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(54) **Rare-earth bonded magnet, material and method for manufacturing the same.**

(57) A rare-earth bonded magnet is improved in its heat resistance by coating rare-earth magnetic powder with heat resisting addition polymerized thermosetting resin consisting mainly of triazine resin because oxidation of the rare-earth magnetic powder is prevented or retarded by triazine rings formed in the coating film of the thermosetting resin consisting mainly of the triazine resin. The heat resistance of the bonded magnet is further improved by curing the thermosetting resin in a vacuum and by adding organometallic salt in the thermosetting resin as a metallic catalyser since the coating film is formed more firmly.

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This invention relates to a rare-earth bonded magnet used widely for industrial products such as automobiles, business machines, domestic electrification machines and sounder machines, to material, a material for such a magnet and a method suitable for manufacturing the rare-earth bonded magnet.

Heretofore, there has been widely used Alnico magnets and Ferrite magnets as permanent magnets.

5 However, rare-earth magnets have been developed, which have excellent magnetic properties as compared with the aforementioned magnets, and the application and demand of the rare-earth magnets has increased remarkably in recent years.

10 The rare-earth magnets contain active metals and are easily oxidized. Therefore, the rare-earth magnets of this kind are inferior in their corrosion resistance and heat-resisting properties, especially in an atmosphere at a temperature higher than room temperature.

Among the rare-earth magnets, R-Fe-B magnets and R-Fe-N magnets have Fe(iron) for their main element in addition to R(rare-earth metals), and are oxidized more remarkably as compared with Sm-Co magnets. Accordingly, the R-Fe rare-earth magnets have excellent magnetic properties. However, they have serious problems from the view point of their oxidation resistance, their corrosion resistance and their
15 temperature characteristics and heat resistance at a temperature higher than room temperature.

Among the rare-earth magnets, the sintered magnet is densified by sintering. Therefore, it is possible to improve the heat resistance of the sintered magnet considerably by coating the surface of the magnet with, for example, Ni, or resin at the final stage of the magnet manufacturing process. Among the bonded magnets, especially in a magnet manufactured by injection molding using thermoplastic resin such as
20 polyamide resin, it is possible to improve its heat resistance by coating the surface of the magnet in a manner similar to that described above in relation to the sintered magnet because the surface of magnetic powder is covered completely with the resin.

For bonded magnets, in a magnet manufactured by compression molding using a binder such as thermosetting resin (for example, epoxy resin), metals or the like, a large number of vacancies exist
25 between the powdered magnetic material and the binder. Therefore, it is not possible to prevent the magnet from oxidizing owing to the internal vacancies even if the surface of the magnet is coated completely, and it is unavoidable to oxidize the magnetic material through the coating layer and the internal vacancies. Consequently, there is a problem in that secular change of the magnetic properties at room temperature and a temperature higher than room temperature becomes large and the heat resistance of the magnet is degraded with the passage of time.
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This invention is made in view of the aforementioned problems of the prior art, it is an aim to provide a rare-earth bonded magnet with improved heat-resistance characteristics by preventing the oxidation of the rare-earth magnetic material as much as possible and decreasing the secular change of the magnetic properties at room temperature and at higher temperatures.

35 The material for the rare-earth bonded magnet according to this invention is characterized by comprising rare-earth magnetic powder coated with heat resisting addition polymerized thermosetting resin consisting mainly of triazine resin, optionally together with binder if necessary.

The rare-earth bonded magnet according to this invention is characterized in that rare-earth magnetic powder coated, optionally by using binder if necessary, with heat resisting addition polymerized thermosetting resin consisting mainly of triazine resin is agglomerated together with the optional binder.
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The method of manufacturing a rare-earth bonded magnet according to this invention is characterized by comprising steps of coating a surface of rare-earth magnetic powder with heat resisting addition polymerized thermosetting resin consisting mainly of triazine resin by adding the thermosetting resin into the rare-earth magnetic powder almost at the same time as addition of binder, subsequently molding a
45 compact by pressing the rare-earth magnetic powder coated with the thermosetting resin together with the binder and curing the thermosetting resin in the compact. The rare-earth magnetic powder may be added with organometallic salt as a metallic catalyser together with the binder and the heat resisting addition polymerized thermosetting resin in a preferred aspect, and the curing of the thermosetting resin may be carried out at a temperature of not lower than 150 °C in a vacuum or in an atmosphere of argon in the other
50 preferred aspects.

The present invention will now be described in greater detail below.

In the present invention, magnetic powder containing rare-earth metals such as R-Fe, R-Fe-B, R-Fe-N and the like are used as rare-earth magnetic powder.

55 As resin to be coated on the surface of the rare-earth magnetic powder of this kind, heat resisting addition polymerized thermosetting resin is used which has triazine resin (polymer having unsaturated triple bonds (cyanato group -R-O-C≡N)) for its main component.

The material for the rare-earth bonded magnet according to this invention comprises rare-earth magnetic powder coated with heat resisting addition polymerized thermosetting resin consisting mainly of

triazine resin, together with binder if need require. In case of coating, various methods may be applied, such as a method of coating the rare-earth magnetic powder by dipping it into a solution (for example, methyl ethyl ketone is used as a solvent) containing the heat resisting addition polymerized thermosetting resin consisting mainly of triazine resin, a method of mixing the rare-earth magnetic powder after adding the heat resisting addition polymerized thermosetting resin consisting mainly of triazine resin in it, and a method of coating the rare-earth magnetic powder by vaporizing the thermosetting resin and depositing it on the surface of the magnetic powder, for example.

The rare-earth bonded magnet according to this invention is formed by agglomerating rare-earth magnetic powder using binder, which magnetic powder is coated with heat resisting addition polymerized thermosetting resin together with binder if need require. In this case, thermosetting resin such as epoxy resin is used similarly as the binder, and the magnetic powder is molded (agglomerated) into a compact having desired shape by forming methods such as compression molding and so on.

After molding the compact, it is preferable to cure the thermosetting resin added as the binder and the thermosetting resin consisting mainly of triazine resin at a temperature of not lower than 150 °C in a non-oxidative atmosphere or in a vacuum. In the curing treatment, the thermosetting resin is hardened, while triazine resin of the thermosetting resin is hardened by heating and triazine rings are formed therein. The triazine ring is remarkably stable to thermal energy, so that the heat resistance of the resin is improved.

In order to coat the thermosetting resin consisting mainly of triazine resin on surfaces of the respective particles of the rare-earth magnetic powder more uniformly, it is desirable to perform the curing at a temperature of not lower than 150 °C in a vacuum because the triazine resin is vapourized temporarily and hardened after depositing on the surface of the rare-earth magnetic powder very uniformly.

In a case of manufacturing the rare-earth bonded magnet in such a manner, it is advisable according to demand to add organometallic salt such as zinc octylate, iron acetylacetonate or the like as a metallic catalyser together with the binder and the heat resisting addition polymerized thermosetting resin. Namely, it is possible to further reduce the secular change of the magnetic properties because adhesiveness between the rare-earth magnetic powder and the thermosetting resin consisting mainly of triazine resin is improved by addition of the organometallic salt as the metallic catalyser, and a firm coating film having heat resistance can be obtained.

In the rare-earth bonded magnet, the material and the method for manufacturing the rare-earth bonded magnet, the rare-earth magnetic powder is coated with the heat resisting addition polymerized thermosetting resin consisting mainly of triazine resin on the surface thereof and the coated magnetic powder is used. Therefore it is possible to retard or prevent the oxidation of the magnetic material. The heat resistance of the magnet is improved and the secular change of the rare-earth bonded magnet at room temperature and at a temperature higher than room temperature is reduced remarkably.

The present invention is illustrated below with reference to the following non-limiting Examples.

EXAMPLE 1

At first, by spraying rare-earth molten magnetic alloy consisting essentially of 28wt% of Nd - 0.9wt% of B - 5.0wt% of Co - Fe (remainder) on the surface of a copper roll rotating at the peripheral speed of 25m/sec, a ribbon of about 30µm in thickness was obtained, and rare-earth magnetic powder was obtained by comminuting the ribbon into the size smaller than 200µm. Subsequently, the rare-earth magnetic powder was annealed for 10 minutes at 550 °C.

Next, epoxy resin which is a thermosetting resin was added into the annealed rare-earth magnetic powder as much as 2wt% as binder, and triazine resin which is the heat resisting addition polymerized thermosetting resin was added into the magnetic powder as much as amount shown in Table 1, respectively. Then, these were mixed uniformly. And, zinc octylate was further added in some of samples as a metallic catalyser as much as 0.0006wt% of the triazine resin content, respectively.

Then, each of the mixed powders was compressed into a compact of 10mm in diameter and 7mm in height, and cured for 1 hour at 170 °C in an atmosphere of argon.

Furthermore, rare-earth bonded magnets were obtained by polarizing the cured compacts in a pulse magnetic field of 50kOe, and open flux values of the polarized magnet were measured, respectively. The open flux values were measured again at room temperature after holding them for 1000 hours at 180 °C, whereby the rates of decrease of the open flux values, that is irreversible demagnetizing factors were obtained. The results of measurement of the irreversible demagnetizing factors are shown in Table 1 together with the triazine resin contents.

Table 1

Sample Number	Triazine resin content (wt%)	Irreversible demagnetizing factor (%)	
		Without zinc octylate	Addition of zinc octylate
Conventional example 1	0	55.0	55.0
2	0.01	38.0	32.5
3	0.05	27.5	20.6
4	0.10	10.8	9.9
Inventive example 5	0.20	9.4	8.4
6	0.30	8.5	7.3
7	0.50	8.2	7.3
8	1.00	8.9	8.2

As shown in Table 1, in the case of the conventional example No.1 which is not coated with triazine resin on the surface of the rare-earth magnetic powder, the irreversible demagnetizing factor after holding it for 1000 hours at 180 °C was considerably large. As compared with above, in the cases of the examples Nos. 2-8 according to this invention which are coated with triazine resin, it was confirmed that the irreversible demagnetizing factor becomes considerably smaller when triazine resin is coated more than some degree. However it is desirable to coat triazine resin not more than 2wt% since the magnetic properties are degraded if the triazine resin is coated in excess. In addition, it was confirmed that the irreversible demagnetizing factor becomes smaller when an organometallic salt is added.

Example 2

By spraying molten rare-earth magnetic alloy consisting essentially of 28wt% of Nd - 0.9wt% of B - 5.0wt% of Co - Fe (remainder) on the surface of the copper roll rotating at the peripheral speed of 25m/sec, a ribbon of about 30μm in thickness was obtained, and rare-earth magnetic powder was obtained by comminuting the ribbon into the size of smaller than 200μm. rare-earth magnetic powder was annealed for 10 minutes at 550 °C.

Secondly, epoxy resin of 2wt% which is the thermosetting resin was added into the annealed rare-earth magnetic resin powder as binder, and triazine resin which is the heat resisting addition polymerized thermosetting resin was added into the magnetic powder as much as amount shown in Table 2, respectively. Then, these were mixed uniformly similar to the case of Example 1. Furthermore, zinc octylate was also added in some of samples as a metallic catalyser as much as 0.0006wt% of the triazine resin content, respectively.

Then, each of the mixed powders was compressed into a compact of 10mm in diameter and 7mm in height, and the compact was cured for 1 hour at 170 °C in a vacuum.

Then, the cured compacts were polarized in a pulse magnetic field of 50 kOe, and open flux values of the polarized magnets were measured, respectively. The open flux values were measured again at room temperature after holding them for 1000 hour at 180 °C, whereby the rates of decrease of the open flux values, that is irreversible demagnetizing factors were obtained. The results of measurement of the irreversible demagnetizing factors are shown in Table 2.

Table 2

Sample Number	Triazine resin content (wt%)	Irreversible demagnetizing factor (%)	
		Without zinc octylate	Addition of zinc octylate
Conventional example 9	0	53.5	53.5
10	0.01	13.6	11.5
11	0.05	10.8	9.1
12	0.10	9.3	8.8
Inventive example 13	0.20	8.5	8.4
14	0.30	8.2	7.7
15	0.50	7.9	7.5
16	1.00	8.0	7.8

As shown in Table 2, in the case of performing the curing in a vacuum, it was confirmed that the irreversible demagnetizing factor after holding for 1000 hours at 180 °C becomes smaller and the heat resistance of the magnet is further improved since the triazine resin is coated more uniformly on the respective surface of the magnetic powder.

Example 3

After obtaining rare-earth magnetic powder consisting essentially of 31.1wt% of Nd - 1.0wt% of B - Fe (remainder) in the same manner as Example 1, 2.0wt% of epoxy resin being the thermosetting resin as binder and 0.3wt% of triazine resin being the heat resisting addition polymerized thermosetting resin were added into the annealed rare- earth magnetic powder, and they were mixed uniformly. In some of samples, zinc octylate was further added as a metallic catalyser as much as 0.0006wt% of the triazine resin content.

Next, each of the mixed powders was compressed into a compact of 10mm in diameter and 7mm in height, and the compacts were cured for 1 hour at 170 °C, in the air as to a part of compacts, in an atmosphere of argon as to another part of compacts and in a vacuum as to the remaining part of compacts, respectively.

Then, the cured compacts were polarized in a pulse magnetic field of 50kOe, and open flux values of the polarized magnets were measured, respectively. The rates of decrease of the open flux values, that is irreversible demagnetizing factors were obtained by measuring the open flux values at room temperature after holding them for 1000 hours at 180 °C. The measured results are shown in Table 3.

Table 3

Sample Number	Triazine resin content (wt%)	Zinc octylate	Curing	Irreversible demagnetizing factor (%)
Conventional example 17	0	None	in Air	32.5
18	0	None	in Argon	41.5
19	0	None	in Vacuum	49.0
Inventive example 20	0.3	None	in Air	4.9
21	0.3	None	in Argon	5.1
22	0.3	None	in Vacuum	3.5
23	0.3	Addition	in Air	4.4
24	0.3	Addition	in Argon	4.6
25	0.3	Addition	in Vacuum	3.0

As is obvious from Table 3, the conventional examples Nos.17-19 which do not include triazine resin nor an organometallic salt showed large irreversible demagnetizing factors after holding them for 1000 hours at 180 °C. As compared with above, in the examples Nos.20-22 which include triazine resin but do not include an organometallic salt and the examples Nos.23-25 which include both the triazine resin and organometallic salt, they showed considerably smaller irreversible demagnetizing factors after holding them for 1000 hours at 180 °C. It was confirmed that the irreversible demagnetizing factor of the magnet cured in

a vacuum is smaller than that of magnet cured in the air and an atmosphere of argon and it is effective to cure in the vacuum for further improving the heat resistance of the magnet. Furthermore, it became clear that it is possible to further decrease the irreversible demagnetizing factor by adding an organometallic salt as a metallic catalyser.

Example 4

An ingot having a composition represented by $\text{Sm}_2\text{Fe}_{17}$ was subjected to a homogenizing treatment by heating it for 24 hours at a temperature of 1100°C , and grinded mechanically into powder of the size passing 120 mesh. Then the powder was subjected to nitriding by heating for 5 hours at a temperature of 550°C in an atmosphere of nitrogen.

Secondly, fine rare-earth magnetic powder was obtained by comminuting the nitrided powder into particles of $3\mu\text{m}$ in mean diameter. Subsequently, the rare-earth magnetic powder was added with epoxy resin of 2wt% as binder, and added with triazine resin of 0.3wt% as the heat resisting addition polymerized thermosetting resin. In some of samples, iron acetylacetonate was further added as a metallic catalyser as much as 0.0015wt% of the triazine resin.

Then, each of the mixed powders was compressed into a compact of 10mm in diameter and 7mm in height in a vertical magnetic field of 15kOe, and the compacts were cured for 1 hour at 170°C , in an atmosphere of argon as to a part of compacts and in a vacuum as to the other part of compacts, respectively.

The results shown in Table 4 were obtained by measuring the irreversible demagnetizing factors after holding for 1000 hours at 180°C in the same manner as Example 1.

The following were typical magnetic properties of these rare-earth bonded magnets; Br (residual magnetic flux density) : 8.0KG, iHc (coercive force) : 8.5kOe, (BH)max (maximum energy product) : 11.8MGOe.

Table 4

Sample Number	Triazine resin content (wt%)	Iron acetylacetonate	Curing	Irreversible demagnetizing factor (%)
Conventional example 26	0	None	in Argon	13.5
Inventive 27 example	0.3	None	in Argon	4.3
28	0.3	None	in Vacuum	2.5
29	0.3	Addition	in Argon	3.1
30	0.3	Addition	in Vacuum	2.0

As shown in Table 4, the conventional example No.26 which does not include triazine resin nor an organometallic salt exhibited a large irreversible demagnetizing factor after holding it for 1000 hours at 180°C . As compared with above, the inventive examples Nos 27, 28 which include triazine resin but not an organometallic salt, and the inventive examples No. 29, 30 which include both the triazine resin and an organometallic salt exhibited considerably smaller irreversible demagnetizing factors after holding them for 1000 hours at 180°C . It was confirmed that the irreversible demagnetizing factor becomes smaller in the case of performing the curing in a vacuum and it is effective to carry out the curing in a vacuum for further improving the heat resistance of the magnet. Additionally, it was also confirmed that it is possible to further decrease the irreversible demagnetizing factor by adding an organometallic salt as a metallic catalyser.

As mentioned above, the rare-earth bonded magnet, the material and the method for manufacturing the rare-earth bonded magnet according to this invention, it is possible to prevent the oxidation of the rare-earth magnetic powder which is easily oxidized and the secular change of the magnetic properties of the rare-earth bonded magnet at room temperature and at a temperature higher than room temperature becomes smaller. Accordingly, an excellent effect can be obtained since it is possible to provide the rare-earth bonded magnet having improved heat resistance.

In this specification the phrase "almost at the same time" means that the thermosetting resin is added into the rare-earth magnetic powder at the same time as addition of the binder, or before or after the addition of the binder.

Claims

1. Material for a rare-earth bonded magnet comprising rare-earth magnetic powder coated with heat resisting addition polymerized thermosetting resin consisting mainly of triazine resin.
- 5 2. A rare-earth bonded magnet characterized by agglomerating rare-earth magnetic powder coated with heat resisting addition polymerized thermosetting resin consisting mainly of triazine resin, optionally, together with binder.
- 10 3. A method for manufacturing a rare-earth bonded magnet by compacting rare-earth magnetic powder together with binder which comprises coating a surface of said rare-earth magnetic powder with heat resisting addition polymerized thermosetting resin consisting mainly of triazine resin by adding said thermosetting resin into the rare-earth magnetic powder almost at the same time as addition of the binder, subsequently molding a compact by pressing the rare-earth magnetic powder coated with the thermosetting resin and curing the thermosetting resin in said compact.
- 15 4. A method for manufacturing a rare-earth bonded magnet as claimed in claim 3, wherein said rare-earth magnetic powder is added with organometallic salt as a metallic catalyser together with the binder and the heat resisting addition polymer-type thermosetting resin.
- 20 5. A method for manufacturing a rare-earth bonded magnet as claimed in claim 3 or claim 4, wherein said curing of the thermosetting resin is carried out at a temperature of not lower than 150 °C in an atmosphere of argon.
- 25 6. A method for manufacturing a rare-earth bonded magnet as claimed in claim 3 or claim 4, wherein said curing of the thermosetting resin is carried out at a temperature of not lower than 150 °C in a vacuum.

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EUROPEAN SEARCH REPORT

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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	PATENT ABSTRACTS OF JAPAN vol. 13, no. 354 (E-802)8 August 1989 & JP-11 14 006 (SANKYO SEIKI MFG CO) 2 May 1989 * abstract *	1-3	H01F1/053
A	--- PATENT ABSTRACTS OF JAPAN vol. 14, no. 344 (E-0955)25 July 1990 & JP-21 17 105 (TDK CORP) 1 May 1990 * abstract *	1-3	
A	--- PATENT ABSTRACTS OF JAPAN vol. 14, no. 134 (C-0701)14 March 1990 & JP-20 06 573 (SANYO SEIKI MGF CO) 10 January 1990 * abstract *		

The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			H01F
Place of search THE HAGUE		Date of completion of the search 16 MARCH 1993	Examiner DECANNIERE L.
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