

of Tl hydride, NdH_3 hydride or α -Fe. These materials did not allow highly corrosion resistant magnets to be obtained, see the examples outside the invention.

The invention will be understood better by means of the following examples:

Tests have been carried out on materials obtained by melting, having the following composition (in at%) which is non-limiting and has a small content of TR in order to obtain the highest residual magnetism. They allowed the passivity of the materials obtained under various conditions according to the invention and outside the invention and the corrosion resistance quality of the final magnets to be tested. The process described in this invention has been successfully applied to other compositions with TR or with B or containing the substitutions and/or additions described in the prior art (see EP-A-101552, EP-A-106558, EP-A-344542), or again to granulates originating from the so-called diffusion reduction process.

	Nd	Dy	B	Al	Fe
C1	13.5	1.5	8	0.75	remainder

The friability was measured by the grain size spectrum (% by weight passing through the sieve without external stress) of the material obtained after the hydride-forming treatment.

The nature of the phases present in the material subjected to hydride formation was determined by X-ray diffraction.

The magnetic characteristics- B_r and H_{cJ} - were determined on the sintered magnets prepared by the process recalled in the introduction and without extreme precautions for the handling atmospheres.

The oxygen content of the magnets obtained lies, as a function of their composition, in the range which is most desirable for the particular use thereof. It is known that the prior art recommends either relatively high oxygen contents in order to improve the corrosion resistance, as is the case in US patent 4,588,439; or, on the other hand, very low contents, as in the patent EP 0.197.712, if high magnetic properties (B_r , $(BH)_{max}$) are to be obtained.

The corrosion resistance of the sintered magnets has been estimated by their life in an autoclave at 115°C under 0.175 MPa at 100% relative humidity. In all cases, the magnets were coated before testing under identical conditions by an epoxy resin after a surface preparation (phosphatation). The content of the coating has been estimated by visual examination (blisters) and by the cross-cutting test.

The results are compiled in Tables 1 to 8 (as follows).

Examples 1, 6 and 7 relate to the prior art or to conditions outside the invention, the other tests (Examples 2 to 5 and 8) relate to the invention.

EXAMPLE 1

Formation of hydrides at 25°C under P = 0.1 MPa of H₂
(outside invention)

Composition	C1
	% (by weight)
Grain size . 0 - 100 μm	1.6
100 - 500 μm	8.5
500 - 1000 μm	89.9
1000 and greater	0
Main phases present	(NdDy) ₂ Fe ₁₄ BH ₃ (NdDy) H ₃ Nd Fe ₄ B ₄
Density (g/cm ³)	7.4
Residual magnetism (T)	1.14
Coercivity (kA/m)	1480
Life in autoclave (days)	4

EXAMPLE 2

Formation of hydrides at 300°C under P = 0.1 MPa of H₂
(invention)

Composition	C1
	% (by weight)
Grain size 0 - 100 μm	1.0
100 - 500 μm	11.3
500 - 1000 μm	87.7
1000 and greater	0
Main phases present	(Nd,Dy) ₂ Fe ₁₄ B. "(Nd,Dy) H ₂ " Nd Fe ₄ B ₄
Density (g/cm ³)	7.5
Residual magnetism (T)	1.16
Coercivity (kA/m)	1616
Life in autoclave (days)	9

EXAMPLE 3

Formation of hydrides at 400°C under P = 0.1 MPa of H₂
(invention)

Composition	C1
	% (by weight)
Grain size 0 - 100 μm	1.2
100 - 500 μm	11.1
500 - 1000 μm	87.7
1000 and greater	0
Main phases present	(Nd,Dy) ₂ Fe ₁₄ B "(Nd,Dy) H ₂ " Nd Fe ₄ B ₄
Density (g/cm ³)	7.5
Residual magnetism (T)	1.16
Coercivity (kA/m)	1608
Life in autoclave (days)	8

EXAMPLE 4

Formation of hydrides at 400°C under P = 0.01 MPa of H₂
 (invention)

Composition	C1
	% (by weight)
Grain size 0 - 100 μm	1.0
100 - 500 μm	12.2
500 - 1000 μm	86.8
1000 and greater	0
Main phases present	(Nd,Dy) ₂ Fe ₁₄ B "(Nd,Dy) H ₂ " Nd Fe ₄ B ₄
Density (g/cm ³)	7.5
Residual magnetism (T)	1.16
Coercivity (kA/m)	1600
Life in autoclave (days)	9

EXAMPLE 5

Formation of hydrides at 400°C under P = 0.001 MPa of H₂
(invention)

Composition	C1
	% (by weight)
Grain size 0 - 100 μm	0.8
100 - 500 μm	9.1
500 - 1000 μm	90.1
1000 and greater	0
Main phases present	(Nd,Dy) ₂ Fe ₁₄ B "(Nd,Dy) H ₂ " Nd Fe ₄ B ₄
Density (g/cm ³)	7.5
Residual magnetism (T)	1.16
Coercivity (kA/m)	1600
Life in autoclave (days)	8

EXAMPLE 6

Formation of hydrides at 550°C under P = 0.1 MPa of H₂
(outside invention)

Composition	C1
	% (by weight)
Grain size 0 - 100 μm	0
100 - 500 μm	0
500 - 1000 μm	30.2
1000 and greater	69.8
Main phases present	(Nd,Dy) ₂ Fe ₁₄ B "(Nd,Dy) H ₂ " Nd Fe ₄ B ₄
Density (g/cm ³)	7.1
Residual magnetism (T)	0.82
Coercivity (kA/m)	320
Life in autoclave (days)	1

EXAMPLE 7

Formation of hydrides at 250°C under P = 100 bar (10MPa)
of H₂ (outside invention)

Composition	C1
	% (by weight)
Grain size 0 <%< 100 μm	1.2
100 <%< 500 μm	10.0
500 <%< 1000 μm	88.8
1000 <%	0
Main phases present	(Nd,Dy) ₂ Fe ₁₄ BH ₃ (Nd,Dy) H _{2.9} Nd Fe ₄ B ₄
Density (g/cm ³)	7.3
Residual magnetism (T)	1.13
Coercivity (kA/m)	1380
Life in autoclave (days)	4

EXAMPLE 8

Formation of hydrides at 700°C under P = 100 bar (10MPa)
of H₂ (invention)

Composition	C1
	% (by weight)
Grain size 0 <%< 100 μm	2.2
100 <%< 500 μm	12.3
500 <%< 1000 μm	85.5
1000 <%	0
Main phases present	(Nd,Dy) ₂ Fe ₁₄ B "(Nd,Dy) H ₂ " Nd Fe ₄ B ₄
Density (g/cm ³)	7.5
Residual magnetism (T)	1.16
Coercivity (kA/m)	1650
Life in autoclave (days)	9

Example 1 shows that under conditions close to those of the prior art (25°C at about 0.1 MPa of H₂) and for the exemplified composition, a duration of 4 days is the maximum which the coated magnet can withstand in the autoclave before blistering which is a sign of corrosion.

Example 2 shows that hydride formation at 300°C under conditions which are representative of the invention leads to a life in an autoclave which is considerably increased (+100%) over Example 1, which is perhaps linked to improved compactness.

A similar result is obtained by hydride formation at 400°C under 0.1 MPa of H₂ (Example 3), under 0.01 MPa of H₂ (Example 4), or under 10⁻³ MPa of H₂ (Example 5).

Example 6 shows that at 550°C there is no more embrittlement. Mechanical precrushing is therefore necessary. Densification becomes difficult; the lives in an autoclave are extremely reduced as well as the magnetic properties, undoubtedly owing to the presence of numerous open pores.

At 250°C under 100 bar (10 MPa) - Example 7 - and identically to Example 1, easy corrosion is found.

At 700°C (Example 8), the magnetic properties as well as the corrosion resistance are at an optimum, similar to those in Example 2.

Apart from the high passivity of the materials obtained and the improved corrosion resistance of the magnets prepared with them, the process according to the invention provides the following economic and technical advantages:

- less consumption of H_2 since the phase which is rich in rare earth and occupies several per cent of the structure is hydrided at its lowest level
- slight desorption of the H_2 during sintering which prevents the appearance of defects such as blow holes or cracks and allows parts having a large unit volume to be obtained
- facility of crushing of the passivated materials
- absence of formation of a ferromagnetic phase $Fe \alpha$ owing to the disproportionation reaction described in the prior art
- lower consumption of TR
- safety improved by the reduced volume of H_2 to be used.



Claims

1. Method of obtaining a friable and relatively inert Fe TR B type magnetic material in divided form containing at least the Tl , $Nd_2 Fe_{14} B$ phase and a rare earth hydride, $TR H_x$ wherein x is between 1.8 and 2.45, allowing highly corrosion resistant sintered permanent magnets to be formed in a hydrogen-containing atmosphere, characterised in that the conditions of absolute pressure (P) and temperature T ($^{\circ}C$) are as follows:

if $P \leq Patm.$, $250 < T < 550^{\circ}C$

if $P > Patm.$, $250+100 \log (P/Patm.) < T < 500+100 \log (P/Patm.)$

in which formulae $Patm.$ denotes atmospheric pressure and $\log$ the logarithm of base 10.

2. Method according to claim 1, characterised in that:

if $P \leq Patm.$, $350 < T < 550^{\circ}C$

if $P > Patm.$, $350+100 \log (P/Patm.) < t < 550+100 \log (P/Patm.)$

3. Method according to one of claims 1 or 2, characterised in that:

if $P \leq Patm.$, $350 < T < 500^{\circ}C$

if $P > Patm.$, $350+100 \log (P/Patm.) < T < 500+100 \log (P/Patm.)$

4. Method according to one of claims 1 to 3, characterised in that the temperature is $> 400^{\circ}C$.

5. Method according to one of claims 1 to 4, characterised in that the pressure P is higher than 50.6 kPa (0.5 atmosphere).

6. Method according to claim 5, characterised in that the pressure P is lower than 101.3 kPa (1 atmosphere).