

The present invention is concerned with the technical field of products endowed with permanent magnetic properties.

More specifically, the invention concerns hydrided products of the rare earth/iron/boron type and with obtaining pulverulent products resulting from the cycle of corresponding hydridation/dehydridation.

One interesting aspect of permanent magnets that contain a rare earth element, and of current research in this area, is presented in the article by Arthur L. Robinson in "Science", Vol. 223, March 2, 1984, pp. 920-922, entitled "Powerful new magnet material found".

The article in question describes, *inter alia*, a magnetic product of formula $\text{Nd}_2\text{Fe}_{14}\text{B}$, its presumed crystalline structure and also its magnetic properties.

This product does, however, have a relatively low Curie temperature (585 K).

In accordance with the invention, a hydridation/dehydridation cycle for rare earth/iron/boron and rare earth/cobalt/boron compounds has now been discovered which results in original hydrides endowed with outstanding magnetic properties which satisfy the following formula:



with $0 < x \leq 5$ and preferably $x \geq 0.1$

where R represents a rare earth element or yttrium and where, in the above formula, iron or cobalt can be partially substituted by other 3d, 4d, 5d transition elements or by Al, C, Si or Ge.

These compounds have a markedly greater magnetic moment than that of the respective unhydrided compounds.

A further object of the invention is therefore also directed to applications exploiting the magnetic properties of the aforementioned compounds.

These compounds prove to be especially useful in fine powder form for, notably, preparing magnetic recording and reproduction media, ferrofluids, incorporation into elastomer and plastic compounds and the like.

Yet another object of the invention is a process for preparing the aforementioned compounds which consists in hydriding the rare earth/iron/boron or rare earth/cobalt/boron compounds at room temperature and at a suitable hydrogen pressure. The hydrogen pressure is varied according to the compound and the desired degree of hydridation. For example, a pressure of more than 10 bars (10×10^5 Pa) and less than 500 bars (500×10^5 Pa) has proved to be satisfactory.

The compounds may be dehydried by heating them at a temperature preferably between 150 and 600°C. However, care must be taken not to reach the decomposition temperature of said compounds. Accordingly, the intermediates wherein $0 < x < 5$ are obtained after mixing an unhydried compound with a hydridation compound $x = 5$ in the desired proportions, and then this mixture is brought to the appropriate dehydration temperature in an impervious enclosure that has minimal dead volume and is capable of maintaining the pressure. Dehydration is preferably performed *in vacuo*.

After recooling, a homogenous hydride is obtained which is characterised by a fine discontinuous spectrum and whose Curie point and lattice parameters lie between the extreme values characteristic of the product, on the one hand, and the hydried product, on the other.

The hydridation/dehydridation process also enables an outstanding dehydrided product to be obtained which is in the form of a fine powder. It should be stressed that it was not previously possible to obtain such a product and the importance of this fineness in the aforementioned applications is appreciated. Typically, after grinding these products have a particle size of between 0.2 and 3 μm , preferably between 0.8 and 1.5 μm .

The invention is also concerned with novel unhydrided compounds with particle sizes between 0.5 and 3 μm . Preferably these compounds have a hydridation degree $x > 3$, because they have excellent magnetic moments for the applications envisaged.

Preferred compounds include those of formula $\text{Nd}_2\text{Fe}_{14}\text{BH}_x$ with $0 < x \leq 5$. This novel hydride is prepared by hydriding the compound $\text{Nd}_2\text{Fe}_{14}\text{B}$. Hydriding is carried out at room temperature, say at a hydrogen pressure of approximately 20 bars ($20 \times 10^5 \text{ Pa}$).

Using this process a compound satisfying the formula $\text{Nd}_2\text{Fe}_{14}\text{BH}_5$ is obtained, characterised by a quadratic crystal mesh having parameters

$$a = 0.8926 \text{ nm}$$

$$b = 1.2334 \text{ nm}$$

and with a Curie point of 403°C , $\theta_c = 403^\circ\text{C}$.

The starting product of formula $\text{Nd}_2\text{Fe}_{14}\text{B}$ is itself obtained by a process similar to that described by Sagawa in European Patent Application No. 0 101 552, following melting in a levitation crucible and annealing. Taking into account the non-congruent melting of compound $\text{Nd}_2\text{Fe}_{14}\text{B}$, neodymium enrichment in relation to stoichiometric composition allows, by lowering the liquid-solid equilibrium temperature, primary iron precipitation in the course of solidification. For this

reason a mixture satisfying the overall composition $\text{Nd}_2\text{Fe}_{1.0.5}\text{B}$ is used. The material so obtained is composed to a large extent of the $\text{Nd}_2\text{Fe}_{1.4}\text{B}$ phase having parameters

$$a = 0.8805 \text{ nm},$$

quadric symmetry

$$\theta_c = 316^\circ\text{C}$$

$$c = 1.2204 \text{ nm}$$

The magnetic moments expressed in electromagnetic units ($\text{A.m}^2/\text{kg}$) are respectively

1) $\text{Nd}_2\text{Fe}_{1.4}\text{B}$ obtained from the starting composition

" $\text{Nd}_2\text{Fe}_{1.0.5}\text{B}$ " having parameters $a = 0.8805 \text{ nm}$

$$c = 1.2204 \text{ nm}$$

$$H = 2.66 \text{ tesla (300K)} \quad M = 129.2 \text{ electromag. units (A.m}^2/\text{kg)}$$

$$H = 15.8 \text{ tesla (4.2K)} \quad M = 164.6 \text{ electromag. units (A.m}^2/\text{kg)}$$

$$H = 15.8 \text{ tesla (300K)} \quad M = 144.3 \text{ electromag. units (A.m}^2/\text{kg)}.$$

2) The hydrided preceding compound having parameters

$$a = 0.8926 \text{ nm}$$

$$c = 1.2334 \text{ nm}$$

$$H = 2.66 \text{ tesla (300K)} \quad M = 150.8 \text{ electromag. units (A.m}^2/\text{kg)}$$

$$H = 15.8 \text{ tesla (4.2K)} \quad M = 169.4 \text{ electromag. units (A.m}^2/\text{kg)}$$

$$H = 15.8 \text{ tesla (300K)} \quad M = 152.4 \text{ electromag. units (A.m}^2/\text{kg)}.$$

We must emphasise that it was not absolutely clear that a product so rich in iron can be hydrided.

It was also to be feared that hydridation would affect (or decompose) the $\text{Nd}_2\text{Fe}_{1.4}\text{B}$ phase and hence the magnetic properties.

In fact, it was found that this was not the case and that, on the contrary, the absorption of hydrogen produces an increase in magnetic moment at room temperature and a reduction in the magnetic field necessary for saturation, compared to the starting compound $\text{Nd}_2\text{Fe}_{1.4}\text{B}$, and an increased Curie point.

This development of the properties is shown in accompanying Figure 1.

The magnetic moment measured from 0 to 2.66 tesla is expressed in μ_B per formula group.

Accompanying Figure 2 represents the curve of magnetisation, at the various temperatures indicated on the graph, of an $Nd_2Fe_{14}BH_8$ powder oriented perpendicularly to the field and made into a block using araldite adhesive.

In the graph temperatures are given in degrees Kelvin and magnetic fields in tesla units.

This graph shows that the field of anisotropy is very high at low temperature. It decreases as the temperature rises.

The results of the magnetic trial are confirmed by Mössbauer spectroscopy, which revealed an increase in the hyperfine fields at the Fe sites at room temperature in relation to those measured for $Nd_2Fe_{14}B$.

At the four Fe sites distinguished under the Mössbauer effect, the average rated hyperfine field ranges from 305 KOe (30.5 tesla) for $Nd_2Fe_{14}B$ to 320 KOe (32 tesla) for the hydride of the invention $Nd_2Fe_{14}H_x$.

It should be noted that the hydridation described above can be reversed without destroying the $Nd_2Fe_{14}B$ phase, and that the hydridation/dehydridation cycle applied to compound $Nd_2Fe_{14}B$ enables said compound $Nd_2Fe_{14}B$ to be in a pulverulent form.

At atmospheric pressure the hydride begins to lose its hydrogen around 150°C. However, temperatures of the order of about 400°C are necessary to eliminate the hydrogen totally in

a primary vacuum (10^{-2} mmHg = 1.3 Pa) and return to starting compound $\text{Nd}_2\text{Fe}_{1.4}\text{B}$.

The non-congruent melting of some $R_2Fe_{14}B$ compounds, particularly $Nd_2Fe_{14}B$, does not allow a pure product to be obtained by melting and solidification of the mixture of the elements in stoichiometric proportions. The material obtained is a mixture containing very predominately the $Nd_2Fe_{14}B$ phase, iron and a compound much richer in neodymium (non-magnetic).

If the foregoing mixture in solid form is subjected to hydridation/dehydridation treatment, the fact that it is reduced to a fine powder makes it far more reactive. Diffusion treatment of the foregoing pulverulent product at around 900°C allows the iron from the primary precipitation to be combined and thus a material of far greater pureness to be obtained.

The property of forming ferromagnetic hydrides is shared by all isomorphic compounds of the quadratic $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound, including solid solutions thereof obtained either by intersubstitution of the rare earths or by partially substituting 3d, 4d or 5d transition elements for the iron and cobalt, and various elements conventionally used in iron substitution, such as Al, Si or Ge.

This iron substitution is total in the case of cobalt, for example resulting in the compound

**Nd₂Co₁₄B θ_c = 708 °C a = 0.86492 nm
c = 1.18558 nm**

ferromagnetic Nd₂Co₁₄BH₉

a = 0.8705 nm
c = 1.1925 nm

Tables I and II below summarise the lattice parameters of some preferred compounds according to the invention, hydrided at

room temperature at a hydrogen pressure of the order of 50 bars ($50 \cdot 10^5$ Pa), and the corresponding unhydrided compounds.

Supplemental examples:

Using the foregoing methods, the following products were obtained:

- 1) $Tb_2Co_{14}BH$
% by weight of fixed hydrogen : 0.37%
- 2) $La_2Co_{14}BH$
% by weight of fixed hydrogen : 0.20%
- 3) $Pr_2Co_{14}BH$
% by weight of fixed hydrogen : 0.15%
- 4) $Gd_2Co_{14}BH$
% by weight of fixed hydrogen : 0.15%
- 5) $Y_2Co_9Mn_5BH$
% by weight of fixed hydrogen : 0.33%
unhydrided product ($Y_2Co_9Mn_5B$):
a) = 0.8697 nm
b) = 1.1969 nm

Figure 3 shows the magnetisation curves at 293 K of compounds $Ce_2Fe_{14}BH_{4.83}$ and $Ce_2Fe_{14}B$.

Likewise, Figure 4 shows the magnetisation curves at 293 K of compounds $Y_2Fe_{14}BH_{3.7}$ and $Y_2Fe_{14}B$.

In both cases a very high level of magnetisation with lower anisotropy was found.

TABLE I

Ln	Ln ₂ Fe ₁₄ B			Ln ₂ Fe ₁₄ BH _x 3			H % by wt.	x
	nm	nm	nm ³	nm	nm	nm		
Ce	a: 0,8757	c: 1,2106	v: 0,928351	a: 0,8921	c: 1,2275	v: 0,977046	0,45	4,83
Pr	0,8810	1,2246	0,950542	0,8923	1,2370	0,985761	0,32	3,44
Nd	0,8805	1,2204	0,946189	0,8926	1,2344	0,983489	0,47	5,08
Sm	0,8791	1,2135	0,937940	0,8919	1,2263	0,975597	0,37	4,05
Gd	0,8789	1,2077	0,932892	0,8891	1,2201	0,964410	0,29	3,22
Tb	0,8767	1,2040	0,925471	0,8879	1,2168	0,959398	0,32	3,56
Dy	0,8759	1,2011	0,921621	0,8866	1,2139	0,954176	0,32	3,58
Ho	0,8745	1,1977	0,915715	0,8853	1,2114	0,949397	0,39	4,39
Er	0,8734	1,1956	0,912059	0,8844	1,2088	0,945570	0,30	3,39
Tm	0,8722	1,1931	0,907715	0,8840	1,2061	0,942423	0,30	3,39
Y	0,8755	1,2018	0,921256	0,8880	1,2156	0,958534	0,38	3,7

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TABLE II

Ln	Ln ₂ Co ₁₄ B			Ln ₂ Co ₁₄ BH _x			H % by wt.	x
	nm	nm	nm ³	nm	nm	nm ³		
La	a: 0,8687	c: 1,1012	v: 0,906573	a: 0,8752	c: 1,2087	v: 0,925786	0,20	2,14
Pr	0,8655	1,1886	0,890383	0,8712	1,1965	0,908237	0,14	1,5
Nd	0,8649	1,1356	0,886916	0,8705	1,1925	0,903602	0,27	2,9
Sm	0,8629	1,1806	0,879220	0,8678	1,1878	0,894649	0,16	1,75
Gd	0,8618	1,1764	0,873813	0,8655	1,1809	0,884656	0,15	1,77
Tb	0,8605	1,1728	0,868511	0,8637	1,1764	0,877631	0,37	4,1
Y	0,8604	1,1718	0,867532	0,8635	1,1758	0,876772	0,42	4,25



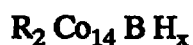
CLAIMS

1. Novel compounds characterized in that they consist in rare-earth/iron/boron or rare-earth/cobalt/boron hydrides, of the formula:

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or

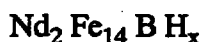


with $0 < x \leq 5$

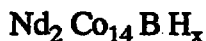
10 where R represents an element of the rare earth or yttrium, in that in the above formula, the iron or cobalt can be partially substituted by other transition elements 3d, 4d, 5d or the elements Al, C, Si, Ge.

2. Novel compound according to claim 1, characterized in that it has the formula:

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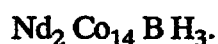


or



with $0 < x \leq 5$

20 in particular $Nd_2 Fe_{14} B H_5$ or



3. Process for preparing the compounds according to claims 1 or 2, characterized in that the hydridation of the rare earth/iron/boron $R_2 Fe_{14} B$ or rare-earth/cobalt/boron $R_2 Co_{14} B$ compound is carried out.

25 4. Process according to claim 3 for preparing the compound according to claim 2, characterized in that compound $Nd_2 Fe_{14} B$ or $Nd_2 Co_{14} B$ is hydrided at room temperature and under a hydrogen pressure at least equal to 1.10^6 Pa and lower than 500.10^5 Pa.

30 5. Applications of the hydrides according to claim 1 or 2 using their magnetic properties, particularly in the form of fine powder, such as the preparation of recording and reading magnetic carriers, ferrofluids, incorporation in elastomer or plastic masses and the like.

6. Process for dehydriding novel compounds of formula $R_2 Co_{14} B H_x$ or $R_2 Fe_{14} B H_x$ according to claim 1 or 2, characterized in that the compounds are
35 heated to at least $150^\circ C$.



7. Process according to claim 6, characterized in that the heating is carried out in vacuum.
8. Process for preparing the compounds of formula $R_2 Fe_{14} B$ or $R_2 Co_{14} B$ where R represents an element of the rare earths, in particular $Nd_2 Fe_{14} B$ or $Nd_2 Co_{14} B$, characterized in that a dehydration is conducted by heating the hydrided compounds of formula $R_2 Fe_{14} B H_x$ or $R_2 Co_{14} B H_x$ with $0 < x \leq 5$, to at least $150^\circ C$, optionally by way of a heating in vacuum, in order to form said compounds of formula $R_2 Fe_{14} B$ or $R_2 Co_{14} B$ in the form of a fine powder of granulometry comprised between 0.2 and $3 \mu m$.
- 10 9. Use of the previously obtained fine powder for preparing, recording and reading magnetic carriers, ferrofluids, elastomer or plastic masses having magnetic properties.