Advanced Materials '93, I / B: Magnetic, Fullerene, Dielectric, Ferroelectric,
Diamond and Related Materials, edited by M. Homma et al.
Trans. Mat. Res. Soc. Jpn., Volume 14B

Dispersion-hardened corrosion-resistant Nd-(FeCoNiTi)-B magnets; properties and microstructure

M. Shimotomai, Y. Fukuda, A. Fujita, Y. Ozaki and Y. Kitano

Technical Research Division, Kawasaki Steel Corporation,
Kawasaki-cho, Chuou-ku, Chiba 260, Japan

Salient features of sintered Nd-(Fe,Co,Ni,Ti)-B magnets with transition metals in a specific alloying range are satisfactory magnetic properties, excellent corrosion-free chemical stability and outstanding mechanical strength. Microscopic origins of these properties are discussed and promising application areas are suggested.

1. INTRODUCTION

It has been reported that magnetic properties and corrosion resistance are compatible in pseudo-ternary sintered magnets of Nd-($Fe_{1-x-y}Co_x Ni_y$)-B with $.2 \leq x \leq .45$ and $.05 \leq y \leq .25$ and that addition of Ti atoms enhances fracture toughness and coercivity as well [1,2]. This class of magnets was registered as NEONICO magnets by Kawasaki Steel Corp. and will be called as such hereinafter.

A chart as shown in Fig.1 qualitatively compares various properties among NEONICO, NdFeB and SmCo magnets; references are those of Sm-Co magnets. The magnetic property of NEONICO at room temperature is equal to or better than that of SmCo magnets. The corrosion resistance of NEONICO to humid air and spray salt is far better than that of NdFeB magnets and comparable to that of SmCo magnets, so that NEONICO magnets are usable without any coating. As the Curie temperature is raised to 550 ℃ in NEONICO magnets owing to Co and Ni additions, their thermal stability is improved, compared to NdFeB magnets. The reversible thermal coefficient of Br are -0.04, -0.03, -0.12 %/℃ for NEONICO, SmCo and NdFeB magnets, respectively.

The mechanical property of Ti-doped NEONICO magnets, as represented by the bending strength, is 4 times better than that of SmCo magnets. Fabrication of NEONICO magnets will be the simplest among the three, because neither a complicated heating process nor a tedious surface coating process is needed for NEONICO. This leads to a prediction of the lowest production cost for NEONICO magnets.

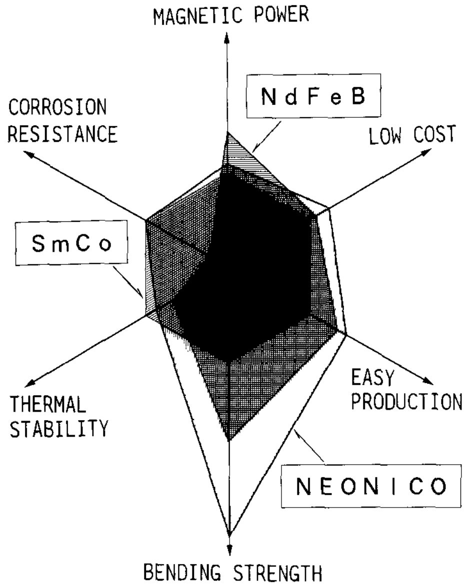

Fig.1. Comparison of rare earth magnets.

In the following, microstructures underlying the excellent properties of NEONICO magnets are discussed. Several remarks on applications are also given.

2. ATOMISTIC STRUCTURE

The double substitution of Co and Ni atoms for Fe atoms in NdFeB magnets is one of key points for NEONICO magnets. To clarify its mechanism, measurements of anisotropy field and saturation magnetization were carried out on single crystals of $Nd_2(FeCoNi)_{14}B$ prepared by the travelling solvent floating zone-melting technique [3]. The result was that double substitution of Co and Ni atoms for Fe atoms in the lattice of $Nd_2Fe_{14}B$ restored values of saturation magnetization and anisotropy field which were lost by single substitution Ni for Fe atoms. Based on this results, an ordered phase of $Nd_2(FeCoNi)_{14}B$ in NEONICO magnet was proposed and is shown in Fig. 2, where Co and Ni atoms occupy k_2 and j_2 sites, respectively.

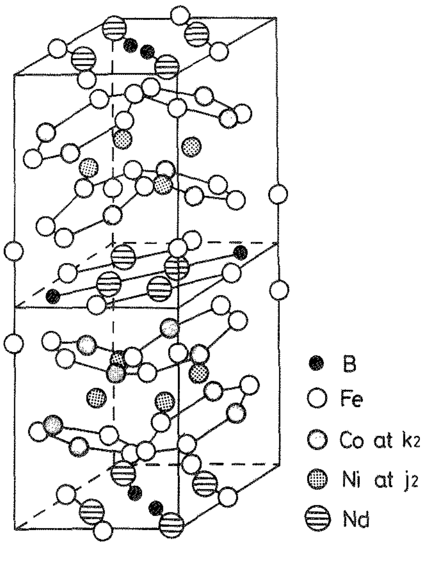

Fig. 2. Site occupation of atoms in an unit cell of $Nd_2(FeCoNi)_{14}B$.

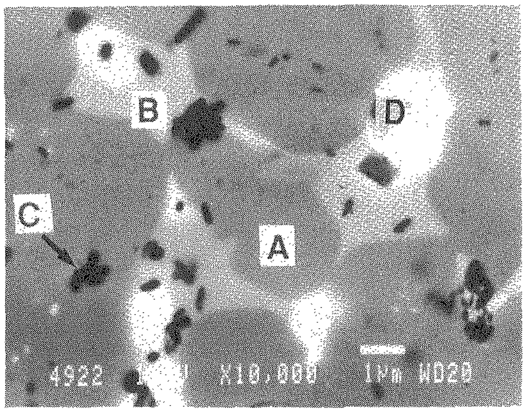

Fig. 3. Backscattered image of NEONICO magnet. A:$Nd_2(FeCoNi)_{14}B$, B:$Nd(FeCoNi)_4B$, C:TiB_2, D:Nd_2O_3.

3. METALLOGRAPHIC STRUCTURE

Since NEONICO magnets are nucleation-type, the nature of intergranular phase has significant effect on the coercivity. Figure 3 shows a scanning electron micrograph of a NEONICO magnet. The phases of $Nd(FeCoNi)_4B$, TiB_2 and Nd_2O_3 are observed in addition to the $Nd_2(FeCoNi)_{14}B$ phase. However, closer observations by TEM have revealed a thin intergranular phase as shown in Fig. 4. The phase was identified as $Nd(Ni_{.85}Co_{.15})$ with CrB structure by the energy-dispersive X-ray analysis and electron diffraction [4]. These phases

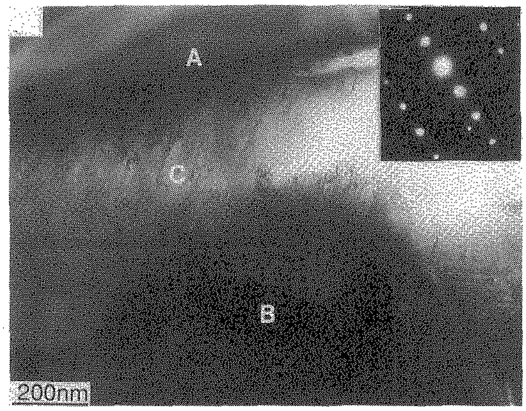

Fig. 4. TEM micrograph of NEONICO magnet. Diffraction pattern is from region C. A:$Nd_2(FeCoNi)_{14}B$, B:$Nd(FeCoNi)_4B$.

suggest that NEONICO magnets are in a regime of Nd-Co-B ternary phase diagram [5] in contrast to NdFeB magnets which obey Nd-Fe-B phase diagram [6]. The precise compositions of the constituent phases in NEONICO magnets were already reported[4] and are indicated in Fig.5. It is noted that Ni atoms are enriched in intergranular phases. The production process of NEONICO magnets involves gas- or oil-quenching after sintering to get high coercivity, because a formation of harmful intermetallic compound inherent to Nd-Co-B system has to be avoided. The NdNi phase has two advantages for high coercivity. One is low Curie point of 28 K [7], and the other is its relatively low melting temperature of 780℃[8]. The latter is very important to promote liquid phase sintering which results in smooth interfaces in NEONICO magnets.

The NdNi phase is also indispensable to the coating-free corrosion resistance of NEONICO magnets to humid air and to salt water. The values of corrosion potential of component phases in NEONICO and NdFeB magnets are plotted in Fig. 5. The small

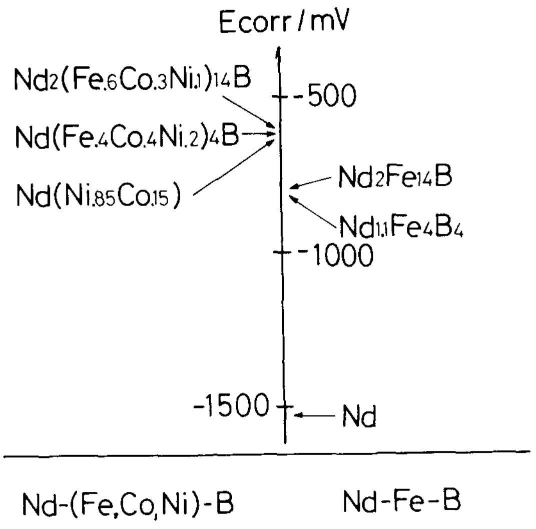

Fig. 5. Corrosion potential of component phases in solution of pH=2.7.

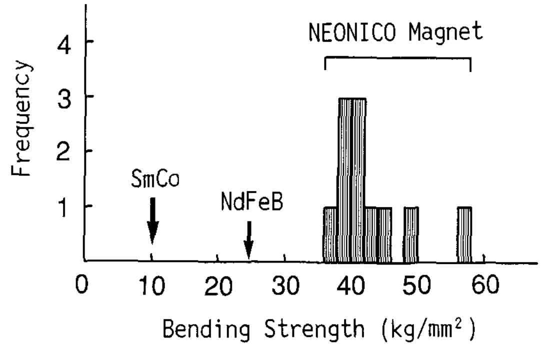

Fig. 6. Distribution of bending strength of NEONICO magnets.

difference of potential among the phases in NEONICO magnets are noteworthy since this is a condition to suppress galvanic corrosion. More details are given in a companion paper [9].

The mechanical property of the magnets is governed by the precipitates of TiB_2 as was shown in Fig.3. It has turned out that TiB_2 rods semicoherently precipitated inside the $Nd_2(FeCoNi)_{14}B$ grains enhance toughness, while TiB_2 clusters at intragranular region deteriorates it. The distribution of bending strength of 11 test pieces is shown in Fig. 6. The value of 50 kg/mm^2 on average is attainable by improved powder-compaction and/or control of precipitation. Interestingly, precipitates of ZrB_2 and HfB_2 were found to decrease the mechanical strength and coercivity in NEONICO magnets. The toughness of magnet has significant influence on the depth of surface layer damaged by by machining as shown in Table 1.

Table 1
Depth of damaged surface by machining.

easy axis	NEONICO(μm)	NdFeB(μm)
perpendicular to surface	6 ± 1	15 ± 1
pararell to surface	2 ± 1	6 ± 1

4. COERCIVITY ENHANCEMENT

Utility of a magnet is partly dependent on the range of its coercivity value. Enhancements of coercivity in NEONICO magnets are achievable through the composition and the process. Figure 7 is a series of demagnetization curves showing the effect of alloying on coercivity. addition of Ti atoms gives rise to precipitates of TiB_2 which inhibit grain growth during sintering. A fine-grained structure is generally favorable to high coercivity. Ga atoms are supposed to lower the Curie temperature of harmful impurity phase like $Nd(FeCoNi)_2$. The substitution of Dy for Nd in $Nd_2(FeCoNi)_{14}B$ increases the coercivity by enhancing the anisotropy field. A coercivity of 22 kOe with BH-product of 22 MGOe was attained with all the additions of Ti, Ga and Dy. Refinements of processes such as α-Fe-free casting, finer jet-milling, minimization of oxidation and better magnetic alignment during compaction of powders will contribute to improve the magnetic properties of NEONICO magnets.

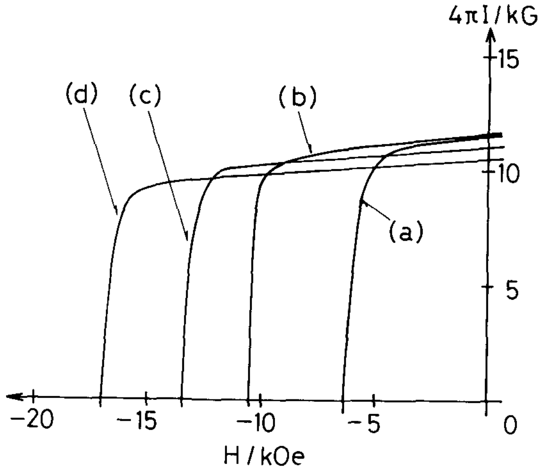

Fig. 7. Enhancement of coercivity of NEONICO magnets by sequential addition of alloying elements. (a):Nd(FeCoNi)B, (b):Nd(FeCoNiTi)B, (c):Nd(FeCoNiTiGa)B, (d):(NdDy)(FeCoNiTiGa)B.

5. INDUSTRIAL APPLICATIONS

The advantages of NEONICO magnets over the other rare-earth magnets are already summarized in Fig. 1. From a standpoint of applications, however, there are two more points to be added. In the first, NEONICO magnets can be machined to a sheet of 50 μm in thickness since they possess enough fracture toughness and moreover are free from any surface coating. This will make it possible to design and produce flatter rigid-disk drives or high thrust density linear motor with smaller size and pitch. In the second, NEONICO magnets is applicable to rotating parts without any outer mechanical protection belt on the side of air gap, because they are able to sustain large centrifugal force. This point will be valuable in the field of electric vehicles.

REFERENCES

1. M. Shimotomai, Y. Fukuda, A. Fujita and Y. Ozaki, IEEE Trans., MAG-26(1990)1939.
2. Y. Fukuda, A. Fujita, Y. Kitano, Y. Ozaki and M. Shimotomai, Proc. 12th Int. Workshop on Rare-Earth Magnet and Their Applications, Canberra, p. 435(1992).
3. Y. Fukuda, A. Fujita and M. Shimotomai, J. Alloys and Compounds, 193(1993)256.
4. Y. Kitano, J. Shimomura, M. Shimotomai, Y. Fukuda, A. Fujita and Y. Ozaki, J. Alloys and Compounds, 193(1993)245.
5. N. S. Bilonizhko and Yu. B. Kuz'ma, Izv. Akad. Nauki SSSR, Neorg. Mater. 19(1983)485.
6. N. F. Chaban, Yu. B. Kuz'ma, N. S. Bilonishko, O. O. Kachmar and N. V. Petrov, 1980, Dopov. Akad. Nauk SSSR, Set. A., Fiz.-Mat. Tekh. Nauki, No. 10(1979)873.
7. R. E. Wallin and W. E. Wallace, J. Chem. Phys., 41(1964)1587.
8. Y. Y. Pan and C. S. Cheng, Acta Physica Sinica, 34(1985)384.
9. Y. Fukuda and M. Shimotomai, presented at this conference.