(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 510 578 A2**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number : **92106791.4**

(51) Int. Cl.^{5} : **H01F 1/053**

(22) Date of filing : **21.04.92**

(30) Priority : **22.04.91 JP 118081/91**

(43) Date of publication of application :
28.10.92 Bulletin 92/44

(84) Designated Contracting States :
DE FR GB

(71) Applicant : **SHIN-ETSU CHEMICAL CO., LTD.**
6-1, Ohtemachi 2-chome
Chiyoda-ku Tokyo (JP)

(72) Inventor : **Ohashi, Ken**
2-20, Kitago 3-chome
Takefu-shi, Fukui-ken (JP)
Inventor : **Yoneda, Yuhito**
1-13, Kitago 4-chome
Takefu-shi, Fukui-ken (JP)

(74) Representative : **Raeck, Wilfrid, Dipl.-Ing.**
Moserstrasse 8
W-7000 Stuttgart 1 (DE)

(54) Rare earth-based alloy for permanent magnet.

(57) Disclosed is a novel rare earth-iron-based magnetic alloy and a permanent magnet having a chemical composition represented by the general formula

$$(R_{1-x}M_x)(Fe_{1-y}Co_y)_z,$$

in which R is a rare earth element, e.g., samarium, M is a non-magnetic additive element selected from the group consisting of zirconium, hafnium, bismuth, tin, indium and lead, the subscript x is a positive number in the range from 0.01 to 0.4, the subscript y is zero or a positive number not exceeding 0.5 and the subscript z is a positive number in the range from 10 to 13.

Jouve, 18, rue Saint-Denis, 75001 PARIS

BACKGROUND OF THE INVENTION

The present invention relates to a rare earth-based alloy for permanent magnets or, more particularly, to a rare earth-based alloy capable of giving a permanent magnet having excellent magnetic properties or, in particular, coercive force as well as to a permanent magnet as prepared from the rare earth-based alloy.

The inventors have previously reported in Japanese Patent Kokai No. 62-241302, No. 62-241303, No. 62-241304, No. 63-248103, No. 63-273302, No. 63-273303, No. 1-53507 and No. 1-67902 that a high-performance permanent magnet can be obtained from an alloy of a rare earth metal and a transition metal of the iron group having a body-centered tetragonal crystallographic structure of the $ThMn_{12}$ type when the alloy is a ternary intermetallic compound of high iron content including, besides the rare earth element, e.g., samarium, and iron, a third element such as titanium, vanadium, chromium, molybdenum, tungsten, silicon and rhenium while no binary intermetallic compound consisting of a rare earth element and iron and having a body-centered tetragonal crystallographic structure of the $ThMn_{12}$ type is hitherto known. Examples of the above mentioned ternary intermetallic compounds are those expressed by the chemical formulas such as $SmTiFe_{11}$, SmV_2Fe_{10}, $SmMo_2Fe_{10}$, $SmWFe_{11}$, $SmSi_2Fe_{10}$ and $SmReFe_{11}$ or generally expressed by the general formula RM_nFe_{12-n}, in which R is a rare earth element not limited to samarium, M is the third element and n is 1 or 2.

The permanent magnets prepared from these rare earth-iron based ternary alloys have, in most cases, a Curie point Tc of 300 °C or higher and, as a consequence of the high iron content, a high saturation magnetic flux density Ms. The ternary intermetallic compounds have a very high magnetic anisotropy when the rare earth element is samarium so that they are quite satisfactory as a material of permanent magnets. In fact, such a permanent magnet sometimes has an extremely high coercive force of 10 kOe or higher when it is prepared by the liquid super-quenching method. The only example of the ternary rare earth-iron based intermetallic compound of high iron content other than the above mentioned is a neodymium-iron-boron alloy of the formula $Nd_2Fe_{14}B$.

Although the ternary compounds of the general formula RM_nFe_{12-n} generally have a very high magnetic characteristics as mentioned above, the compound of the formula $SmTiFe_{11}$ as compared with the compound of the formula $Nd_2Fe_{14}B$ has a considerably lower saturation magnetization than the latter despite the approximately identical atomic percentages of the iron atoms presumably due to the substitution of the atoms of the non-magnetic third element for the iron atoms. Accordingly, it is eagerly desired to develop a permanent magnet of high saturation magnetization prepared from a ternary compound of the general formula RM_nFe_{12-n}, in which the atomic fraction of the third element M can be decreased as far as possible approaching zero. Despite the extensive investigations so far undertaken with this object, no successful results can be obtained to decrease the atomic fraction of the third element M below the composition corresponding to the formula $RMFe_{11}$.

SUMMARY OF THE INVENTION

The present invention accordingly has an object to provide a novel rare earth-iron based ternary intermetallic compound or alloy having the crystallographic structure of the $ThMn_{12}$ type capable of giving a high-performance permanent magnet as an alternative solution of the above described problem, in which the ternary compound of a rare earth element, iron and a third element has a composition corresponding to the replacement of the rare earth element with the third element in place of the replacement of iron with the third element.

Thus, the magnetic alloy provided by the present invention and suitable as a material of a permanent magnet has a chemical composition represented by the general formula

$$(R_{1-x}M_x)(Fe_{1-y}Co_y)_z \qquad (I)$$

in which R is a rare earth element such as yttrium and samarium or, preferably, samarium, M is a non-magnetic additive element selected from the group consisting of zirconium, hafnium, bismuth, tin, indium and lead, x is a positive number in the range from 0.01 to 0.4, y is zero or a positive number not exceeding 0.5 and z is a positive number in the range from 10 to 13.

The above defined magnetic alloy of the invention can be processed into a high-performance permanent magnet by the powder metallurgical method well established in the art.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As is understood from the above given general formula (I) and the definition of each symbol, the most characteristic feature of the inventive magnetic alloy is that the rare earth element is partly replaced with a specific non-magnetic additive element M in a limited proportion so as to give a fully stabilized crystallographic structure of the $ThMn_{12}$ type.

It is presumable that, when the atomic radius of the non-magnetic additive element M is slightly larger than that of the iron atom, the crystallographic structure of the $ThMn_{12}$ type could be stabilized with some expansion of the crystalline lattice by the partial replacement of the iron atoms with the atoms of the additive element. It is also known that, when the additive element is an element having a wide range of solid solubility such as vanadium, the crystalline lattice shrinks with decrease in the amount of the additive element. In other words, the crystalline lattice diminishes in the absence of the additive element M so that the rooms inherently for the iron atoms would be too small to include the iron atoms. When the atom of the additive element M has an atomic radius substantially larger than that of the iron atom, the crystalline lattice must be expanded to a great extent so that the crystallographic structure of the $ThMn_{12}$ type cannot be stabilized. This is a presumable reason for the limited kinds of the additive element M and the limited amount of substitution thereof for the stabilization of the ternary compound of the general formula RM_nFe_{12-n}.

The above described consideration has led the inventors to an idea that the $ThMn_{12}$ type crystallographic structure of a ternary compound of a rare earth element, iron and a third element could be stabilized when, instead of the replacement of the iron atoms with other atoms having a slightly larger atomic radius than iron atoms, the atoms of the rare earth element are replaced with other atoms having a slightly smaller atomic radius than the rare earth atoms so that the crystalline lattice may have rooms large enough to accept the iron atoms. Being led by this idea, the inventors have conducted extensive investigations and arrived at a discovery that the crystallographic structure of the $ThMn_{12}$ type can be stabilized by selecting the additive element M from those having such an atomic radius which is slightly smaller than that of the rare earth element as R as the substituent atoms in the sites for the atoms of R but too large to substitute for the iron atoms. The conclusion obtained after detailed experimentation is that the additive element should be selected from the group consisting of zirconium, hafnium, bismuth and so on above named.

In the general formula (I), R is a rare earth element including yttrium and the elements of the atomic numbers from 58 to 71 inclusive or, preferably yttrium and samarium or, more preferably, samarium. If it were not for the problem of radioactivity, thorium also can be used as a substitute of the rare earth element. These rare earth elements can be used either singly or as a combination of two kinds or more according to need.

The additive element denoted by M in the general formula (I) is selected from the group consisting of zirconium, hafnium, bismuth, tin, indium and lead or, preferably, from the group consisting of zirconium, hafnium and bismuth in order to obtain good stabilization of the crystallographic structure of the alloy. This selection of the additive element M is based on the experimental results that most remarkable improvements can be obtained in the magnetic properties of the permanent magnet prepared from the magnetic alloy when the additive element M has an atomic radius intermediate between that of the atoms of the rare earth element R and that of the iron atom. The degree of substitution of the additive element M for the rare earth element R should be in such a range that the subscript x in the general formula (I) is in the range from 0.01 to 0.4 or, preferably, from 0.1 to 0.2. When the value of the subscript x is too small, the $ThMn_{12}$ type crystallographic structure cannot be fully stabilized eventually to cause phase separation into the phases of R_2Fe_{17} and Fe. When the value of x is too large to decrease the fraction of the rare earth element R correspondingly, on the other hand, the resulting magnetic alloy would have magnetic properties not quite satisfactory, in particular, in respect of the magnetic anisotropy since the magnetic anisotropy is an inherency of the rare earth element R. It is optional that two kinds or more of the additive elements M are used in combination according to need.

As is indicated by the general formula (I) and definition of the subscript y, iron as the major constituent of the inventive magnetic alloy can be partly replaced with cobalt in such a limited amount that the subscript y in the general formula (I) does not exceed 0.5. Partial replacement of iron with cobalt has an effect to increase the Curie point of the permanent magnet and to improve the thermal stability of the magnetic properties with a slight increase in the saturation magnetization. When the amount of cobalt is too large, however, the crystalline magnetic anisotropy of the magnetic alloy is rather decreased. The subscript z in the general formula (I) is a positive number in the range from 10 to 13. When the value of z is too small, the phase of R_2Fe_{17} would be stabilized while the major crystallographic phase of the alloy would be the phase of iron when the value of z is too large.

The magnetic alloy of the invention can be prepared by melting together each in a specified and weighed amount of the respective constituent elements in the form of a metal in an atmosphere of an inert gas such as argon followed by casting and solidification of the melt into an ingot. The constituent metals should have a purity as high as possible or, desirably, at least 99% by weight.

The thus obtained inventive magnetic alloy can be processed into a permanent magnet by a process well established in the art after pulverization using a jet mill and the like under an atmosphere of an inert gas into a fine powder having an average particle diameter not exceeding 10 μm. The pulverization of the alloy can be performed also by the method of liquid super-quenching, mechanical alloying, gas atomizing and the like. Typically, a permanent magnet can be prepared from the alloy powder by the powder metallurgical method. Namely, the alloy powder is compression-molded in a magnetic field to orient the particles into a green body which is sintered by heating at a temperature in the range from 1000 to 1300 °C followed by an aging treatment at a temperatrure in the range from 500 to 900 °C. Alternatively, a resin-bonded permanent magnet can be prepared from the alloy powder by blending the alloy powder with an organic resin as a binder in the form of a liquid and the blend is molded in a magnetic field followed by heating the molded body to effect curing of the organic resin.

In the following, the magnetic alloy of the invention and the permanent magnet prepared therefrom are illustrated in more detail by way of examples and comparative examples, which, however, are never limitative of the scope of the invention.

Example 1.

Nine magnetic alloys No. 1 to No. 9 were prepared each from samarium metal having a purity of 99%, iron metal having a purity of 99.9%, cobalt metal having a purity of 99.9% and a metal of zirconium for No. 2 to No. 7, hafnium for No. 8 and bismuth for No. 9 as the additive element M in the formulations shown in Table 1 given below by taking each a weighed amount of the respective metals and melting them together in a high-frequency induction furnace under an atmosphere of argon followed by casting the melt into a copper mold and cooling to effect solidification of the melt into an ingot. No additive element was used for the alloy No. 1 for comparative purpose. The ingot was coarsely crushed and then finely pulverized in a jet mill using nitrogen as the jet gas into fine particles having a particle diameter in the range from 3 to 5 μm.

The fine powder of the magnetic alloy was compression-molded in a magnetic field of 15 kOe by pressing in a direction perpendicular to the magnetic field under a pressure of 1 ton/cm^2 into a green body having dimensions of 20 mm by 15 mm by 10 mm, the direction of the 10 mm long side being the direction of the magnetic field. The green body was subjected to sintering by heating in an atmosphere of argon at a temperature of 800 °C for about 1 hour followed by an aging treatment for 1 hour at a temperature of 650 °C and then quenching to room temperature.

The permanent magnets prepared in the above described manner were subjected to the measurement of the coercive force using an automatic fluxmeter to give the results shown in Table 1. As is clear from these results, no permanent magnet could be obtained with the coercive force substantially equal to zero when the additive element M was not contained in the alloy. The coercive force of the permanent magnet No. 5 was considerably lower than the others presumably because the content of cobalt relative to iron was close to the upper limit defined by the subscript y in the general formula (I). Similarly, the coercive force of the permanent magnet No. 7 was also inferior as compared with the others presumably because the content of zirconium as the additive element M was close to the upper limit defined by the subscript x in the general formula (I).

Table 1

No.	Content in the alloy, % by weight				Coercive force, Oe
	Samarium	Iron	Cobalt	Element M	
1	18.3	81.7	-	-	ca. 0
2	16.6	82.3	-	1.1	7700
3	16.5	68.0	14.4	1.1	7200
4	16.4	54.0	28.5	1.1	6100
5	16.3	40.2	42.4	1.1	4200
6	14.8	68.5	14.5	2.2	6400
7	11.3	69.5	14.7	4.5	4800
8	14.4	67.1	14.2	4.3	6200
9	14.3	66.6	14.1	5.0	6000

Claims

1. A magnetic alloy having a chemical composition represented by the general formula

   $$(R_{1-x}M_x)(Fe_{1-y}Co_y)_z,$$

   in which R is a rare earth element, M is a non-magnetic additive element selected from the group consisting of zirconium, hafnium, bismuth, tin, indium and lead, the subscript x is a positive number in the range from 0.01 to 0.4, the subscript y is zero or a positive number not exceeding 0.5 and the subscript z is a positive number in the range from 10 to 13.

2. The magnetic alloy as claimed in claim 1 in which the rare earth element denoted by R is samarium.

3. The magnetic alloy as claimed in claim 1 in which the non-magnetic additive element denoted by M is selected from the group consisting of zirconium, hafnium and bismuth.

4. The magnetic alloy as claimed in claim 1 in which the subscript x is a positive number in the range from 0.1 to 0.2.

5. A permanent magnet which is a shaped body of a powder of a magnetic alloy having a chemical composition represented by the general formula

   $$(R_{1-x}M_x)(Fe_{1-y}Co_y)_z,$$

   in which R is a rare earth element, M is a non-magnetic additive element selected from the group consisting of zirconium, hafnium, bismuth, tin, indium and lead, the subscript x is a positive number in the range from 0.01 to 0.4, the subscript y is zero or a positive number not exceeding 0.5 and the subscript z is a positive number in the range from 10 to 13.