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(54) **CORROSION-RESISTANT TM-B-RE TYPE MAGNET AND METHOD OF PRODUCTION THEREOF**

KORROSIONSBESTÄNDIGER MAGNET VOM TM-B-RE-TYP UND DESSEN HERSTELLUNGSVERFAHREN

AIMANT A BASE DE TM-B-RE RESISTANT A LA CORROSION ET PROCEDE DE PRODUCTION DE CET AIMANT

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(73) Proprietor: **KAWASAKI STEEL CORPORATION**  
**Chuo-Ku, Kobe-Shi Hyogo-Ken (JP)**

(72) Inventors:  
• **OZAKI, Yukiko**  
**Kawasaki Steel Corporation Technical**  
**Chiba-shi Chiba260 (JP)**  
• **SHIMOTOMAI, Michio Kawasaki Steel Corp.**  
**Chiba-shi Chiba 260 (JP)**  
• **FUKUDA, Yasutaka Kawasaki Steel Corporation**  
**Chiba-shi Chiba 260 (JP)**

- **FUJITA, Akira Kawasaki Steel Corporation**  
**Chiba-shi Chiba 260 (JP)**
- **KITANO, Yoko Kawasaki Steel Corporation**  
**Chiba-shi Chiba 260 (JP)**
- **SHIMOMURA, Junichi**  
**Kawasaki Steel Corporation**  
**Chiba-shi 260 (JP)**

(74) Representative: **Grünecker, Kinkeldey,**  
**Stockmair & Schwanhäusser Anwaltssozietät**  
**Maximilianstrasse 58**  
**80538 München (DE)**

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**Description**

## TECHNICAL FIELD

5 This invention relates to rare earth metal-transition metal boron series magnets having not only excellent magnetic properties but also improved corrosion resistance and temperature-dependent properties and a method of producing the same.

## BACKGROUND ART

10 EP-A-261579 refers to a rare earth metal-iron-boron permanent magnet and a method for producing same. Rare earth metal-iron-boron magnets are known for their good magnetic properties. However, this conventional material has a problem in that it rusts easily in ordinary environments. The unsatisfactory corrosion resistance is one of the most significant properties of said conventional RE-Fe-B magnets for commercial use.

15 In order to improve the corrosion resistance of these conventional magnets, it has become common practice to provide a protective surface coating to shield the magnet against environmental effects.

In this respect, reference is made to EP-A-261579, page 28, lines 1 through 8, as well as in the subsequent Table 25, which indicates that anti-corrosion tests with the conventional magnet were effected after nickel platings and Zn-chromating surface treatments were provided after copper plating was applied as a base plating. Obviously, the conventional magnets would have failed in the corrosion tests without having a protective coating provided thereon.

20 As a typical permanent magnet manufactured at the present, there are mentioned Alnico magnets, ferrite magnets, rare earth metal magnets and the like. The Alnico magnets are manufactured from the old time, but their demand is lowering in accordance with the development of cheap ferrite magnets and rare earth metal magnets having higher magnetic properties. On the other hand, the ferrite magnets are chemically stable and low in the cost because oxides are used as a main starting material, so that they are the main current as a magnet material even at the present, but they have a drawback that maximum energy product is small.

25 Recently, Sm-Co series magnets having a combination of magnetic isotropy inherent to rare earth metal ion and magnetic moment inherent to transition metal element have been developed, whereby the conventional value of maximum energy product is largely increased. However, the Sm-Co series magnet is mainly composed of resourceless Sm and Co, so that it is obliged to become expensive.

30 Now, it has been attempted to develop cheap magnet alloys containing no expensive Sm and Co and having high magnetic properties, and consequently Sagawa et al developed stable ternary alloys by sintering process (Japanese Patent Application Publication No. 61-34242 and Japanese Patent laid open No. 59-132104) and J. J. Groat et al developed alloys having a high coercive force by liquid quenching process (Japanese Patent laid open No. 59-64739). These magnets are composed of Nd, Fe and B, and their maximum energy product exceeds that of Sm-Co series magnet.

35 However, Nd-Fe-B series magnets contain greater amounts of a light rare earth element such as Nd having very high activity or the like and a corrosive Fe as a main component, so that the corrosion resistance is poor and hence the magnetic properties are degraded to damage the reliability as an industrial material.

40 Therefore, in order to improve the corrosion resistance, there are taken countermeasures such as surface plating (Japanese Patent laid open No. 63-77103), coating treatment (Japanese Patent laid open No. 60-63901) and the like on the sintered magnets, and surface treatment on resin bonded type magnets before kneading magnet powder with a resin and the like, but they can not be said to be an effective rustproof treatment over a long period of time, and the cost becomes higher due to such a treatment and further there are caused problems such as magnetic flux loss due to the presence of protective film and the like.

45 As a solution on the above problems, the inventors have previously proposed rare earth metal-transition metal-boron series magnet alloys in which Fe in the Nd-Fe-B series magnet is replaced with high concentrations of Co and Ni (Japanese Patent laid open No. 2-4939).

50 Such magnets are excellent in the corrosion resistance and high in the Curie point, so that the reliability as a magnet material is largely increased.

The invention is concerned with rare earth metal-transition metal series magnets of two phase structure further developed from the above magnet.

55 Moreover, magnets having excellent magnetic properties through two alloying process in which rare earth rich phase and rare earth poor phase are mixed and sintered at liquid phase state have previously been proposed as Nd series magnet of two phase structure (Japanese Patent laid open No. 63-93841 and No. 63-164403). In this case, the magnetic properties are improved, but there is still remained a problem on the corrosion resistance.

## DISCLOSURE OF INVENTION

The invention is to advantageously solve the aforementioned problems and to propose rare earth metal-transition metal series magnets of two phase structure being excellent in not only the magnetic properties but also the corrosion resistance and a method of advantageously producing the same.

At first, details of elucidating the invention will be described.

The inventors have made various metallographical studies on the above magnet using high resolution electron microscope or the like, and confirmed that this magnet contains  $\text{Nd}_2(\text{Fe, Co, Ni})_{14}\text{B}$  phase having a large saturated magnetic flux density, and intergranular phases surrounding crystal grains of the above phase and developing a strong coercive force such as  $\text{Nd}_2(\text{Fe, Co, Ni})_{17}$ ,  $\text{Nd}(\text{Fe, Co, Ni})_5$ ,  $\text{Nd}_2(\text{Fe, Co, Ni})_7$ ,  $\text{Nd}(\text{Fe, Co, Ni})_4\text{B}$  and  $\text{Nd}(\text{Fe, Co, Ni})_{12}\text{B}_6$  and further  $\text{Nd}_{1-x}\text{TM}_x$  of CrB structure (TM is mainly Ni) and the like.

Furthermore, it has been found that better corrosion resistance is exhibited as the amount of Nd phase being a point of causing corrosion is less and the concentration of Ni or Co in the above intergranular phase becomes high.

Now, the inventors have made further studies with respect to this point and found that the above intergranular phase hardly appears in a range of Nd-Fe-B ternary phase diagram other than  $\text{Nd}_2(\text{Fe, Co, Ni})_{17}$  and is rather a phase appearing only in the range of Nd-Co-B system.

For the reference, Nd-Fe-B ternary phase diagram is shown in Fig. 1 (N. F. Chaban, Yu. B. Kuzma, N. S. Bilonizhko, O. O. Kachmar and N. U. Petrov, Akad Nauk, SSSR, SetA, Fiz.-Mat. Tekh, Nauki No. 10 (1979) 873), and Nd-Co-B ternary phase diagram is shown in Fig. 2 (N. S. Bilonizhko and Yu. B. Kuzma, Izv. Akad. Nauk SSSR Neorg. Mater, 19 (1983) 487) (In the original report,  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase and  $\text{Nd}_2\text{Co}_{14}\text{B}$  phase are misinterpreted as  $\text{Nd}_2\text{Fe}_9\text{B}$  phase and  $\text{Nd}_2\text{Co}_9\text{B}$  phase, so that they are corrected in Figs. 1 and 2).

In Fig. 1, a phase of number 1 is  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase, and  $\text{NdFe}_4\text{B}_4$  phase (phase of number 2), Nd phase,  $\text{Nd}_2\text{Fe}_{17}$  phase and Fe phase appear as a composition near thereto. In Fig. 2, however,  $\text{Nd}_2\text{Co}_{17}$  phase,  $\text{NdCo}_5$  phase,  $\text{Nd}_2\text{Co}_7$  phase,  $\text{NdCo}_4\text{B}$  phase (phase of number 2) and  $\text{NdCo}_{12}\text{B}_6$  phase (phase of number 7) appear in a magnet prepared from a composition near to  $\text{Nd}_2\text{Co}_{14}\text{B}$  phase of number 1, and Nd phase does not naturally appear at an equilibrium state.

As previously mentioned, Nd phase is not only a point of causing rust but also a magnetically useless phase, so that it should be eliminated.

It is, therefore, an object of the invention to provide permanent magnets having excellent magnetic properties and corrosion resistance by using magnetically useful two phases, i.e.  $\text{RE}_2\text{TM}_{14}\text{B}$  phase having a high residual magnetic flux density and a low melting point RE-TM phase or RE-TM-B phase enhancing the sinterability and possessing a cleaning action against grain boundary of main phase and further forming an electrochemically noble composition as a starting material to prepare a two phase magnet.

That is, the invention lies in a corrosion-resistant rare earth metal-transition metal-boron series permanent magnet having a rusted surface area ratio of 5% or less after a 48 hour exposure test in air at a temperature of 70°C and a humidity of 95%, consisting essentially of RE: not less than 10 at% but not more than 25 at%, where RE is one or more of Y, Sc and lanthanides, B: not less than 2 at% but not more than 20 at% and the remainder being substantially TM, TM is one or more of Fe, Co and Ni, whose metallographic structure being comprised of a phase of  $\text{RE}_2\text{TM}_{14}\text{B}$  having  $\text{Nd}_2\text{Fe}_{14}\text{B}$  structure and a phase of  $\text{RE}_1\text{TM}_1$  intermetallic compound (wherein TM is Ni) with CrB structure.

Furthermore, the invention lies in a method of producing a corrosion-resistant rare earth metal-transition metal-boron series permanent magnet as claimed in claim 1, which comprises subjecting a mixture of powder composed of  $\text{RE}_2\text{TM}_{14}\text{B}$ -type phase (TM is one or more of Fe, Co and Ni) and a powder composed of  $\text{RE}_1\text{TM}_1$  intermetallic compound (wherein TM is Ni) to a compression molding and then sintering it, wherein a ratio of  $\text{RE}_2\text{TM}_{14}\text{B}$  to  $\text{RE}_1\text{TM}_1$  intermetallic compound phase is about 95:5 to 40:60 as a formula unit.

In the invention, in order to more improve the corrosion resistance, it is effective to make the intergranular phase electrochemically more noble than the main phase, so that it is preferable that a ratio of Ni and/or Co in TM of the low melting point RE-TM and RE-TM-B series phases is higher than that in  $\text{RE}_2\text{TM}_{14}\text{B}$  phase. Particularly, the increase of Ni ratio is effective to the improvement of corrosion resistance and the reduction of cost.

In the invention, it is favorable that a ratio of  $\text{RE}_2\text{TM}_{14}\text{B}$  intermetallic compound phase to RE-TM, RE-TM-B series intermetallic compound phase is about 95:5 to 40:60 as a formula unit. Because, when this ratio is outside the above range, there is caused a disadvantage of bringing about considerable degradation of coercive force and saturated magnetic flux density. The term "formula unit" used herein corresponds to a case that  $\text{Nd}_2\text{Fe}_{14}\text{B}$  is considered as one molecule (this is called as formula in case of solid). The particle size of each of the above powders to be mixed is desirable to be about 0.5-5  $\mu\text{m}$  for handling easiness and homogeneous mixing.

A typical composition of RE-TM series intermetallic compound phase (inclusive of eutectic structure, same as above) is  $\text{RE}_1\text{TM}_1$ .

Moreover, powder composed mainly of the above  $\text{RE}_2\text{TM}_{14}\text{B}$ , RE-TM series and RE-TM-B series intermetallic compound phases can be obtained as follows.

That is, constitutional elements are weighed so as to have a given composition and shaped into an ingot by arc melting or high frequency melting under vacuum or in an inert gas atmosphere. Then, the ingot is held at a temperature of 600-1000°C under vacuum or in an inert gas atmosphere for 1-30 days to form a single phase of intermetallic compound. In general, the intermetallic compound phase has frequently a solid solution range to a certain extent (~20%), so that the starting composition is allowed to have a composition width in accordance therewith.

The single phase of the intermetallic compound is roughly ground by means of a hammer mill and then finely divided into a particle size of 0.5-5 μm by using a jet mill or an attritor. Moreover, when the hardness is low and the pulverization is difficult in the low melting point RE-TM phase, hydrogen brittleness is previously carried out within a temperature range of room temperature to about 350°C for several hours before the grinding with a hammer mill, whereby the subsequent pulverization is made easy.

According to the invention, powder composed mainly of the previously prepared intermetallic compound having a composition of RE<sub>2</sub>TM<sub>14</sub>B is mixed with at least one powder composed mainly of the previously prepared RE-TM series intermetallic compound, pressed and sintered, whereby high magnetic properties and high corrosion resistance can simultaneously be provided.

This is considered to be due to the fact that the powder having a melting point lower than that of the powder composed mainly of RE<sub>2</sub>TM<sub>14</sub>B intermetallic compound phase promotes the sintering and forms an intergranular phase between crystal grains of RE<sub>2</sub>TM<sub>14</sub>B to improve coercive force.

In RE<sub>2</sub>TM<sub>14</sub>B phase, Nd and Pr are desirable as RE from viewpoints of magnitude of magnetic moment and magnetic coupling with TM atom as well as the cost, but it is needless to say that the other RE or a combination of Nd, Pr therewith may be used.

As to TM, one or more of Fe, Co and Ni is sufficient, and particularly it is preferable to increase the ratio of Ni from a viewpoint of high corrosion resistance of the magnet. Further, RE<sub>2</sub>TM<sub>14</sub>B phase bears the saturated magnetic flux density of the magnet, so that the ratios of Fe, Co and Ni in TM are desirable to be not less than 10 at% but less than 73 at% in Fe, not less than 7 at% but not more than 50 at% in Co and not less than 5 at% but not more than 30 at% in Ni. Even when the main phase is RE<sub>2</sub>TM<sub>14</sub>B phase in which Fe as TM is 100%, the corrosion resistance of the permanent magnet according to the invention is superior to that of the conventional RE-TM-B magnet, so that the above phase can naturally be used as a main phase in accordance with the use purpose of the magnet.

As RE in the low melting point phase of RE-TM system, light rare earth element such as La, Ce, Pr, Nd or the like is advantageously adaptable importantly considering the cost, and middle to heavy rare earth elements from Sm to Lu and Y, Sc and the like are adaptable for more enhancing the corrosion resistance.

As to TM, the presence of Ni is effective to improve the corrosion resistance, so that according to the invention Ni is necessarily contained as TM.

The effect of Ni is as follows.

- i) The melting point of RE-TM system is lowered, and the wetting of liquid phase in the liquid phase sintering is promoted to increase the sintering density and enhance the residual magnetic flux density.
- ii) The effect of cleaning grain boundary in liquid phase is enhanced in the liquid phase sintering to more increase the coercive force by the same reason as in the above item i).
- iii) It is effective to the improvement of corrosion resistance.
- iv) The magnetically useless Nd phase can be eliminated, so that the residual magnetic flux density increases and hence the maximum energy product (BH)<sub>max</sub> also increases.

In this connection, even when an alloy having an average composition as a whole magnet is melted from the first as in the conventional technique, pulverized, pressed and sintered so as to approach to an equilibrium state, the Nd phase is not obtained. For this purpose, it is necessary to conduct the heating at a high temperature for long time, during which abnormal growth of crystal grain is undesirably caused to considerably degrade the coercive force.

Moreover, it is not necessary that the same element is used in RE of the main phase and RE of the low melting point phase. And also, in the magnet consisting of the above two phases, the effect of the invention is not lost even when a part of RE and TM is replaced with at least one of Mg, Al, Si, Ti, V, Cr, Mn, Cu, Ag, Au, Cd, Rh, Pd, Ir, Pt, Zn, Ga, Ge, Zr, Nb, Mo, In, Sn, Hf, Ta and W in an amount up to 8 at% of a full magnet.

As to the production method, there may be carried out a method wherein a mixture of powder of RE<sub>2</sub>TM<sub>14</sub>B composition and powder composed mainly of low melting point RE-TM series and/or RE-TM-B series intermetallic compound phases is placed in an iron pipe under vacuum and then sintered while hot rolling as a method of producing large size magnets in addition to the method in which the above powder mixture is subjected to compression molding and then sintered.

BRIEF DISCLOSURE OF DRAWINGS

Fig. 1 is a Nd-Fe-B three component phase diagram; and  
Fig. 2 is a Nd-Co-B three component phase diagram.

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BEST MODE FOR CARRYING OUT THE INVENTION

Example 1

10 An alloy button was prepared by arc melting neodymium, transition metal and boron at an atomic ratio of 2:14:1, which was subjected to a normalizing treatment in a vacuum furnace at 950°C for 7 days and further to rough grinding and fine pulverization, whereby fine powder having a particle size of few microns was obtained. In this case, the ratios of Fe, Co, Ni in the transition metal were varied to produce a plurality of alloy powders.

15 Similarly, powder having a ratio of neodymium or (neodymium + dysprosium) to nickel of 1:1 was prepared. In this case, the normalizing treatment conditions were 680°C and 5 days.

Then, powders selected from the above two groups were mixed at a mixing ratio shown in Table 1, pressed while applying a magnetic field of 15 kOe, sintered at 1000°C under vacuum for 2 hours and then quenched to room temperature.

20 The magnetic properties and corrosion property of the thus obtained samples were measured to obtain results shown in Table 1. Moreover, the corrosion property was evaluated by exposing the sample to an environment at a temperature of 70°C and a humidity of 95% for 48 hours and measuring a rusted area ratio on the surface of the sample.

For the comparison, the measured results of a sample produced by the conventional method in which a full composition for the sintered magnet was melted at once and subjected to rough grinding - fine pulverization - pressing in magnetic field - sintering steps are also shown in Table 1.

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Table 1

No.	Powder mixing ratio (formula unit.ratio %)	Ratio of transition metals (atomic ratio %)	Composition of magnet (at%)						Br (T) (kG)	iH <sub>c</sub> (kA/m) (kOe)	(BH) <sub>max</sub> (MGOe) (kJ/m <sup>3</sup> )	Rusted area (%)	Remarks
			Nd	Dy	Fe	Co	Ni	B					
1	Nd <sub>2</sub> Tm <sub>14</sub> B <sub>1</sub> Nd <sub>1</sub> Ni <sub>1</sub>	Fe : Co : Ni 100 : 0 : 0	15.79	-	73.69	-	5.26	5.26	1.2 (12.0)	576 (7.2)	260 (32.5)	11	Acceptable Example 1
2	Arc melting of the above whole composition		"	-	"	-	"	"	1.33 (13.3)	456 (5.7)	281.6 (35.2)	30	Comparative Example 1
3	Nd <sub>2</sub> Tm <sub>14</sub> B <sub>1</sub> Nd <sub>1</sub> Ni <sub>1</sub>	Fe : Co : Ni 75 : 25 : 0	15.12	-	56.34	18.78	4.39	5.37	1.18 (11.8)	464 (5.8)	238.4 (29.8)	2	Acceptable Example 2
4	Arc melting of the above whole composition		"	-	"	"	"	"	1.25 (12.5)	320 (4.0)	224 (28.0)	9	Comparative Example 2
5	Nd <sub>2</sub> Tm <sub>14</sub> B <sub>1</sub> Nd <sub>1</sub> Ni <sub>1</sub>	Fe : Co : Ni 65 : 30 : 5	15.8	-	47.9	22.1	8.9	5.3	1.15 (11.5)	1056 (13.2)	256 (32.0)	0	Acceptable Example 3
6	Arc melting of the above whole composition		"	-	"	"	"	"	1.2 (12.0)	320 (4.0)	211.4 (26.4)	6.5	Comparative Example 3
7	Nd <sub>2</sub> Tm <sub>14</sub> B <sub>1</sub> Nd <sub>1</sub> Ni <sub>1</sub>	Fe : Co : Ni 65 : 30 : 5	16.6	-	46.8	21.6	9.9	5.1	1.16 (11.6)	640 (8.0)	236.8 (29.6)	0	Acceptable Example 4
8	Arc melting of the above whole composition		"	-	"	"	"	"	1.2 (12.0)	296 (3.7)	176 (22.0)	2	Comparative Example 4
9	Nd <sub>2</sub> Tm <sub>14</sub> B <sub>1</sub> (Nd <sub>0.99</sub> Dy <sub>0.01</sub> ) <sub>1</sub> Ni <sub>1</sub>	Fe : Co : Ni 100 : 0 : 0	15.74	0.05	73.69	-	5.26	5.26	1.14 (11.4)	776 (9.7)	352 (31.5)	1	Acceptable Example 5
10	Arc melting of the above whole composition		"	"	"	-	"	"	1.28 (12.8)	680 (8.5)	280 (35.0)	28	Comparative Example 5
11	Nd <sub>2</sub> Tm <sub>14</sub> B <sub>1</sub> (Nd <sub>0.99</sub> Dy <sub>0.01</sub> ) <sub>1</sub> Ni <sub>1</sub>	Fe : Co : Ni 80 : 20 : 0	15.08	0.04	56.34	18.78	4.39	5.37	1.13 (11.3)	648 (8.1)	240 (30.0)	3	Acceptable Example 6
12	Arc melting of the above whole composition		"	"	"	"	"	"	1.26 (12.6)	460 (5.0)	253.6 (31.7)	7	Comparative Example 6

As seen from the above table, the rare earth metal-transition metal series magnets of two phase structure according

to the invention considerably improve not only the magnetic properties but also corrosion resistance as compared with those obtained by melting the full composition from the first as in the conventional technique.

5 **Claims**

1. A corrosion-resistant rare earth metal-transition metal-boron series permanent magnet having a rusted surface area ratio of 5% or less after a 48 hour exposure test in air at a temperature of 70°C and a humidity of 95%, consisting essentially of RE: not less than 10 at% but not more than 25 at%, where RE is one or more of Y, Sc and lanthanides, B: not less than 2 at% but not more than 20 at% and the remainder being substantially TM, TM is one or more of Fe, Co and Ni, whose metallographic structure being comprised of a phase of RE<sub>2</sub>TM<sub>14</sub>B, having Nd<sub>2</sub>Fe<sub>14</sub>B structure and a phase of RE<sub>1</sub>Ni intermetallic compound with CrB structure.
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2. The corrosion-resistant rare earth metal-transition metal-boron series permanent magnet according to claim 1, wherein a part of RE and TM is replaced with not more than 8 at% of at least one of Mg, Al, Si, Ti, V, Cr, Mn, Cu, Ag, Au, Cd, Rh, Pd, Ir, Pt, Zn, Ga, Ge, Zr, Nb, Mo, In, Sn, Hf, Ta and W.
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3. A method of producing a corrosion-resistant rare earth metal-transition metal-boron series permanent magnet as claimed in claim 1, which comprises subjecting a mixture of powder composed of RE<sub>2</sub>TM<sub>14</sub>B-type phase, TM is one or more of Fe, Co and Ni and a powder composed of RE<sub>1</sub>TM<sub>1</sub> intermetallic compound (wherein TM is Ni) to a compression molding and then sintering it, wherein a ratio of RE<sub>2</sub>TM<sub>14</sub>B to RE<sub>1</sub>TM<sub>1</sub> intermetallic compound phase is about 95:5 to 40:60 as a formula unit.
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4. The method according to claim 3, wherein a part of RE and TM is replaced with at least one of Mg, Al, Si, Ti, V, Cr, Mn, Cu, Ag, Au, Cd, Rh, Pd, Ir, Pt, Zn, Ga, Ge, Zr, Nb, Mo, In, Sn, Hf, Ta and W in an amount up to 8 at% of a full magnet.
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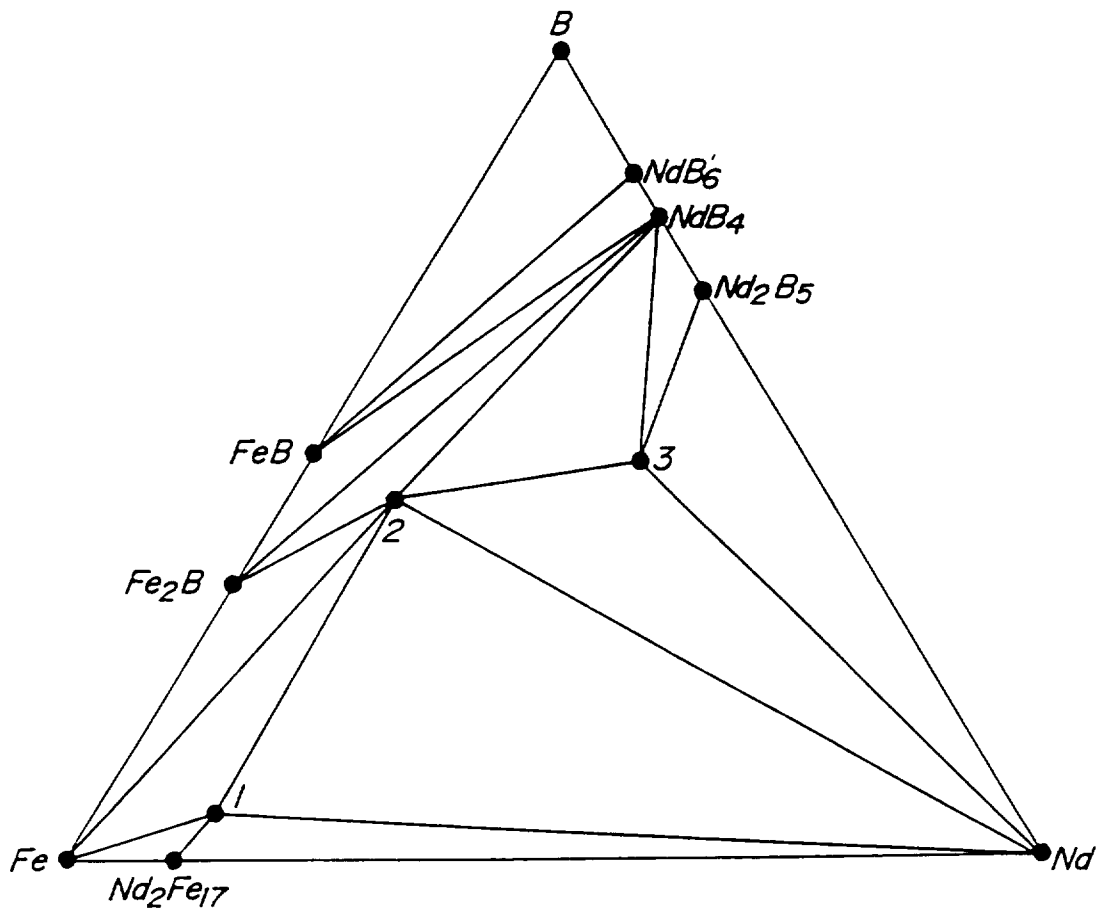
30 **Patentansprüche**

1. Korrosionsbeständiger Dauermagnet der Seltenerdmetalle-Übergangsmetalle-Elemente der Borgruppe mit einem rostigen Oberflächenbereich von 5% oder weniger nach einem 48 stündigen Aussetzen in Luft, bei einer Temperatur von 70°C und einer Feuchtigkeit von 95%, im wesentlichen bestehend aus einem Seltenerdmetall (RE): nicht weniger als 10 Atom.-%, jedoch nicht mehr als 25 Atom.-%, wobei RE ein oder mehrere Element(e) gewählt aus Y, Sc und Lanthaniden ist, B: nicht weniger als zwei Atom.-%, jedoch nicht mehr als 20 Atom.-% und wobei der Rest im wesentlichen TM ist, wobei TM ein oder mehrere Element(e) gewählt aus Fe, Co oder Ni ist, deren metallographische Struktur eine RE<sub>2</sub>TM<sub>14</sub>B-Phase umfaßt, mit einer Nd<sub>2</sub>Fe<sub>14</sub>B-Struktur und eine Phase aus einer intermetallischen RE<sub>1</sub>Ni-Verbindung mit CrB-Struktur.
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2. Korrosionsbeständiger Dauermagnet der Metalle der Seltenerd-metalle-Übergangsmetalle-Elemente der Borgruppe gemäß Anspruch 1, wobei ein Teil des RE und des TM durch nicht weniger als acht Atom.-% wenigstens eines aus Mg, Al, Si, Ti, V, Cr, Mn, Cu, Ag, Au, Cd, Rh, Pd, Ir, Pt, Zn, Ga, Ge, Zr, Nb, Mo, In, Sn, Hf, Ta und W ersetzt wird.
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3. Verfahren zur Herstellung eines korrosionsbeständigen Dauermagneten der Seltenerdmetalle-Übergangsmetalle-Elemente der Borgruppe nach Anspruch 1, umfassend das Unterwerfen einer Mischung eines Pulvers bestehend einer Phase vom RE<sub>2</sub>TM<sub>14</sub>B-Typ, wobei TM ein oder mehrere Element(e) gewählt aus Fe, Co und Ni ist, und eines Pulvers bestehend aus einer intermetallischen RE<sub>1</sub>TM<sub>1</sub>-Verbindung (wobei TM Ni ist) einem Kompressionsformen und einem anschließenden Sintern, wobei ein Verhältnis von RE<sub>2</sub>TM<sub>14</sub>B zu RE<sub>1</sub>TM<sub>1</sub> intermetallischer Verbindungsphase bei ungefähr 95: 5 bis 40 : 60 als eine Formeleinheit liegt.
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4. Verfahren nach Anspruch 3, wobei ein Teil des RE und TM durch wenigstens ein Element gewählt aus Mg, Al, Si, Ti, V, Cr, Mn, Cu, Ag, Au, Cd, Rh, Pd, Ir, Pt, Zn, Ga, Ge, Zr, Nb, Mo, In, Sn, Hf, Ta und W in einer Menge bis zu acht Atom.-% eines ganzen Magneten zu ersetzt wird.
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**Revendications**

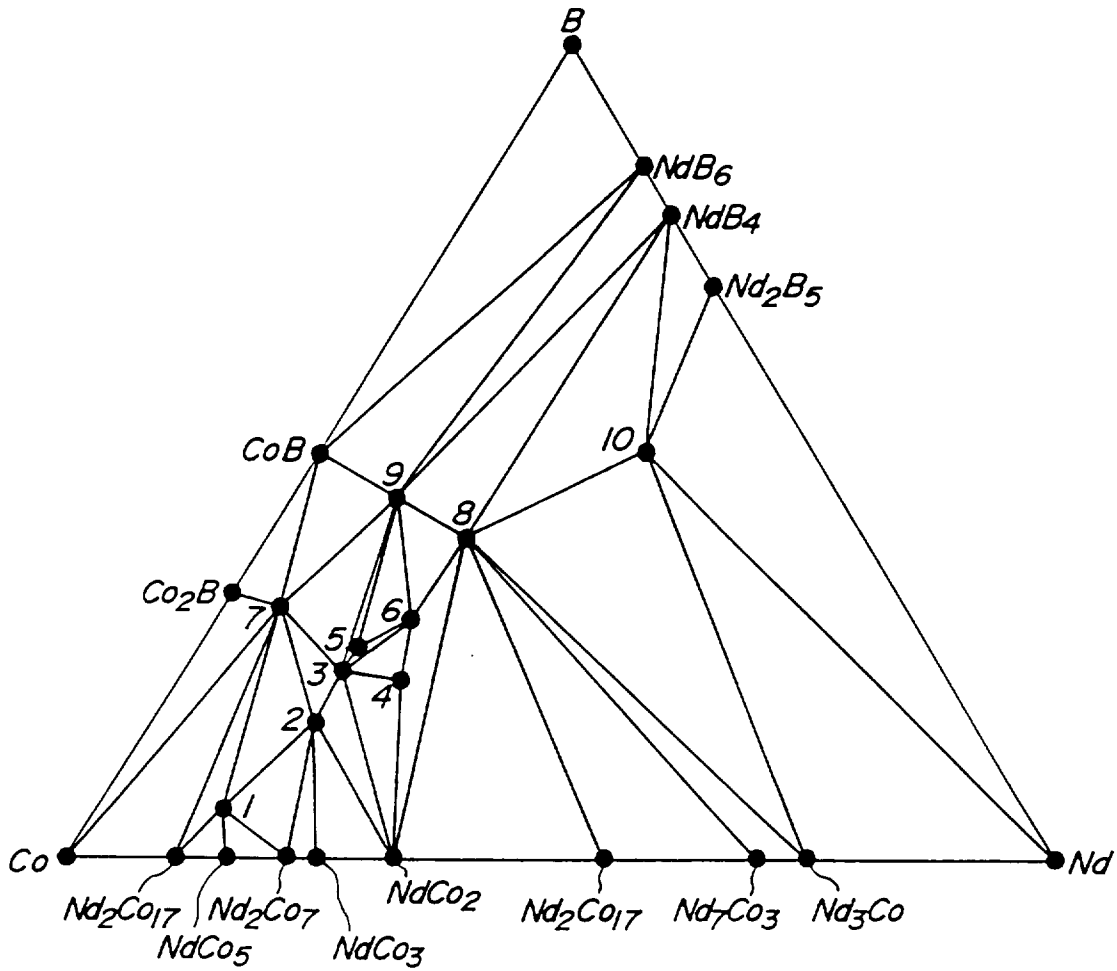
- 5 1. Aimant permanent série résistant à la corrosion à base de métal de terre rare, de métal de transition et de bore ayant un rapport de superficie rouillée inférieur ou égal à 5% après un essai d'exposition à l'air de 48 heures, à une température de 70°C et une humidité relative de 95%, consistant essentiellement en un métal de terre rare (TR), qui est présent dans une quantité comprise entre 10% atom. et 25% atom., où le métal de terre rare est un ou plusieurs membres du groupe constitué de Y, Sc et lanthanides, en B, qui est présent dans une quantité comprise entre 2% atom. et 20% atom., le reste consistant sensiblement en métal de transition (MT), le métal de transition étant un ou plusieurs membres du groupe constitué de Fe, Co et Ni, dont la structure métallographique est constituée d'une phase de  $TR_2MT_{14}B$ , ayant une structure de type  $Nd_2Fe_{14}B$ , et d'une phase de composé intermétallique de type  $TR_1Ni$  avec une structure CrB.
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- 15 2. Aimant permanent série résistant à la corrosion à base de métal de terre rare, de métal de transition et de bore selon la revendication 1, dans lequel une partie du métal de terre rare et du métal de transition est remplacée par 8% atom. maximum d'au moins un membre du groupe Mg, Al, Si, Ti, V, Cr, Mn, Cu, Ag, Au, Cd, Rh, Pd, Ir, Pt, Zn, Ga, Ge, Zr, Nb, Mo, In, Sn, Hf, Ta et W.
- 20 3. Procédé de production d'un aimant permanent série résistant à la corrosion à base de métal de terre rare, de métal de transition et de bore selon la revendication 1, qui comprend la soumission d'un mélange de poudre constituée d'une phase de type  $TR_2MT_{14}B$ , le MT étant composé d'un ou plusieurs membres du groupe constitué de Fe, Co et Ni, et de poudre constituée d'un composé intermétallique  $TR_1MT_1$  (dans lequel le MT est Ni) à un moulage par compression, puis à un frittage, dans lequel un rapport de la phase de  $TR_2MT_{14}B$  sur la phase du composé intermétallique  $TR_1MT_1$  est d'environ 95/5 à 40/60 en tant qu'unité de formule.
- 25 4. Procédé selon la revendication 3, dans lequel une partie du métal de terre rare et du métal de transition est remplacée par au moins un membre du groupe constitué de Mg, Al, Si, Ti, V, Cr, Mn, Cu, Ag, Au, Cd, Rh, Pd, Ir, Pt, Zn, Ga, Ge, Zr, Nb, Mo, In, Sn, Hf, Ta et W dans une quantité allant jusqu'à 8% atom. d'un aimant entier.
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- 50
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**FIG. 1**



- 1 --- Nd<sub>2</sub>Fe<sub>14</sub>B
- 2 --- NdFe<sub>4</sub>B<sub>4</sub>
- 3 --- Nd<sub>2</sub>FeB<sub>3</sub>

FIG. 2



- 1 ---  $Nd_2Co_{14}B$
- 2 ---  $NdCo_4B$
- 3 ---  $Nd_3Co_1B_4$
- 4 ---  $Nd_2Co_5B_2$
- 5 ---  $Nd_2Co_7B_3$
- 6 ---  $\sim Nd_2Co_5B_3$
- 7 ---  $NdCo_{12}B_6$
- 8 ---  $NdCo_2B_2$
- 9 ---  $NdCo_4B_4$
- 10 ---  $\sim Nd_2CoB_3$