	Pitting potential (V)
E	-0.6	0.6
F	-0.5	0.3
G	-0.3	0.4
H	-0.9	0.3
I	-0.6	0.1
J	-0.5	-0.2
K	-0.7	0.4
L	-0.7	-0.6
M	-0.4	-0.1
N	-1.4	-1.2
O	-0.7	-0.6
P	-0.5	-0.3

magnet, the corrosion potentials of constituent phases become nobler as compositions. Because of the marked change in Nd-rich phase, corrosion potential differences among constituent phases decrease and a electrochemical corrosion is inhibited. In neutral and alkaline solutions, constituent phases of Nd-(Fe,Co,Ni)-B magnets form the passive oxide films and these films are supposed to make the passive state of Nd-(Fe,Co,Ni)-B sintered magnet in alkaline solution [7].

In conclusion, it is demonstrated that the excellent corrosion resistance of Nd-(Fe,Co,Ni)-B magnet is attributable to the inhibition of electrochemical corrosion, which is achieved by the decrease of corrosion potential differences among constituent phases.

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