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Magnetic Properties and Corrosion Characteristics of Nd-(Fe, Co, Ni)-B Pseudo-Ternary Systems

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Synopsis :

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Magnetic Properties and Corrosion Characteristics of Nd-(Fe, Co, Ni)-B Pseudo-Ternary Systems*



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1 Introduction

Reflecting the recent needs for high performance, miniaturization, and low noise in machines and equipment, rare earth magnets of a large maximum energy-product have been applied to voice coil motors, magnetic resonance imagers, and miniature coreless motors, and their production is increasing steadily. The first rare earth magnets developed were the Sm-Co magnets.^{1,2)} After the discovery of the ternary intermetallic compound consisting of Nd, Fe and B by Chaban et al. in 1979,³⁾ Sagawa et al.⁴⁾ and Croat et al.⁵⁾ respectively announced a Nd-Fe-B sintered magnet and a Nd-Fe-B melt-spun magnet in 1983. Patents for the latter two inventions were applied for in 1982. The maximum energy-product of the Nd-Fe-B magnets exceed the value of 30 MGOe of conventional Sm-Co magnets. It is predicted that Nd-Fe-B magnets will replace Sm-Co magnets.⁶⁾

The crystallographic phase which produces the high magnetic properties of the Nd-Fe-B magnet is $Nd_2Fe_{14}B$, a tetragonal compound. Its crystal structure is shown in Fig. 1.⁷⁾ The unit cell consists of fifty six Fe atoms which occupy crystallographically inequivalent sites of c, e, j₁, j₂, k₁, and k₂, eight Nd atoms which occupy sites of f and g, and four B atoms which occupy sites of g.

Magnetically, the 4f electrons of the Nd atom and the 3d electrons of the Fe atom bring about magnetocrystal-

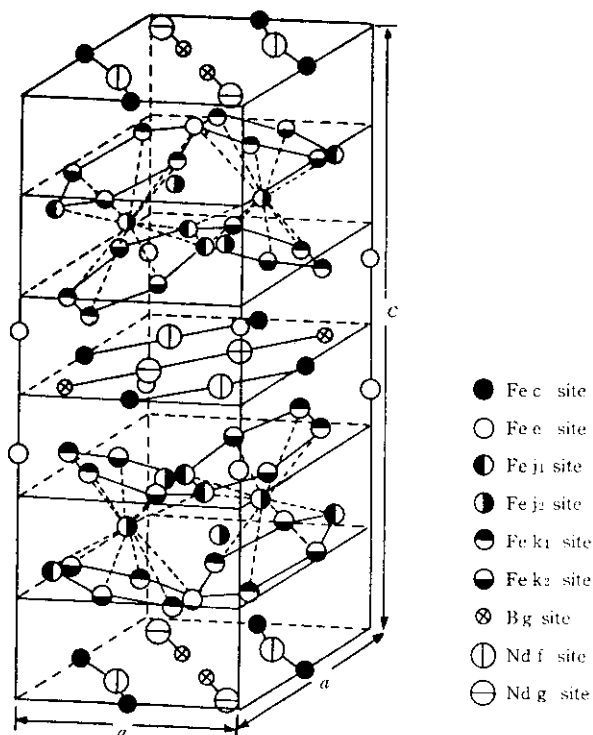


Fig. 1 Tetragonal unit cell of $Nd_2Fe_{14}B$

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line anisotropy and the magnetic moment. The 4f electrons are localized in a trivalent Nd ion, and the 3d electrons itinerate to form a band. Therefore it is possible to discuss the high magnetic properties of the Nd-Fe-B magnet by dividing its properties into the contribution of the Nd sublattice, that of the Fe sublattice, and the interaction between the two sublattices.

Studies on the effect of adding other elements to the Nd magnet have been made since the initial period of its development. The effects of addition can be broadly classified into two cases, one in which the alloying element replaces the atoms of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, and the other in which a new precipitate is formed by the alloying element. Typical examples of replacement include substitution of the other rare earth elements for the Nd atoms, substitution of Co atoms for Fe atoms, or substitution of C atoms for B atoms. Additive elements which form precipitates are represented by Al,⁸⁾ Ga,⁹⁾ and Nb.¹⁰⁾ It is reported that Al and Ga are effective in increasing intrinsic coercivity by improving the grain boundary phase,^{8,9)} while Nb increases intrinsic coercivity by precipitating into the main phase grains.¹⁰⁾

The present study is related to the magnetic properties and corrosion characteristics of a $\text{Nd}_{15}(\text{Fe}_{1-x-y}\text{Co}_x\text{Ni}_y)_{77}\text{B}_8$ magnet alloy in which the Fe atoms are replaced by Co and Ni atoms in combination. According to the past reports, Co can replace the total amount of Fe,¹¹⁾ and this substitution increases Curie temperature¹¹⁾ and lowers the anisotropy field.¹²⁾ Further, it has been determined by NMR spectroscopy that the Co atom does not occupy the Fe sites randomly but preferentially enters the k_2 site.¹³⁾ The Ni atom substitutes for up to about 20% of the Fe atoms,¹⁴⁾ increasing the Curie temperature^{15,16)} and lowering the anisotropy field.¹⁶⁾ It has been reported from measurements of the Mössbauer effect that the preferential substitution sites are the k_2 and j_2 sites.¹⁷⁾ In combined substitution of Co and Ni, the substituted sites should change from those seen in single substitution. It is of scientific as well as technical interest to see whether the magnetic moment and the anisotropy field will show values different from the simple dilution effect in combined-substituted magnets. Furthermore, since both Co and Ni are electrochemically nobler metals than Fe, the corrosion characteristics of magnets containing these elements are also expected to change.

The objective of this study lies in manufacturing $\text{Nd}_{15}(\text{Fe}_{1-x-y}\text{Co}_x\text{Ni}_y)_{77}\text{B}_8$ pseudo-ternary sintered magnets and in investigating the composition dependences of Curie temperature, saturation magnetization, intrinsic coercivity, and corrosion properties when Fe atoms are replaced by Co and Ni atoms in combination.

2 Experimental Procedure

Button-shaped ingots having compositions of $\text{Nd}_{15}(\text{Fe}_{1-x-y}\text{Co}_x\text{Ni}_y)_{77}\text{B}_8$ ($0 \leq x \leq 0.5$, $0 \leq y \leq 0.3$)

were prepared by arc-melting in an Ar atmosphere, rough-crushed into 32 mesh, and then jet-milled to a diameter of 2 to 4 μm . The fine powders were aligned in a magnetic field of 12 kOe, followed by pressing under a load of 2 to 3 t/cm². The resulting compacts were sintered in a vacuum at temperatures between 1 000 to 1 100°C. Subsequently, aging treatment was given to the sintered specimens as necessary.

Magnetic properties were investigated by applying saturation magnetization to the sintered bodies in a pulse field of 90 kOe, and then drawing a $4\pi I-H$ curve using a recording fluxmeter. Corrosion characteristic tests were conducted in the atmosphere of a thermostatic oven at a temperature of 70°C and a relative humidity of 95%. To quantify the corrosion results, the rusty specimen surfaces were subjected to graphic analysis.

3 Results and Discussion

3.1 Combined-Substitution Effects

3.1.1 Magnetic characteristics

The relation between the percentage ratio of Fe, Co, and Ni and Curie temperature T_C when Fe is replaced by Co and Ni in combination is shown in Fig. 2. The element Co significantly raises the Curie temperature of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. Ni also raises the Curie temperature, but not as effectively as Co. In contrast, however, as the contour diagram in Fig. 2 shows, in combined substitution, the effect of Ni substitution is to lower the Curie temperature, as the Co content increases. This suggests that the preferential sites for Ni may change depending upon whether single substitu-

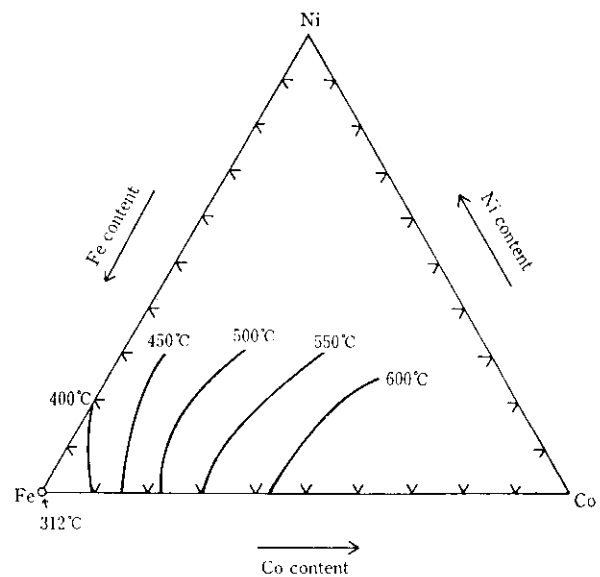


Fig. 2 Composition dependence of the Curie temperature for $\text{Nd}_{15}(\text{Fe}_{1-x-y}\text{Co}_x\text{Ni}_y)_{77}\text{B}_8$ sintered magnets

tion or combined substitution is adopted. Thus it is possible to make the following conjecture: In the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, a negative exchange-interaction takes place in Fe-Fe pairs whose inter-atomic distance is 2.44 Å or below, presumably causing a drop in Curie temperature.¹⁸⁾ The Fe-Fe pairs of 2.44 Å or below in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase are the j_1-j_1 pair (2.433 Å) and j_1-k_2 pair (2.396 Å). It has been argued that the reason why the Curie temperature increases upon substitution of Ni, which is lower in Curie temperature and smaller in atomic radius than Fe, is that substitution takes place at sites of less than 2.44 Å, namely, j_1 and k_2 sites, reducing the negative exchange interaction.¹⁴⁾ However, measurements of the Mössbauer effect by Dai et al.¹⁷⁾ support j_2 and k_2 sites, while, in substitution by Co, measurement by NMR spectroscopy¹³⁾ supports the k_2 site. Since Ni, on the contrary, lowers the Curie temperature in combined substitution, Co is considered to preferentially occupy the k_2 site when combined substitution occurs, displacing Ni to other sites. The j_2 site, as Dai et al.¹⁷⁾ reported, may be considered as a candidate for the new site occupied by Ni, since at this site, Ni may lower Curie temperature.

The composition dependence of saturation magnetization $4\pi I_s$, is shown in Fig. 3. On the Fe-Co pseudo-binary line, a slight peak occurs near $x = 0.15$, and the graph exhibits behavior similar to that of the Slater-Pauling curve. On the other hand, dense contour lines run along the Fe-Ni pseudo binary line, and saturation magnetization decreases rapidly. This behavior is different from that of the Fe-Ni binary alloy.

Changes in magnetization in Fe-Co and Fe-Ni binary alloys are caused by changes in the localized state-den-

sity of Fe due to alloying of Fe with Co and Ni. Hamada¹⁹⁾ indicates that the state-density of Fe in Fe-Co and Fe-Ni alloys varies significantly depending upon the numbers of Co and Ni atoms located at the nearest positions. Binary alloys of the Fe-Co and Fe-Ni types are disordered alloys, while Co and Ni occupy preferential substitution sites, as mentioned earlier, in alloys of the Nd-(Fe, Co)-B and Nd-(Fe, Ni)-B types, which thus become ordered alloys. Therefore, the changes in the pseudo-binary lines of Fe-Co and Fe-Ni of Fig. 3 may have been caused by changes in the localized state-density of Fe due to the well-defined nearest-neighbor arrangements.

Another important necessary requirement for permanent magnet materials is to show significant intrinsic coercivity. The relationship between the percentage ratio of Fe, Co, and Ni and intrinsic coercivity H_c is shown in Fig. 4. On the Fe-Co pseudo-binary line, intrinsic coercivity sharply drops in the vicinity of 7% and then rises. After it reaches a peak value in the range of 20 to 40%, it again drops suddenly near 50%. On the Fe-Ni pseudo-binary line, intrinsic coercivity decreases remarkably from near 7%, and after showing a slight recovery at 13 to 20%, almost vanishes above 30%. When combined substitution is performed using Co and Ni, however, the peak of intrinsic coercivity at Co 20 to 40% is extended in the direction of high Ni concentration. Within this range, therefore, the magnetic material in question is considered promising.

One of the factors which govern the magnitude of intrinsic coercivity is the anisotropy field. Both Co and Ni are substitution elements which lower the anisotropy field, and it is known that at 10% substitution, either Co

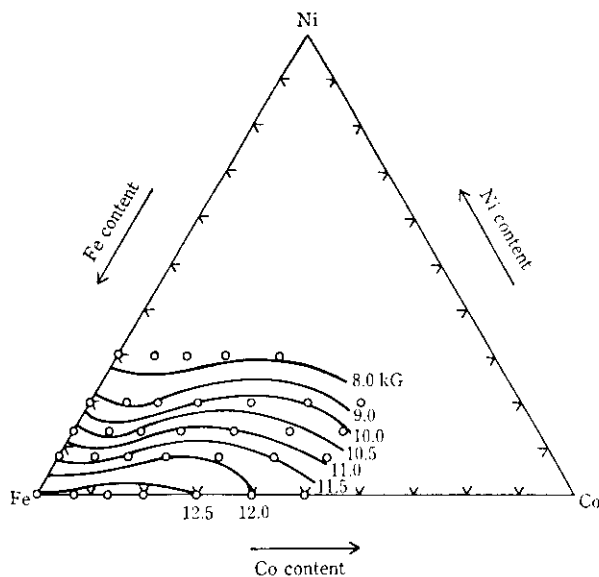


Fig. 3 Composition dependence of the saturation magnetization for $\text{Nd}_{15}(\text{Fe}_{1-x-y}\text{Co}_x\text{Ni}_y)_{77}\text{B}_8$ sintered magnets

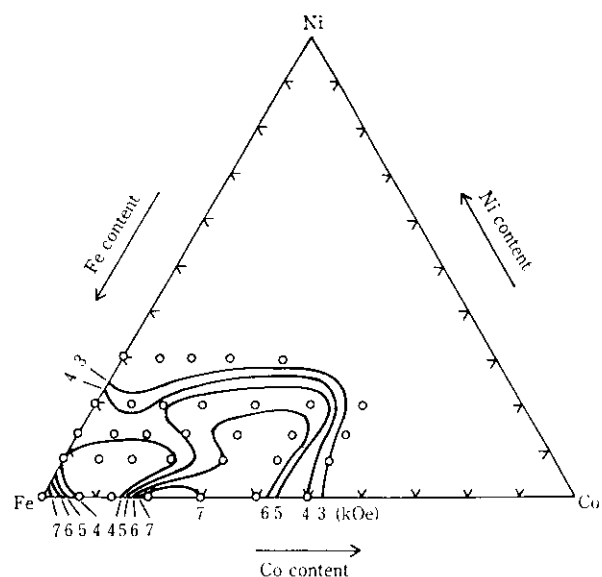


Fig. 4 Composition dependence of the intrinsic coercivity for $\text{Nd}_{15}(\text{Fe}_{1-x-y}\text{Co}_x\text{Ni}_y)_{77}\text{B}_8$ sintered magnets

or Ni lowers the anisotropy field by about 3.5%.^{12,15,16)} When several phases exist in addition to the main phase, as in a sintered magnet, other factors such as the metallographical and magnetic properties of these phases also affect intrinsic coercivity. Precipitation of the soft magnetic phase is believed to be cause the nucleation of reversed magnetic domain, which significantly lowers intrinsic coercivity. In Fig. 4, the lowering of intrinsic coercivity on the low Co concentration side of the Fe-Co pseudo-binary line is ascribed to the presence of a Nd(Fe, Co)₂ Laves phase, which has a Curie temperature higher than room temperature.^{8,20)} The lowering of intrinsic coercivity in the Fe-Ni pseudo-binary system is considered to be caused by precipitation of α Fe. The reason why intrinsic coercivity increases when combined substitution is carried out is unknown at the moment. Considered from the viewpoint of the anisotropy field, the preferential substitution sites in combined substitution are different from those in single substitution. Therefore, a possibility exists that the atomic array, which resembles an ordered alloy, causes an increased anisotropy field. According to X-ray diffraction analysis, the Nd(Fe, Co, Ni)₄B phase is formed within the range of $x + y > 0.4$. Therefore, there is also a possibility that this phase affects intrinsic coercivity.

3.1.2 Corrosion characteristics

The Nd magnet is reportedly inferior in corrosion resistance to the Sm-Co magnet.^{21,22)} This fact raises questions of its reliability in long-time service and is considered one of the disadvantages of this magnet.⁶⁾ It has been reported that in 1 N HCl solution, its electrode potential becomes smaller in the order of B-rich phase (NdFe₄B₄ phase), Nd₂Fe₁₄B phase, and Nd-rich grain boundary phase.²³⁾ Also severe intergranular corrosion has been observed in an atmosphere which contains chloride ions.²⁴⁾

The rusty surface area fraction when Nd-(Fe, Co, Ni)-B magnets were tested at a temperature of 70°C and a relative humidity of 95% for 48 h is shown in Fig. 5, which indicates that the quantity of rust is greatly dependent on Ni concentration and improvement is small with Co single substitution. It is important to note that combined substitution produces greater improvement than Ni single substitution.

Using an electron probe micro-analyzer (EPMA), it was found that although the grain boundary phase in the Nd-Fe-B system is a high Nd-concentration phase of about 95 at.% Nd and 5 at.% Fe, the Nd content is small at Nd 60 at.%, and transition metals are about 40 at.% in the Nd-(Fe, Co, Ni)-B system. This difference in composition may have contributed significantly to the improvement of corrosion characteristics.

3.2 Ti Addition Effect

As mentioned above, it was found that the Nd-(Fe, Co, Ni)-B alloy has a composition range in which

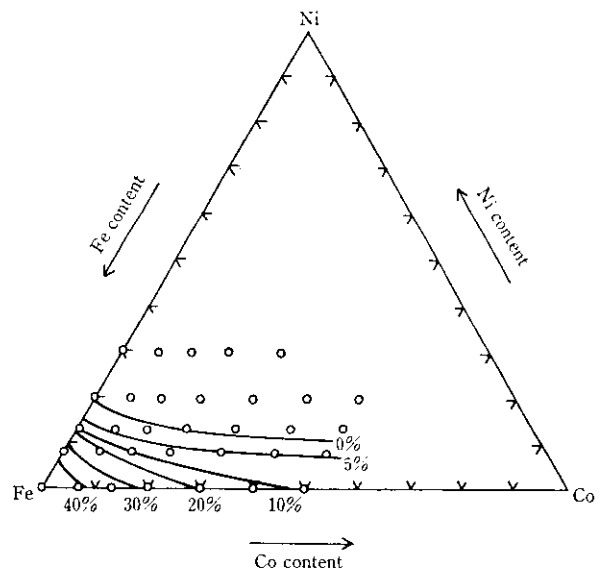


Fig. 5 Composition dependence of the rusty surface area fraction in Nd₁₅(Fe_{1-x-y}Co_xNi_y)₇₇B₈ sintered magnets—(Corrosion tests were carried out in 95% relative humidity at 75°C for 48 h.)

Table 1 Examples of properties of sintered magnets

Compositions	B_r (KG)	H_c (kOe)	$(BH)_{max}$ (MGOe)	T_c (°C)
Nd ₁₅ (Fe _{.60} Co _{.30} Ni _{.10}) ₇₇ B ₈	11.5	6	23	550
Nd ₁₅ (Fe _{.587} Co _{.30} Ni _{.10} Ti _{.013}) ₇₇ B ₈	11.9	10	34	550

saturation magnetization and intrinsic coercivity will both have favorable values. In addition, it was found that if the amount of substituted Ni is greater than a certain fixed amount in this area, corrosion resistance will emerge. Thus, if the combined substitution quantities of Co and Ni are skillfully selected, it is possible to realize a corrosion-resistant Nd magnet.

A frequently adopted method of improving the intrinsic coercivity of the sintered magnet is reforming of the grain boundary phase by a small addition of alloying elements. As an example, the authors attempted Ti addition. The results of the trial are shown in Table 1. When Ti is added, intrinsic coercivity is increased to 10 kOe, and further, the demagnetization curve becomes more rectangular, increasing the maximum energy-product to 34 MGOe. The mechanism of the increase in intrinsic coercivity by Ti addition is currently under study.

4 Conclusions

The Nd-(Fe, Co, Ni)-B sintered magnets were investi-

gated to determine the effect of Co and Ni combined substitution on magnetic properties and corrosion resistance. As a result, the following was clarified:

- (1) Curie temperature increases with single substitution of either Co or Ni, but in combined substitution, the substitution effect of Ni decreases, as the Co concentration increases, until at a certain point the Curie temperature begins to decrease. This suggests that Co and Ni tend to occupy preferential sites of Fe atoms.
- (2) Saturation magnetization during combined substitution reaches a maximum with a 25–30% substitution of Co for the Fe site; maximum values of saturation magnetization shift into the high ranges of Co and Ni concentration as Co and Ni contents increase.
- (3) Intrinsic coercivity shows a peak in the 20–40% Co substitution region. It was also found that Ni combined substitution extends the area of intrinsic coercivity to the level of Ni 20% substitution.
- (4) It was found that corrosion resistance is significantly improved by high-concentration Co and Ni combined substitution, and in the combined-substitution area of Ni 5 to 20% and Co 30% or above, magnetic properties and corrosion resistance become compatible.
- (5) It was determined that in the combined substitution area described in (4), Ti addition improves intrinsic coercivity and the maximum energy-product to practical-use levels.

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