⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 517 355 A1**

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: **92302851.8**

㉒ Date of filing: **01.04.92**

(51) Int. Cl.^{5}: **H01F 1/053**, H01F 1/08, C22C 38/10, C22C 38/14

㉚ Priority: **07.06.91 US 711879**

㊸ Date of publication of application:
09.12.92 Bulletin 92/50

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU MC NL PT SE

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(54) Corrosion resistant permanent magnet alloy and method for producing a permanent magnet therefrom.

(57) A permanent magnet alloy of a Nd-Fe-B composition having a major $Nd_2Fe_{14}B$ permanent magnet phase, with alloying additions of cobalt, aluminum and zirconium, in combination. The permanent magnet alloy may be produced as prealloyed particles by inert gas atomization. The particles are magnetically aligned and consolidated, as by cold isostatic pressing, and then sintered within the temperature range of 950-1100 °C to produce a fully dense alloy article. After heating at a temperature within the range of 850 to 950 °C for 30 to 120 minutes, the article is cooled at a cooling rate of 5-50 °C/min. to a temperature of 400-550 °C and thereafter aged at a temperature within the range of 500-750 °C, preferably 550 to 700 °C. Prior to consolidating, the particles may be blended with zinc stearate and comminuted to reduce the size thereof.

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Field of the Invention

This invention relates to a permanent magnet alloy, and method for manufacturing a permanent magnet therefrom, wherein an improved combination of corrosion resistance and intrinsic coercivity are achieved without sacrificing remanence and energy product.

Description of the Prior Art

It is known that permanent magnets of one or more rare earth elements, iron and boron, and particularly of neodymium, iron and boron having the well known $Nd_2Fe_{14}B$ major permanent magnetic phase exhibit outstanding magnetic properties. Magnets of these compositions may, however, exhibit poor corrosion resistance, particularly in humid, elevated temperature applications.

The poor corrosion resistance is attributable to the rare-earth rich phases which are highly oxidizable, particularly in humid environments. In service, corrosion of these magnets results in degradation of the magnetic properties and also results in the production of contaminants that may be detrimental to the magnetic circuits in which the magnets are used.

Various coating techniques and surface treatments have been proposed to improve the corrosion resistance of these magnets. Although these treatments have been somewhat successful, the highly oxidizable character of these magnetic alloys results in detrimental corrosion in the presence of even slight imperfections or discontinuities in any protective surface coating.

SUMMARY OF THE INVENTION

It is accordingly a primary object of the present invention to provide a permanent magnet alloy that is inherently resistant to corrosion while maintaining or improving intrinsic coercivity (H_{ci}), without sacrificing remanence (B_r)and energy product (BH_{max}).

Another object of the invention is to provide a method for producing a permanent magnet from the alloy of the invention wherein the desired aforementioned permanent magnet properties may be achieved without requiring complex heat-treating practices.

Broadly, in accordance with the invention, the permanent magnet alloy thereof includes the conventional Nd-Fe-B composition having a major $Nd_2Fe_{14}B$ type permanent magnet phase. In accordance with the invention, this conventional composition is modified by the alloying additions of cobalt, aluminum and zirconium, in combination. In weight percent, cobalt is present within the range of 2.5 to 20%, preferably 2.5 to 15%, aluminum is present within the range of 0.1 to 1.2%, preferably 0.2 to 1.2% and more preferably 0.2 to 0.6%, and zirconium is present within the range of 0.5 to 3%, preferably 0.5 to 2%.

Dysprosium may be present as an additional rare earth element substituted for a portion of the neodymium. An amount of Dy not exceeding 5% may be present with the major permanent magnet phase being $(Nd\text{-}Dy)_2Fe_{14}B$. Oxygen should be controlled as a residual element in an amount equal to or less than 1.0%, preferably equal to or less than 0.8%.

In accordance with the method of the invention a permanent magnetic alloy in accordance with the above may be produced as prealloy particles. The prealloy particles may be produced in the well known manner by either inert gas atomization or comminution of a casting. The particles are magnetically aligned and consolidated, as for example by cold isostatic pressing, and then sintering at a temperature within the range of 950 to 1100 ° C to produce a fully dense magnet article. The sintered magnet article is heated at a temperature of 850 to 950 ° C for 30 to 120 minutes, cooled at a cooling rate of 5-50 ° C/min. to 400-550 ° C and thereafter is aged at a temperature within the range of 500 to 750 ° C, preferably 550 to 700 ° C.

Prior to consolidating the particles, the particles may be blended with a carbon-containing lubricant, such as an organometallic compound, such as a metallic fatty acid compound, such as zinc stearate, or a lubricant of a hydrocarbon compound and comminuted to reduce the size thereof. The zinc stearate may be blended in an amount of approximately 0.1%.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The sample materials and magnets used in the experimental work and specific examples of the invention described hereinbelow were prepared by powder metallurgy techniques from induction melted permanent magnet alloys. The alloys contained at least neodymium or a combination of neodymium plus a minor amount of other rare earth elements, along with iron, cobalt, zirconium, aluminum and boron. Other transition elements, such as vanadium or niobium, were also added as a substitute for zirconium in some alloys.

The alloys were produced by vacuum induction melting of a prealloyed charge to produce a molten mass of the desired alloy composition. The molten mass was poured into a mold or atomized into fine powder using an argon gas jet for atomization. The cast ingot or atomized powder was hydrided at 1 to 30 atmospheres. The cast ingot was crushed and pulverized into coarse particles. The coarse particles or atomized powder were then ground to reduce the size thereof by jet milling with argon or nitrogen gas. A portion of the pulverized powder and the atomized powder were blended with 0.1% zinc stearate to improve the jet milling operation. Additional powder samples were jet milled without blending with zinc stearate. The average particle size of the jet milled powders was in the range of 1 to 4 microns by Fisher sub-sieve size measurement.

The prealloy powders, prepared as described above, were placed in a rubber bag, aligned in a magnetic field, and compacted by cold isostatic pressing. The cold-pressed compacts were then sintered to approximately full theoretical density in a vacuum furnace at 950 to 1100°C for 1 to 2 hours. The resulting sintered magnets were further heat-treated at about 900°C for one hour, followed by slow cooling at 20°C per minute to 500°C, and then cooled rapidly by gas blowing. Thereafter, the magnets were aged at a temperature within the range of 550 to 700°C. The aged magnets were ground into a cylindrical shape.

The magnetic properties of the magnets were measured with a hysteresigraph. The accelerated corrosion tests, the results of which are reported hereinafter, were conducted in an autoclave at 5-10 psi of steam pressure at a temperature of 110-115°C. These tests are recognized in the art as providing accurate and reliable data with regard to the long-term corrosion behavior of rare earth, iron and boron magnets. After this autoclave testing, the weight loss of the samples was measured with a balance, after removing the corrosion products from the sample, to obtain an indication of the degree of corrosion for each sample.

Four permanent magnet alloy compositions were produced, as set forth in Table 1, and magnets were produced from each of these compositions by the practice set forth above.

TABLE 1

Alloy Compositions of Nd-Dy-Fe-Co-B-Al alloys containing V, Nb, or Zr.

Alloy No.	Alloy Compositions (wt.%)								
	Nd	Dy	Fe	Co	B	Al	V	Nb	Zr
RT8	33.5		65.4		1.1				
RT7	29.7	3.7	57.5	4.5	1.3	0.2	3.1		
RT3	31.0	3.0	58.8	5.0	1.1	0.35		0.7	
RT5	31.0	3.0	58.5	5.0	1.1	0.35			1.0

The corrosion rate was estimated by measuring the weight loss of the magnets after 96 hours of autoclave testing at 5-10 psi of steam pressure at a temperature of 110-115°C.

TABLE 2

Magnetic Properties and weight losses of alloys described in Table 1.

Alloy No.	Magnetic Properties				Wt. Loss (mg/cm^2 96 Hr
	B_r,KG	H_kKOe	H_{ci},KOe	BH_{max},MGO	
RT8	11.3	9.9	13.9	30.7	422.0
RT7	10.0	9.0	24.4	22.5	3.7
RT3	11.0	15.0	20.5	28.7	5.2
RT5	10.9	14.6	21.2	28.5	0.3

As shown in Table 2, the sample magnets containing cobalt and aluminum along with zirconium, vanadium, or niobium, exhibit substantially reduced weight loss. Of these samples, only the cobalt, aluminum and zirconium containing magnet exhibited near zero weight loss. The other two magnets containing cobalt and aluminum along with vanadium or niobium exhibited small weight losses but nevertheless had observable corrosion on the surface thereof.

The intrinsic coercivity was substantially increased by combined additions of dysprosium, cobalt and aluminum, along with vanadium, columbium or zirconium. The remanence and energy product were substantially reduced, however, in the magnet sample containing vanadium. These test results indicate that only the Nd-Dy-Fe-Co-B-Al-Zr magnet samples satisfy the requirements of high-performance magnetic properties and excellent corrosion resistance.

Since the Nd-Dy-Fe-Co-B-Al-Zr alloy produced a magnet having a combination of high magnetic properties and excellent corrosion resistance, the effects of aluminum and zirconium in the base Nd-Dy-Fe-Co-B alloy on the magnetic properties and corrosion resistance were investigated with the three alloy compositions reported in Table 3.

TABLE 3

Alloy compositions of Nd-Dy-Fe-Co-B alloys with and without Al and/or Zr.

Alloy No.	Alloy Compositions (wt.%)						
	Nd	Dy	Fe	Co	B	Al	Zr
RT1	31	3	59.9	5	1.1		
RT12	31	3	59.5	5	1.1	.35	
RT5A	31	3	58.5	5	1.1	.35	1.0

The alloys were made into magnets in accordance with the above described powder metallurgy practice. Some of the alloy powders were blended with 0.1% zinc stearate before jet milling, and others were jet milled without zinc stearate. When these magnets were aligned by the use of a magnetic field to achieve anisotropy, a different coil was employed than used for the aligning of the samples of Table 1. This resulted in a higher field and higher remanence values compared to the Table 1 samples. After sintering the pressed compacts at 1000°C, the magnets were heat-treated at 890°C, followed by slow cooling at 20°C/minute to 500°C and thereafter rapid gas cooling. The magnet samples were then aged at 610°C for one hour.

As shown in Table 4, magnet samples made from prealloyed powder particle blends with 0.1% zinc stearate exhibited much lower weight loss than magnets made from unblended particles.

TABLE 4

Magnetic Properties and weight losses of alloys described in Table 3.

Alloy No.	Magnetic Properties				Wt. Loss (mg/cm^2	
	B_r,KG	H_k,KOe	H_{ci},KOe	BH_{max},MGO	144Hr	240Hr
RT1	11.7	13.0	14.6	32.9	75	188
RT1ZS	11.8	14.6	15.8	33.7		5.0
RT12	11.6	14.7	17.0	32.3	45	150
RT12ZS	11.6	16.8	17.9	32.6		3.5
RT5AZS	11.8	20.0	23.9	34.1	0.3	0.3

*ZS represents the alloy blended with 0.1 % zinc stearate which increases carbon content about 0.05 %.

The coercivities of these alloys have also slightly increased as a result of the blending with zinc stearate. When 0.35% aluminum was added to the Nd-Dy-Fe-Co-B alloy, the coercivity was increased about 2kOe, and the corrosion resistance was slightly improved. When both aluminum (0.35%) and zirconium (1.0%) were added to the same alloy composition, both the coercivity and corrosion resistance were significantly improved. This indicates the significance of zirconium when added to the Nd-Dy-Fe-Co-B alloy composition.

Nd-Fe-B alloys containing zirconium were made with varying cobalt and aluminum additions to determine the cobalt and aluminum effect on both coercivity and corrosion resistance. These compositions are reported in Table 5.

TABLE 5

Alloy compositions of Nd-Fe-B-Zr alloys with and without Al and/or Co.						
Alloy No.	Nd	Fe	Co	B	Al	Zr
RT18	33	64.6	-	1.1	0.3	1.0
RT19	33	59.6	5	1.1	0.3	1.0
RT20	33	64.9	-	1.1	-	1.0

Table 6 shows the magnetic properties and weight loss as a function of corrosion resistance of the magnet samples of Table 5 after autoclave testing as affected by the cobalt and aluminum contents and zinc stearate blending.

TABLE 6

Magnetic properties and weight loss of alloys as described in Table 5.					
Alloy No.	Magnetic Properties				Wt. Loss (mg/cm^2 96 Hr
	B_r,KG	H_k,KOe	H_{ci},KOe	BH_{max},MGO	
RT18	10.6	3.2	6.0	23.1	24.2
RT18ZS	11.0	7.6	10.6	28.0	0.5
RT19	10.9	10.5	15.2	27.5	0.4
RT19ZS	11.7	10.9	14.3	32.4	0.4
RT20	10.8	7.3	9.8	26.6	0.4
RT20ZS	11.8	9.2	10.8	33.0	13.3

*ZS indicates the alloy blended with 0.1 % zinc stearate which increases carbon content about 0.05 %.

Nd-Fe-B magnets containing zirconium or zirconium and aluminum in combination exhibit relatively low coercivity and fairly good corrosion resistance. The simultaneous addition of cobalt to Nd-Fe-B-Zr-Al alloys substantially improves both coercivity and corrosion resistance. This establishes cobalt as a significant element in a zirconium-containing Nd-Fe-B permanent magnet. The corrosion resistance of alloy RT18 (Nd-Fe-B-Al-Zr) and alloy RT20 (Nd-Fe-B-Zr) is affected by zinc stearate blending, while the corrosion resistance of sample RT19 (Nd-Fe-Co-B-Al-Zr) is not affected by zinc stearate blending and shows an outstanding combination of magnetic and corrosion resistant properties.

As reported in Table 7, alloys of Nd-Fe-Co-B-Al-Zr were made for comparison with identical compositions not containing aluminum or zirconium. These compositions are reported in Table 7.

TABLE 7

Alloy compositions of Nd-Fe-Co-B alloys with Al and/or Zr.						
Alloy No.	Nd	Fe	Co	B	Al	Zr
RT25	33	60.0	5	1.1	0.3	-
RT30	33	59.6	5	1.1	0.3	1.0
RT31	33	59.9	5	1.1	-	1.0

As shown in Table 8, the omission of zirconium or aluminum causes deterioration of the magnetic properties, particularly intrinsic coercivity. The corrosion resistance is also degraded when zirconium is omitted from the alloy. It may be seen, therefore, that cobalt, zirconium and aluminum must be present in combination to achieve the desired combination of magnetic properties and corrosion resistance in accordance with the invention.

TABLE 8

Magnetic properties and weight loss of alloys as described in table 7.					
Alloy No.	Magnetic Properties				Wt. Loss (mg/cm^2) 96hr
	B_r,KG	H_k,kOe	H_{ci},KOe	BH_{max},MGO	
RT25	11.9	7.1	10.7	33.7	7.4
RT25ZS	12.1	7.4	11.9	34.8	0.03
RT30	11.8	12.3	16.2	32.8	0.15
RT30ZS	12.3	11.8	14.7	36.2	0.06
RT31	12.1	5.6	6.7	32.5	0.12
RT31ZS	12.2	7.7	8.9	35.2	0.06

*ZS indicates the alloy blended with 0.1 % zinc stearate which increases carbon content about 0.05 %.

Table 9 presents the magnetic properties and the corrosion rate of the reported alloy composition as a function of the zirconium contents.

TABLE 9

Magnetic Properties and Weight Loss of Fe-33Nd-5Co-1.1B-0.3A1-xZr Alloy as a Function of Zr Content.					
Wt.% of Zr	Magnetic Properties				Wt. Loss (mg/cm^2) 96Hr
	B_r,kG	H_k,kOe	H_{ci},KOe	BH_{max},MGO	
0	11.9	7.1	10.7	30.8	60.7
0 ZS	12.1	7.4	11.9	31.9	0.02
0.5	11.8	8.8	12.5	33.0	13.5
0.5 ZS	11.8	8.9	13.4	33.0	0.18
1.0	12.1	8.9	12.1	34.5	0.11
1.0 ZS	12.3	9.4	13.8	35.6	0.63
1.5	11.8	7.6	10.3	33.0	0.19
1.5 ZS	11.9	10.4	12.8	33.7	1.0
2.0	10.6	3.4	9.1	24.4	0.19
2.0 ZS	11.0	7.1	11.7	27.5	0.33
3.0	7.4	0.4	5.9	4.5	1.27
3.0 ZS	8.8	0.5	7.5	7.2	0.26
4.0	5.0	0.1	1.1	-	4.49
4.0 ZS	6.6	0.1	2.3	-	0.36
8.0	-	-	-	-	6.23
8.0 ZS	-	-	-	-	2.29

It may be seen that the corrosion rate decreases rapidly as the zirconium content is increased from 0 to 1% and then remains near zero weight loss when the zirconium content is varied between 1 and 2%. When the zirconium content exceeds 3%, the corrosion rate gradually increases. If the alloys are blended with 0.1% zinc stearate prior to jet milling, the corrosion rate is further reduced. The coercivity increases as the zirconium content increases from 0 to 0.5%, and then reaches a maximum when the zirconium content is varied between 0.5 to 1.5%. When the zirconium content exceeds 2.0%, the coercivity begins to decrease rapidly and becomes less than 1kOe when zirconium is greater than 3.0%.

TABLE 10

Magnetic Properties and Weight Loss of Fe-33Nd-1.1B-0.3A1-1.0Zr-xCo Alloy as a Function of Co Content.					
Wt.% of Co	Magnetic Properties				Wt. Loss (mg/cm^2) 96Hr
	B_r,kG	H_k,kOe	H_{ci},KOe	BH_{max},MGO	
0	11.7	2.3	2.7	19.5	30.5
2.5	12.0	8.6	9.6	34.5	0.04
5.0	11.9	11.8	15.0	33.6	0.03
7.5	12.0	12.2	13.4	35.4	0.01
10.0	12.0	10.6	11.6	34.8	0.04
15.0	11.9	8.6	12.7	31.9	0.09
20.0	11.3	4.5	9.0	25.2	0.01
25.0	10.8	1.4	2.0	12.4	0.06

Table 10 lists the magnetic properties and the corrosion rate of the reported alloy as a function of the cobalt content. The magnet samples of Table 10 were made from powders blended with 0.1% zinc stearate. The corrosion rate of the samples rapidly decreases with cobalt additions as small as 2.5%. The reported weight losses are nearly zero when the cobalt content is within the range of 2.5 to 25%. The coercivity increases rapidly as the cobalt content is increased from 0 to 2.5% to 5.0%. Further increases in the cobalt content up to 15% do not significantly change coercivity. Within the range of 2.5 to 15%, the remanence remains unchanged. When the cobalt content exceeds 20%, the remanence is somewhat reduced and intrinsic coercivity is drastically reduced.

TABLE 11

Magnetic Properties and Weight Loss of Fe-33Nd-1.1B-5Co-1.0Zr-xA1 Alloy as a Function of A1 Content.					
Wt.% of A1	Magnetic Properties				Wt. Loss (mg/cm^2) 96Hr
	B_r,kG	H_k,kOe	H_{ci},KOe	BH_{max},MGO	
0	12.0	7.7	8.9	33.4	0.07
0.1	11.9	10.7	12.5	33.9	0.08
0.2	11.9	12.6	14.3	33.9	0.04
0.3	11.9	11.8	15.0	33.6	0.03
0.4	12.0	14.8	16.7	34.8	0.04
0.5	11.8	14.6	17.0	33.3	0.42
0.6	11.9	14.0	16.6	34.5	0.06
0.9	11.7	12.8	16.3	32.9	0.09
1.2	11.3	12.4	15.8	30.4	0.06
1.5	10.9	12.8	18.5	28.6	0.06

Table 11 presents the magnetic properties and corrosion rates of the reported alloy as a function of the aluminum content. The magnet samples were made from powders blended with 0.1% zinc stearate. The corrosion rate of the samples is close to zero weight loss, regardless of the aluminum content. The magnetic properties, however, of the alloy samples are very dependent upon the aluminum content. The coercivity increases rapidly as aluminum is increased from 0 to 0.2%, and then gradually increases with further increases in the aluminum content up to 0.5%. Further increases in aluminum up to 1.2% slightly reduces coercivity. The remanence and energy product remain the same with aluminum contents within the range of 0 to 0.6%. Further increases in aluminum begin to reduce the remanence and energy product. When aluminum exceeds 1.2% the remanence and energy product decrease substantially.

TABLE 12

Magnetic Properties and Weight Loss of Fe-33.5(Nd,Dy)-1.1B-5Co-1Zr-0.3A1 Alloy as a Function of Dy Content.					
Wt.% of Dy	Magnetic Properties				Wt. Loss (mg/cm^2) 96hr
	B$_r$,kG	H$_k$,kOe	H$_{ci}$,KOe	BH$_{max}$,MGO	
0	11.8	11.1	14.5	33.5	0.36
1	11.7	14.6	18.0	33.2	0.29
2	11.9	16.9	20.6	34.7	0.15
3	11.4	>20.0	23.9	31.9	0.35

Magnets of neodymium, iron and boron with cobalt, zirconium and aluminum additions in accordance with the invention were produced with dysprosium substituted for a portion of the neodymium. These magnet samples were made from powders blended with 0.1% zinc stearate. As may be seen from Table 12 the corrosion rate of the alloy is not affected by the dysprosium content. The intrinsic coercivity, however, increases at a rate of about 3kOe/1wt.% dysprosium as the dysprosium content is increased from 0 to 3%. This indicates that a very high coercivity magnet can be made with small additions of dysprosium to this alloy composition. The remanence and energy product did not change until dysprosium was increased up to 2%. Further increases in dysprosium begin to decrease the remanence and energy product.

TABLE 13. Alloy compositions of various Nd-Fe-Co-B-Al-Zr alloys.

Alloy No.	Alloy Compositions (wt.%) Nd	Fe	Co	B	Al	Zr	O	N	C
RT18	33	64.6	-	1.1	0.3	1.0	0.24	0.12	0.04
RT18-A		"					0.55	"	
RT18ZS		"					0.26	0.07	0.11
RT18ZS-A				"			0.53	"	
RT25	33	60.6	5.0	1.1	0.3	-	0.16	0.08	0.05
RT25-A		"					0.47	"	
RT25ZS		"					0.25	0.06	0.11
RT25ZS-A		"					0.53	"	
RT30	33	59.6	5.0	1.1	0.3	1.0	0.18	0.10	0.05
RT30-A		"					0.51	"	
RT30ZS		"					0.29	0.06	0.11
RT30ZS-A		"					0.53	"	

*-A: Magnet made from powder oxidized by bleeding air into a jar containing powder for 4 hours

*ZS: Magnet made from powder blended with 0.1% zinc stearate

The effects of oxygen, carbon and nitrogen on magnetic properties and corrosion resistance were investigated with respect to the specific compositions set forth in Table 13. These alloys were jet milled with and without 0.1% zinc stearate blending. Some of the magnet samples were made from jet-milled powder and others were made from powders oxidized by air bleeding for four hours. The magnet samples were measured for magnetic properties and tested for corrosion in an autoclave environment for 240 hours.

TABLE 14

Magnetic properties and weight loss of alloys described in table 13.

Alloy No.	Magnetic Properties				Wt. Loss (mg/cm^2) 240Hr
	B_r,kG	Hk,kOe	Hci,KOe	BH_{max},MGO	
RT18	10.6	3.2	6.0	23.1	23
RT18-A	11.1	1.4	1.9	12.0	0.12
RT18ZS	11.0	7.6	10.6	28.0	173
RT18ZS-A	11.7	1.4	1.8	13.2	0.10
RT25	11.9	7.1	10.7	33.7	181
RT25-A	11.9	8.6	10.9	33.4	14
RT25ZS	12.1	7.4	11.9	34.8	2.0
RT25ZS-A	12.2	9.6	11.4	35.6	0.11
RT30	11.8	12.3	16.2	32.8	0.14
RT30-A	12.0	7.3	7.7	34.2	1.09
RT30ZS	12.3	11.8	14.7	36.2	0.09
RT30ZS-A	12.2	6.5	7.0	34.6	0.23

As shown in Table 14, the coercivity values of the zirconium-containing magnet samples are significantly affected by the oxygen content, while these values for magnets without zirconium are not affected by the oxygen content. Specifically, when the oxygen content exceeds 0.5% the RT18 magnet samples exhibited significant loss of coercivity and the RT30 samples exhibited a loss of more than half of their coercivity. This indicates that high oxygen content is detrimental to the magnetic properties of these zirconium-containing magnets. Increased oxygen content of about 0.5% in magnets not containing zirconium (RT25) is beneficial to improve the corrosion resistance without degrading the magnetic properties. The addition of zinc stearate prior to jet milling generally increases carbon content to improve the corrosion resistance. The remanence is also improved. The intrinsic coercivity is increased initially and then begins to slowly decrease as the carbon content exceeds 0.1%.

TABLE 15. Alloy compositions of various Nd-Fe-Co-B-Al-Zr magnets.

Alloy No.		Air Blend Hrs.	Alloy Compositions (wt.%)						
			Nd	Fe	Co	B	Al	Zr	O
RT54	A	0	33	56.9	7.5	1.1	0.5	1.0	0.16
"	B	8				"			0.72
"	C	16				"			0.82
RT54ZS	A	0				"			0.14
"	B	8				"			0.67
"	C	16				"			0.75
RT56	A	0	33	57.4	10.0	1.1	0.5	1.0	0.14
"	B	8				"			0.63
"	C	16				"			0.68
RT56ZS	A	0				"			0.18
"	B	8				"			0.69
"	C	16				"			0.73

TABLE 16. Magnetic properties and density of magnets described in Table 15.

Alloy No.		Density g/cc	Magnetic Properties			
			Br,KG	Hk,kOe	Hci,kOe	BHmax,MGO
RT54	A	7.57	12.0	9.4	12.3	34.0
"	B	7.47	12.0	9.7	14.4	34.1
"	C	7.43	12.0	12.2	14.1	34.3
RT54ZS	A	7.55	11.6	13.4	15.7	32.1
"	B	7.43	12.1	13.2	14.4	34.8
"	C	7.33	11.8	12.1	13.2	33.0
RT56	A	7.54	12.1	8.9	11.9	35.2
"	B	7.30	12.1	9.7	12.6	34.5
"	C	7.21	12.0	9.8	11.7	33.8
RT56ZS	A	7.56	11.9	11.8	13.7	34.1
"	B	7.42	12.1	12.2	13.5	34.7
"	C	7.33	12.0	11.8	12.0	33.8

It is noted, however, that although the Zr containing magnets without Co (RT18) lost most of their coercivity values, the 5% Co and 1% Zr containing magnets (RT30) lost only about half of their coercivity values when the oxygen content increased to over 0.5% in the magnets. This suggests that increased Co may reduce the detrimental effect of oxygen in a Zr containing alloy. Therefore, two alloys were made with an increased Co content of 7.5 and 10%, as shown in Table 15. The alloys were jet milled with and without 0.1% zinc stearate addition. The jet milled powders were oxidized by bleeding air for 8 and 16 hours prior to compaction. The oxygen contents were increased from 0.1~0.2% to 0.6~0.8% by air bleeding into the powders, as shown in Table 15.

Table 16 shows the magnetic properties of the higher Co content magnets with different oxygen contents. When the oxygen content exceeds 0.6%, the density starts to decrease and the coercivity starts to slowly decrease. Unlike the 5% Co containing magnets, the adverse effect of oxygen on the coercivity of a higher Co containing magnet is not significant. Therefore, when the Co content is 7.5% in a Zr containing alloy, the oxygen content can be increased up to 0.8% or 1.0% with no significant affect on the magnetic properties. When Co approaches 10%, the magnetic properties (coercivity) start to decrease. As shown in Tables 13 and 14, the corrosion resistance is significantly improved by adding 5% Co in Zr containing magnets. The increase of the oxygen content in a 5% Co containing alloy (RT30) does not affect the corrosion resistance. A further increase of Co content up to 7.5 and 10% still results in excellent corrosion resistance, as shown in Table 10. Therefore, when the Co content is about 7.5 to 10%, the detrimental effect of high oxygen on the magnetic properties of Zr containing alloys is diminished and the corrosion resistance is still excellent.

TABLE 17

Coercivity of various Fe-33Nd-1.1B-Co-0.3A1-1.OZr magnets as a function of aging temperature (° C).

	H_{ci},kOe							
	570	580	590	600	610	630	650	670
RT19ZS	11.8	14.2	13.5	14.0				
RT25+RT26ZS			14.7		14.5	14.4	14.1	
RT3OZS					13.5	12.9	12.7	13.6

TABLE 18

Coercivity of a Fe-33Nd-1.1B-5Co-0.3A1-1.OZr magnet (RT30) as a function of aging time (Hr) and temperature (° C).			
	H_{ci},kOe		
	610° C	630° C	650° C
1 Hr	13.9	14.3	14.6
2 Hrs	13.6	14.4	14.7
3 Hrs	14.2	14.7	15.7

The permanent magnet alloys in accordance with the invention not only exhibited excellent corrosion resistance and magnetic properties as demonstrated by the data presented and discussed above, but also are characterized by ease of processing into permanent magnets. Most neodymium, iron, boron permanent magnet alloys containing cobalt require rapid cooling from the sintering temperature and any post sintering heat-treatment temperature, as well as a narrow aging temperature range, to obtain the desired high coercivity values. The rapid cooling and narrow aging temperature range make the mass production of magnets from these compositions difficult using conventional production facilities.

As shown by the data presented in Tables 17 and 18, for the listed alloy compositions in accordance with the invention, high coercivity values were obtained using slow cooling at a rate of about 20° C/min as opposed to conventional rapid cooling from sintering temperatures and from post-sintering heat-treatment temperatures. The coercivity is relatively independent of the aging temperature and time when aging is conducted within a temperature range of 580 to 700° C for 1, 2 or 3 hours, as shown by the data presented in Table 17 and Table 18. Since high coercivity may be obtained by slow cooling from sintering and heat-treatment temperatures with these alloys of the invention, and by aging within a wide temperature range, these alloys may be easily produced into permanent magnets having high magnetic properties and corrosion resistance using conventional production facilities.

All percentages are in percent by weight unless otherwise indicated, and all temperatures are in degrees Centigrade unless otherwise indicated.

The term "$Nd_2Fe_{14}B$ type permanent magnet phase" as used herein is defined as a primary phase of the permanent magnet alloy with this primary phase having a tetragonal crystal structure wherein Nd is a major rare element, with optional additional rare earth elements including but not limited to Dy and Pr, and Fe as a major transition element, with optional additional transition elements including but not limited to Co, Al and Zr, and B.

Claims

1. A permanent magnet alloy characterised in that it comprises, Nd-Fe-B, with a major $Nd_2Fe_{14}B$ type permanent magnet phase, 2.5 to 20 wt % Co, 0.1 to 1.2 wt % Al, and 0.5 to 3 wt 5 Zr.

2. A permanent magnet alloy according to claim 1 comprising, Dy in an amount not exceeding 5 wt %, with a major $(Nd\text{-}Dy)_2Fe_{14}B$ type permanent magnet phase.

3. A permanent magnet alloy according to claim 1 or 2, wherein Zr is within the range of 0.5 to 2 wt %.

4. A permanent magnet alloy according to any one of claims 1 to 3, wherein Co is within the range of 2.5 to 15 wt %.

5. A permanent magnet alloy according to any one of the preceding claims, wherein Al is within the range of 0.2 to 1.2 wt 5.

6. A permanent magnet alloy according to claim 5, wherein Al is within the range of 0.2 to 0.6 wt %.

7. A permanent magnet alloy according to any one of the preceding claims wherein the oxygen content is ≦ 1.0 wt %.

8. A method for producing a permanent magnet comprising, producing prealloyed particles of a permanent magnet alloy comprising, Nd-Fe-B, with a major $Nd_2Fe_{14}B$ type permanent magnet phase, 2.5 to 20 wt % Co, 0.1 to 1.2 wt % Al, and 0.5 to 3 wt % Zr, characterised by magnetically aligning and consolidating said particles including sintering at a temperature within the range of 950 to 1100 ° C to produce a fully dense article, heating said article at a temperature of 850 to 950 ° C for 30 to 120 minutes, cooling said article at a rate of 5-50 ° C/min to 400-550 ° C, and thereafter aging said article at a temperature within the range of 500 to 750 ° C.

9. A method according to claim 8, wherein said aging is at a temperature within the range of 550 to 700 ° C.

10. A method according to claim 8 or 9, wherein prior to said consolidating, the particles are blended with a carbon-containing lubricant and comminuted to reduce the size thereof.

11. A method according to claim 8 or 9, wherein prior to said consolidating, the particles are blended with a lubricant of an organometallic compound and comminuted to reduce the size thereof.

12. A method according to claim 11, wherein said lubricant is zinc stearate.

13. A method according to claim 8 or 9, wherein prior to said consolidating, the particles are blended with a lubricant of a hydrocarbon compound and comminuted to reduce the size thereof.

14. A method according to any one of claims 8 to 13, wherein said permanent magnet alloy comprises, Nd-Fe-B, with Dy in an amount not exceeding 5 wt %, with a major $(Nd\text{-}Dy)_2Fe_{14}B$ permanent magnet phase.

15. A method according to any one of claims 8 to 14, wherein the oxygen content is $\leqq$ 1.0 wt %.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92302851.8

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	CHEMICAL ABSTRACTS, vol. 109, no. 18, October 31, 1988, Columbus, Ohio, USA FUKUNO AKIRA et al. "Permanent magnet with improved corrosion resistance and its manufacture" pages 878,879, abstract-no. 162 176h & Jpn. Kokai Tokkyo Koho JP 63 62 204 --	1,8	H 01 F 1/053 H 01 F 1/08 C 22 C 38/10 C 22 C 38/14
A	CHEMICAL ABSTRACTS, vol. 110, no. 16, April 17, 1989, Columbus, Ohio, USA AKIOKA KOJI et al. "Rare earth-iron-boron system alloy anisotropic magnets" page 785, abstract-no. 146 467u & Jpn. Kokai Tokkyo Koho JP 63 213 323 --	1,8	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**
A	CHEMICAL ABSTRACTS, vol. 110, no. 16, April 17, 1989, Columbus, Ohio, USA KOBAYASHI OSAMU et al. "Rare earth-iron-boron system alloy anisotropic magnets" page 785, abstract-no. 146 468v & Jpn. Kokai Tokkyo Koho JP 63 213 322 ----	1,8	H 01 F C 22 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	25-08-1992	LUX

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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