



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 028 437 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
16.08.2000 Bulletin 2000/33

(51) Int. Cl.⁷: **H01F 7/02**

(21) Application number: **98950380.0**

(86) International application number:
PCT/JP98/04829

(22) Date of filing: **23.10.1998**

(87) International publication number:
WO 99/23675 (14.05.1999 Gazette 1999/19)

(84) Designated Contracting States:
DE FR GB NL

(30) Priority: **30.10.1997 JP 31643597**
17.11.1997 JP 33368197
10.02.1998 JP 4455898
10.02.1998 JP 4455998
12.02.1998 JP 4882798
12.02.1998 JP 4882898
19.02.1998 JP 5604498
12.03.1998 JP 8301198
12.03.1998 JP 8301298
30.03.1998 JP 10349698

(71) Applicant:
SUMITOMO SPECIAL METALS COMPANY LIMITED
Osaka-shi, Osaka 541-0041 (JP)

(72) Inventors:
• **YOSHIMURA, Kohshi**
Amagasaki-shi, Hyogo 661-0012 (JP)
• **NISHIUCHI, Takeshi**
Ibaraki-shi, Osaka 567-0035 (JP)
• **KIKUI, Fumiaki**
Minamikawachi-gun, Osaka 587-0032 (JP)
• **ISOZAKI, Takahiro**
Ibaraki-shi, Osaka 567-0035 (JP)

(74) Representative: **Butler, Lance**
Barker Brettell
10-12 Priests Bridge
London SW15 5JE (GB)

(54) **HIGH CORROSION-RESISTANT R-Fe-B-BASE BONDED MAGNET AND METHOD OF MANUFACTURING THE SAME**

(57) A method of efficiently manufacturing R-Fe-B-base bonded magnets of various shapes such as ring shape and disk shape having a high corrosion resistance and capable of being plated electrically with ease, wherein the corrosion resistance of the magnet is improved by forming a conductive film of a metal on the surface thereof with tight adhesion, uniformity and efficiency. The method comprises filling the holes of the magnet with polishing powder, inorganic powder and polishing chips, fixing these materials in the holes by fat of a vegetable medium and sealing the resultant holes, and barrel-polishing the magnet by a barrel unit in the dry process with indefinitely shaped, i.e. spherical, massive or acicular (wiry) pieces of a required size of Cu, Sn, Zn, Pb, Cd, In, Au, Ag, Fe, Ni, Co, Cr and Al and such pieces of alloys thereof used as a metallic medium. Said fine pieces of metals such as Cu are press fitted into a resin surface and holes of the bonded magnet and cover the surface and holes and further, cover the surfaces of particles of magnetic powder whereby a very uniform conductive film can be formed on the surface of the bonded magnet, so that it becomes possible to subject the bonded magnet to

electric plating excellently and obtain a plated R-Fe-B-base bonded magnet of a high corrosion resistance and with minimum deterioration of the magnetic properties.

EP 1 028 437 A1

Description

TECHNICAL FIELD

5 **[0001]** This invention relates to R-Fe-B-base bonded magnets made in various shapes such as rings or discs, the corrosion resistance whereof is improved with a very clean metal film, and to high corrosion-resistant R-Fe-B-base bonded magnets exhibiting sharply improved corrosion resistance and adhesion properties, and a method of manufacturing the same, wherein, after filling pores therein with polishing powder, bonded magnet polishing chips, and inorganic powder by dry-process barrel polishing to seal the pores and smooth the surface, or, alternatively, without performing
 10 that sealing process, dry-process barrel polishing with a metal medium of pieces of Cu, Sn, Zn, Pb, Cd, In, Au, Ag, Fe, Ni, Co, Cr, Al and alloys thereof is used to press-fit fine ground pieces of those metals into the pores and resin surface on the surface of the bonded magnets, effecting a coating, or adequate electrical conductivity is imparted to the magnet surface by coating the magnet powder surfaces with fine metal pieces, making it possible to implement electrolytic plating directly, without non-electrolytic plating, or, after forming the aluminum coating layer noted above, deploying a highly
 15 corrosion-resistant plating layer that can be formed efficiently with good mass-productivity, by performing a zinc substitution treatment, without limiting the electrolytic nickel plating or other plating of a post-process.

BACKGROUND ART

20 **[0002]** Today, in the rubber magnets and plastic magnets called bonded magnets, which are made in various shapes such as rings and discs, advances are being made toward higher performance, moving from conventional isotropic bonded magnets to anisotropic bonded magnets, and from ferrite-based bonded magnets to rare earth-base bonded magnets which exhibit higher magnetic strength, and also from Sm-Co magnetic materials to R-Fe-B bonded magnets which use R-Fe-B magnetic materials exhibiting, in sintered magnets, high magnetic properties, with a maximum energy product of 50 MGOe or higher.

25 **[0003]** There is a problem with R-Fe-B magnets in that they rust easily due to their magnet alloy composition which contains large quantities of iron and a component phase that oxidizes extremely readily, and the surfaces thereof have been coated with resin layers of various compositions by electrodeposition, spraying, immersion, or impregnation, etc. (cf. Japanese Patent Application Laid-Open No. H1-166519/1989, Japanese Patent Application Laid-Open No. H1-245504/1989).

[0004] With the resin coating methods used to date for enhancing the corrosion resistance of R-Fe-B bonded magnets, as in the case of ring-shaped bonded magnets using a spraying method, for example, coating material loss is great and many process steps are involved due to the necessity of reversing the front and back, and there has also been the problem of deterioration in film thickness uniformity.

35 **[0005]** With the electrodeposition method, moreover, although the film thickness is uniform, each magnet must be attached to an electrode. In addition, the electrodes leave marks that must be removed after the coating is made, thus requiring a touch-up operation. Hence this method is problematic in that it requires a great number of process steps and is particularly unsuitable for small magnets.

[0006] Using the immersion method, it is very difficult to obtain coated films of certain uniform thickness due to dripping of the coating material and other problems. With porous bonded magnets, moreover, the pores are not adequately filled in, resulting in such problems as swelling during drying and the products sticking together.

[0007] When the volume productivity of methods for generating metal coating films is considered, one possibility is to implement metal electroplating conducted with sintered R-Fe-B magnets (cf. Japanese Patent Application Laid-Open No. S60-54406/1985, and Japanese Patent Application Laid-Open No. S62-120003/1987), but the surfaces of R-Fe-B
 45 bonded magnets are porous and expose a resin portion of low electrical conductivity. As a consequence, plating solution remains, the plating film is not adequately produced on the resin part resulting in pin holes (unplated portions), and rusting occurs.

[0008] Thereupon, proposals have been made for selecting plating solutions that are harmless even if they penetrate into a porous bonded magnet and remain there (Japanese Patent Application Laid-Open No. H4-276092/1992), and for methods of plating after forming a resin coating on the underlayer (Japanese Patent Application Laid-Open No. H3-11714/1991, Japanese Patent Application Laid-Open No. H4-276095/1992).

[0009] It is very difficult, however, to adjust the pH of plating solutions or render them completely harmless, and no solution liquids exhibiting good film-forming efficiency have been found. Also, the variation in the thickness of the underlayer is a destabilizing factor in plating layers, and to apply an undercoating of sufficient thickness would lead to the contradiction of the plating layer on the surface becoming unnecessary.

55 **[0010]** Plating solutions of specific compositions have been proposed as a method for implementing nickel plating with good film-forming efficiency on R-Fe-B bonded magnets (Japanese Patent Application Laid-Open No. H4-99192/1992), but here again there is still a danger that such solutions will penetrate into the bonded magnet, remain

there, and cause rusting.

[0011] In terms of the structural material, on the other hand, the copper strike plating customarily performed prior to nickel plating is either strongly alkaline or strongly acidic, and hence is not suitable for processing R-Fe-B bonded magnets.

[0012] In order to impart wear resistance to electronic components, furthermore, and as an anticorrosion treatment for automobile steel panels and the like, practical NiP plating has been developed of a high-temperature acidic solution type, but this is unsuitable for application to R-Fe-B bonded magnets because it causes corrosion in the interior of the magnet.

[0013] Thereupon, in the interest of providing R-Fe-B bonded magnets, and a method of manufacture therefore, configured such that plating solutions and cleaning fluids, etc., are prevented from penetrating into and remaining in porous R-Fe-B bonded magnets, wherewith a nickel-electroplated layer or other plating layer can be formed efficiently, and wherewith corrosion resistance can be sharply improved, the following methods have been proposed.

(1) Method of coating the surface of an R-Fe-B-base bonded magnet with a mixture of resin and electrically conductive powder to form an electrically conductive film layer on the surface of the base material.

(2) Method of forming a resin layer exhibiting tackiness to the surface of an R-Fe-B-base bonded magnet, bonding magnetic powder thereto, and forming an electrically conductive coating layer on the surface of the base material (Japanese Patent Application Laid-Open No. H5-302176/1993).

(3) Method of coating surface of an R-Fe-B-base bonded magnet with a mixture of resin and electrically conductive powder to form an electrically conducting coating layer, and then performing a surface smoothing treatment (Japanese Patent Application Laid-Open No. H9-186016/1997).

[0014] In the three methods described above, however, various resins are used for sealing the pores in the base material, resulting inevitably in the processes becoming intricate, involving resin coating (impregnation) and hardening (smoothing treatment), which is undesirable.

[0015] In methods which coat (impregnate) the base material with a resin, moreover, it is very difficult to uniformly coat the resin onto the base material surface, and it is difficult to obtain plated products exhibiting outstanding dimensional precision, even if barrel polishing is performed in a subsequent process. Furthermore, with electrically conductive coating layers, electrically conductive matter or metal powder is included in the resin layer, whereupon, even though the exposed resin portions of the bonded magnet at the surface is improved over the R-Fe-B-base bonded magnet base material, in the manufacture there will still be considerable exposed area in the coating resin, and portions of low electrically conductive will be present on the surface, therefore making it very difficult to obtain surfaces exhibiting good, uniform electrically conductivity, and pinholes will develop readily during electroplating.

[0016] Thereupon, the inventors proposed a method wherein, using as a medium a mixture of a polishing agent and either a vegetable medium or a vegetable medium the surface whereof has been modified with an inorganic powder, barrel-polished is performed in a dry process, polishing agent powder and bonded magnet polishing chips are bonded with the fatty component of the vegetable medium to the pores in the bonded magnet, both sealing the pores and smoothing the surface thereof, and an electrically conductive layer is formed by non-electrolytic copper plating using an alkaline bath.

[0017] There are problems with this method, however, in that, with non-electrolytic copper plating, the useful life of the plating solution is short, and the solution management needed for obtaining good plated coatings is difficult. Furthermore, while corrosion resistance and dimensional precision are superior compared to the prior art, even higher corrosion resistance is now required to cope with many applications.

DISCLOSURE OF THE INVENTION

[0018] One object of the present invention is to provide R-Fe-B bonded magnets that exhibit extremely high corrosion resistance, not rusting even in long-duration high-temperature high-humidity tests, and another object thereof is to provide a manufacturing method wherewith various corrosion-resistant coating films can be formed on the R-Fe-B bonded magnets uniformly and with extremely high bonding strength in order to realize high corrosion resistance.

[0019] Another object of the present invention is to provide a manufacturing method, for highly corrosion-resistant R-Fe-B bonded magnets, comprising optimum industrial process steps for effecting corrosion-resistant coating films with high bonding strength and good dimensional precision on magnet surfaces that prevent plating solutions and cleaning fluids, etc., from penetrating into and remaining in porous R-Fe-B bonded magnets, as in conventional non-electrolytic plating methods.

[0020] The inventors, focusing on the importance of imparting extremely uniform electrically conductivity to base material surfaces in electroplating techniques for R-Fe-B-base bonded magnets exhibiting outstanding corrosion resistance and surface cleanness, conducted various investigations on methods for forming those electrically conductive

films. As a result thereof, they discovered that, by subjecting R-Fe-B-base bonded magnets to barrel polishing in a dry process with a barrel apparatus, using copper pieces of undefined shape, whether spherical, massive, or aricular (wire-form), of desired dimensions, as the metal medium, fine pieces of pulverized copper are press-fit into the porous portions and resin surface of the bonded magnet surface, effecting a coating, and copper pieces are also coated on the magnetic powder surfaces so that an electrically conductive film can be applied with extreme uniformity to the surface of the R-Fe-B-base bonded magnet, whereupon good electroplating is made possible, and R-Fe-B-base bonded magnet products having plating films can be obtained which exhibit outstanding corrosion resistance and little deterioration in magnetic properties.

[0021] The inventors furthermore made various investigations with a view to resolving the problems noted earlier in cases where smoothness is desired in bonded magnet surfaces, and, as a result learned that, by barrel-polishing a porous R-Fe-B bonded magnet in a dry process, using as a medium a mixture of a polishing agent formed by sintering an inorganic powder of Al_2O_3 , SiC, or the like, and a vegetable medium such as fruit rind, corncobs, or the like, or, alternatively, a mixture of the polishing agent noted above and a vegetable medium the surface whereof has been modified with an inorganic powder noted above, it is possible to bond the polishing chips of the surface-oxidized layers of the magnetic powder configuring a bonded magnet, the modifying inorganic powder, and the polishing agent powder to the porous portions of that magnet, by the fatty component in the vegetable medium, thus sealing the pores therein, and simultaneously to smooth the surface thereof, and hence learned that an electrically conductive film can be formed directly to the surface of the magnet base material, after dry-process barrel polishing, whereupon an R-Fe-B-base bonded magnet exhibiting improved smoothness and even more outstanding corrosion resistance can be obtained.

[0022] The inventors further learned that other materials can be used for the metal medium in dry-process barrel polishing besides the copper pieces noted above, namely soft metal pieces of Sn, Zn, Pb, Cd, In, Au, and Ag having a Vickers hardness of 80 or below, and also Fe, Ni, Co, and Cr.

[0023] The inventors further discovered that by performing dry-process barrel polishing in a barrel apparatus, using aluminum pieces of undefined shape as the medium, fine pulverized aluminum pieces are press-fit into the porous portions and resin surface on the surface of the bonded magnet, forming a coating, or by performing a zinc substitution treatment on the surface of the aluminum coating layer formed on the surface of the R-Fe-B-base bonded magnet, with fine aluminum pieces similarly being coated to the surface of the magnetic powder, aluminum effluence during electroplating is prevented, making good electroplating possible, whereupon R-Fe-B-base bonded magnet plate-coated products can be obtained which exhibit outstanding corrosion resistance and little deterioration in magnetic properties. Thus the present invention was perfected.

BEST MODE FOR CARRYING OUT THE INVENTION

[0024] Characteristic of a high corrosion-resistant R-Fe-B-base bonded magnet according to the present invention is that it has a metal coating layer on the surface of the magnet formed with metal pieces of Cu, Sn, Zn, Pb, Cd, In, Au, Ag, Fe, Ni, Co, Cr, and Al, or of alloys thereof, press-fitted in and coated on the porous portions and resin surface configuring the surface of the R-Fe-B-base bonded magnet, or with fine metal pieces coated on the surfaces of the magnetic powder configuring the surface, and an electrolytic plating layer formed with that metal coating layer intervening.

[0025] Also characteristic of a high corrosion-resistant R-Fe-B-base bonded magnet according to the present invention is that it has the metal coating layer on the surface of the magnet formed with the metal pieces noted above press-fitted in and coated on the porous portions and resin surface configuring the surface of the R-Fe-B-base bonded magnet, or with fine metal pieces coated on the surfaces of the magnetic powder configuring the surface, after the porous portions forming the surface of the R-Fe-B-base bonded magnet have been sealed by the bonding thereto, with the fatty component in a vegetable medium, of polishing agent powder, bonded magnet polishing chips, and an inorganic powder, and an electrolytic plating layer formed with that metal coating layer intervening.

[0026] Further characteristic of a high corrosion-resistant R-Fe-B-base bonded magnet according to the present invention is that it has an aluminum coating layer formed, either with fine aluminum pieces press-fitted in and coated on the porous portions and resin surface configuring the surface thereof, or with fine aluminum pieces coated on the surfaces of the magnetic powder configuring the surface, has a zinc layer provided by a zinc substitution treatment on the surface of the magnet, and also has an electrolytic plating layer formed with that metal coating layer intervening.

[0027] In the present invention, the R-Fe-B-base bonded magnets in view are both isotropic bonded magnets and anisotropic bonded magnets. They may be obtained, in the case of compression molding, for example, by, after adding and kneading in a thermosetting resin, coupling agents, and lubricants, etc., to the magnetic powder of the wanted composition and properties, performing compression molding, heating, and resin curing, and in cases of injection molding, extrusion molding, or rolling molding, by, after adding and kneading in a thermoplastic resin, coupling agents, and lubricants, etc., to the magnetic powder, performing injection molding, extrusion molding, or rolling molding.

[0028] For the R-Fe-B magnetic powder, either isotropic or anisotropic powder can be used which has been obtained by any of a number of manufacturing methods including a fusion-pulverizing method wherein the desired R-

Fe-B alloy is melted, cast, and then pulverized, a direct reduction diffusion method for obtaining powder directly by Ca reduction, a quick-cooling alloy method wherein the desired R-Fe-B alloy is melted, ribbon foil is obtained with a jet-caster, and that is pulverized and annealed, a gas atomizing method wherein the desired R-Fe-B alloy is melted, made into powder by gas atomizing, and heat-treated, a mechanical alloying method wherein the desired raw-material metal is made into powder, then made into fine powder by mechanical alloying and heat-treating, or a method (HDDR method) wherein the desired R-Fe-B alloy is heated in hydrogen to break it down and recrystallize it.

[0029] In the present invention, the rare earth element R used in the R-Fe-B magnet powder accounts for 10 at.% to 30 at.% of the composition, but it is preferable that at least one element from the group Nd, Pr, Dy, Ho, and Tb be contained, or additionally that at least one element from the group La, Ce, Sm, Gd, Er, Eu, Tm, Yb, Lu, and Y be contained. Ordinarily, one type of R will be sufficient, but in actual practice, because of the ease of obtaining mixtures of two types or more thereof (such as misch metal or didymium), etc., such can be used. This It need not be a pure rare earth element, moreover, and, within the scope of what is industrially available, such as contains unavoidable impurities due to manufacturing may be used without any difficulty.

[0030] R is a mandatory element in the types of magnet powders noted earlier. At less than 10 at.%, the crystalline structure becomes a cubic crystalline structure identical to that of α -iron, wherefore high magnetic properties, such as high coercive force in particular, are not obtained. When 30 at.% is exceeded, on the other hand, there will be many R-rich non-magnetic phases, the residual flux density (Br) will decline, and permanent magnets with outstanding properties will not be obtained. Thus the R content should be within the range of 10 at.% to 30 at.%.

[0031] B is a mandatory element in the magnet powders noted earlier. At less than 2 at.%, a rhombohedral structure becomes the dominant phase, and high coercive force (iHc) is not obtained. When 28 at.% is exceeded, on the other hand, there will be many B-rich non-magnetic phases, and the residual flux density (Br) will decline, wherefore outstanding permanent magnets will not be obtained. Thus the B content should be within the range of 2 at.% to 28 at.%.

[0032] Fe is a mandatory element in the magnet powders noted earlier. At less than 65 at.%, the residual flux density (Br) declines, whereas when 80 at.% is exceeded, high coercive force is not obtained. Hence the Fe content should be from 65 at.% to 80 at.%.

[0033] By partially replacing the Fe with Co, the temperature characteristics can be improved without impairing the magnetic properties of the magnet. However, when the amount of Co replacement exceeds 20% of the Fe, the magnetic properties conversely deteriorate, so that is undesirable. When the Co replacement quantity is from 5 at.% to 15 at.% in the total quantity of Fe and Co, Br will increase as compared to when no replacement is made, wherefore that is desirable in order to obtain high magnetic flux.

[0034] In addition to R, B, and Fe, moreover, the presence of impurities that are unavoidable in industrial manufacture is permissible. For example, the permanent magnet fabricability can be improved and lower costs realized by partially replacing B with at least one element from among the group C (4.0 wt.% or less), P (2.0 wt.% or less), S (2.0 wt.% or less), and Cu (2.0 wt.% or less), in a total quantity that is 2.0 wt.% or less.

[0035] At least one element from the group Al, Ti, V, Cr, Mn, Bi, Nb, Ta, Mo, W, Sb, Ge, Ga, Sn, Zr, Ni, Si, Zn, and Hf can also be added to the magnet powder to realize the benefit or improving the coercive force, improving the squareness of the magnetism reduction curve, improving fabricability, or reducing costs. The upper limit of the added quantity should be within such range as will satisfy the various conditions required to realize the desired values for the (BH)max and (Br) of the bond magnet.

[0036] In the present invention, furthermore, the binder used with injection molding may be a resin such as 6PA, 12PA, PPS, PBT, or EVA, that used with extrusion molding, calendar rolling, or rolling molding may be PVC, NBR, CPE, NR, or Hypon, etc., and that used with compression molding may be an epoxy resin, DAP, or a phenol resin, etc. If necessary, a known metal binder can be used. Other auxiliary agents may also be used, such as a lubricant to facilitate molding, a bonding agent for the resin and inorganic filler, or a silane-based or titanium-based coupling agent.

[0037] In the present invention, the medium used when barrel-polishing in the sealing and smoothing treatment is either a mixture of a polishing agent such as ceramic material wherein inorganic powder of Al_2O_3 , SiC, etc., is sintered, or metal balls, and a vegetable medium such as vegetable husks, sawdust, fruit rind, or corncobs, or a mixture of a polishing agent noted above and a vegetable medium noted above the surface whereof has been modified with an inorganic powder of Al_2O_3 , SiC, etc., noted above. By performing the barrel-polishing treatment using such a mixture as the medium, it is possible to perform a smoothing-sealing treatment on bond magnets.

[0038] In the dry barrel polishing performed in this invention to effect the sealing and smoothing treatment and to form the metal coating layer on the surface of the bonded magnet, a known barrel can be used, and a common revolving barrel with a turning speed of 20 to 50 rpm, a centrifugal barrel with a turning speed of 70 to 200 rpm, or a vibrating barrel method wherein the vibration amplitude is 0.5 mm or greater but less than 50 mm can be used.

[0039] Ordinarily, moreover, the atmosphere in this barrel polishing may be atmospheric air. However, in cases where, depending on the medium, there is a worry about the magnet being oxidized due to heat of friction during barrel polishing, an inert gas atmosphere such as N_2 , Ar, or He gas, used singly or in a mixture, may be used.

[0040] In this invention, when performing the sealing and smoothing treatment, and the barrel used is a revolving or vibrating barrel, if the total quantity of bond magnet polishing agent and vegetable medium loaded into the barrel is less than 20%, the treatment quantity will be too small to be practical, whereas when 90% is exceeded, stirring will be insufficient and adequate polishing cannot be effected. Thus 20% to 90% of internal capacity is desirable.

[0041] There is no particular limitation on the polishing agent used in the sealing and smoothing treatment in this invention. Nevertheless, a mixture should be used containing a polishing agent with a particle size of 1 to 7 mm and preferably 3 to 5 mm or so, and a vegetable medium with a length of 0.5 to 3 mm and preferably 1 to 2 mm or so, or, alternatively, a mixture of the polishing agent noted above and a vegetable medium noted above wherein the surface has been modified with an inorganic powder. The magnet and medium mixture should be evenly stirred, performed under conditions wherein relative shifting motion is effected.

[0042] For the vegetable medium wherein the surface has been modified with an inorganic powder noted earlier, use is made of such a vegetable medium wherein a fatty component such as a wax has been coated by kneading onto the surface thereof, wherein the surface has then been evenly covered with an inorganic powder of Al_2O_3 , SiC, ZrO, or MgO having a particle size of 0.01 to 3 μm , bonding that powder thereto. The powder of the polishing agent noted above that is a sealant the inorganic powder for modifying the surface of the vegetable medium, and the polishing chips from the bond magnet have a particle size of 0.01 to 3 μm .

[0043] The ratio between the vegetable medium and polishing agent in the medium (vegetable medium/abrasive agent) must be from 1/5 to 2, with a mixture having a ratio of 1 being preferred. The mixture ratio between the bond magnet and medium (bond magnet/medium) may be made 3 or lower.

[0044] In the present invention, the polishing agent noted above functions to effectively grind away the surface oxidation layer of the magnet to smooth the surface thereof, and to beat and harden the sealing materials constituted by the polishing agent powder, the inorganic powder for modifying the vegetable medium surface, and the bond magnet polishing chips. The vegetable medium noted above functions to enhance the bonding strength of the sealing materials by effectively releasing the fatty component thereof.

[0045] In the present invention, it is possible to lower the porosity of the bond magnet after the surface smoothing treatment to 3% or lower. It is possible not only to perform the smoothing-sealing treatment on the bond magnet surface, but also to remove the surface oxidation layer from the magnet and thus obtain active R-Fe-B magnetic powder surfaces.

[0046] In this invention, any known barrel apparatus, whether revolving, vibrating, or centrifugal, etc., can be used for the dry-process barrel polishing with the metal pieces. Metal pieces of undefined shape can be used, whether spherical, massive, or aricular (wire-form), etc. As to the sizes of the metal pieces, below a size of 0.1 mm, too much time is required for adequate press-fitting and coating, so that is impractical, whereas at sizes exceeding 10 mm, the surface irregularities become great, making it impossible to cover the entire surface with the metal being used. Hence metal pieces of sizes ranging from 0.1 to 10 mm are desirable, with 0.3 to 5 mm being preferable, and with a range of 0.5 to 3 mm being most preferable.

[0047] In this invention, moreover, the metal pieces loaded into the dry-process barrel need not all be of the same shape or dimensions, but may be a mixture of different shapes and dimensions. It is also permissible to mix fine metal powder in with the metal pieces of undefined shape. These may, furthermore, be only the metal used, or an alloy, or a copper composite metal wherein copper is coated on cores of a different metal such as iron, nickel, or aluminum, etc.

[0048] It is also desirable that the ratio of loading in the dry-process barrel polishing, namely the volumetric ratio between the magnet and the metal pieces (magnet/metal) be 3 or less. When 3 is exceeded, too much time is required for metal press-fitting and coating, making that impractical, and granules of magnetic powder also comes loose from the surface of the bonded magnet.

[0049] It is preferable that the quantity of bonded magnet and metal pieces loaded into the barrel polishing machine be from 20% to 90% of the internal capacity of the polishing machine. Below 20%, the process quantity is too small, making that impractical, while when 90% is exceeded, stirring is inadequate, whereupon thorough polishing cannot be accomplished.

[0050] The press-fitted and coated fine metal pieces are powder or needle-shaped pieces. When the size thereof exceeds a length of 5 μm , the bonding with the magnet surface is poor, leading to bonding flaws and peeling, etc., during electrolytic plating, wherefore this length should be 5 μm or less. A preferable range is 2 μm or less.

[0051] In this invention, with respect to the press-fitting and coating of the fine metal pieces, the fine metal pieces are press-fitted into and coated on the soft resin surface and porous portions in the surface of the bonded magnet and coated onto the magnet powder surfaces in the surface of the bonded magnet. The quantity press-fitted in the resin surface and porous portions is greater closer to the surface, while the quantity contained in the interior of the resin layer gradually diminishes.

[0052] In this invention, the thickness of the press-fitted layer of metal on the resin surface and porous portions should be 0.1 μm or greater but no more than 2 μm . Below 0.1 μm , adequate electrical conductivity is not obtained, whereas when 2 μm is exceeded, even though there are no problems in terms of performance, more work time is

required, making that impractical.

[0053] The thickness of the metal coating layer on the surfaces of the magnetic powder on the bonded magnet surface should be 0.2 μm or less. The reaction between the magnetic powder surfaces and the fine metal pieces is a type of mechanochemical reaction, and bonding properties deteriorate when 0.2 μm is exceeded.

[0054] The speed of revolution during dry-process barrel polishing in this invention should be 20 to 50 rpm for a revolving barrel, and 70 to 200 rpm for a centrifugal barrel, while the vibrating frequency should be 50 to 100 Hz in vibrating barrel polishing with a vibration amplitude of 0.3 to 10 mm.

[0055] In this invention, when fine metal pieces are being press-fitted and coated to the magnet surface by the barrel polishing method, the atmosphere in the barrel polishing method may be atmospheric air. There is a danger, however, that the heat of friction in the pulverized fine metal pieces, the magnetic powder on the surface of the magnet, and the metal pieces of undefined shape used as the medium will induce oxidation causing a decline in electrically conductivity, so that uniform electrolytic plating cannot be realized, resulting in a decline in the corrosion resistance. Therefore it is preferable that the atmosphere used in the barrel polishing method be an inert or inactive gas, or mixture of such gasses, such as N_2 , Ar, or He.

[0056] In this invention, the aluminum coating surface is subjected to zinc substitution in order to prevent aluminum effluence during the electroplating which follows thereafter. The zinc substitution method should be one that is performed with a solution containing zinc oxide, sodium hydroxide, ferric chloride, or Rossel salt, etc. The process conditions should be immersion in a bath temperature of 10 to 25°C and treatment time of 10 to 120 seconds.

[0057] The processing order in the zinc substitution procedure should be washing→zinc substitution→washing. If there are contaminants or other adhering materials on the aluminum surface, washing should be performed by immersion degreasing in a solution of sodium carbonate and sodium triphosphate. The zinc layer should be formed so that the extreme surface layer is of the form ZnO_x (where $x = 0$ to 1), with the thickness of the zinc layer formed being 0.1 μm or less. If the thickness of this layer exceeds 0.1 μm , bonding flaws will result, so that should be avoided.

[0058] In this invention, the electroplating method should contain at least one type of metal selected from among Ni, Cu, Sn, Co, Zn, Cr, Ag, Au, Pb, and Pt, or have B, S, or P contained in an alloy thereof, with nickel plating being particularly desirable. The plating thickness should be 50 μm or less, and preferably from 10 to 30 μm . In this invention, plating is possible using a common watt bath in order that the press-fitting and coating of the fine metal pieces in the resin surface and porous portions described earlier function effectively, wherewith outstanding bonding characteristics and corrosion resistance are obtained.

[0059] In a plating method using a nickel plating bath, in particular, the order of process steps should be washing→nickel electroplating→washing→drying, and the pH of the nickel plating bath should be adjusted with basic nickel carbonate to a pH of 4.0 to 4.6, and the process temperature should be 50 to 60°C.

[0060] In nickel plating, a prescribed current should be drawn using the plating bath described above and electrolytic nickel plates for the anodes. Nickel electroplating is conducted to stabilize the deposition of the nickel of the nickel anode plates, and it is desirable to use Estland nickel chips containing sulfur in the electrodes. The process order in the plating method using a nickel plating bath should be washing→electroplating→washing→drying, with drying preferably performed at a temperature of 70°C or higher.

[0061] Various bath tanks can be used as the plating bath tank, depending on the shape of the bonded magnet, with a rack plating or barrel plating process being preferable for ring-shaped bonded magnets.

EMBODIMENTS

Embodiment 1

[0062] To an alloy powder having an average particle size of 150 μm and a composition of 12 at.% Nd, 77 at.% Fe, 6 at.% B, and 5 at.% Co, made in a super-rapid-cooling method, 2 wt.% of an epoxy resin were added. This was kneaded and subjected to compression molding under a pressure of 7 ton/cm², and then cured at 170°C for 1 hour to yield ring-shaped bonded magnets having an external diameter of 22 mm, an internal diameter of 20 mm, and a height of 3 mm. The properties of the bonded magnets so obtained were $B_r = 6.7$ kG, $iH_c = 8.9$ kOe, and $(BH)_{\text{max}} = 9.0$ MGOe.

[0063] The bonded magnets obtained were placed in a vibrating barrel and subjected to dry-process barrel polishing using short rod-shaped copper pieces having diameters of 1 mm and lengths of 1 mm to form an electrically conductive coating layer made of fine copper pieces. The thickness of the press-fitted and coated fine copper pieces on the resin surface was approximately 0.7 μm and the thickness of the coating on the magnetic powder surfaces was 0.1 μm .

[0064] The conditions under which the barrel polishing treatment was conducted were an atmosphere of argon gas, loading 50 bond magnets (having an apparent volume of 0.15 liters and weight of 100 g) and the copper pieces (having an apparent volume of 2 liters and weight of 10 kg) of the dimensions noted above into a vibrating barrel having a capacity of 3.5 liters, vibration frequency of 70 Hz, and vibration amplitude of 3 mm, constituting a total load volume that

was 60% of the interior barrel capacity. The treatment was performed for 3 hours.

[0065] Washing was then performed, and nickel electroplating was conducted in a rack plating apparatus. The film thickness after plating was 20 μm on the inner diameter side and 22 μm on the outer diameter side. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 1. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are noted in Table 2.

[0066] The nickel electroplating conditions were a current density of 2 A/dm², plating time 60 minutes, pH 4.2, and bath temperature 55°C, with a plating solution composition of 240 g/l nickel sulfate, 45 g/l nickel chloride, titrated nickel carbonate (for pH adjustment), and 30 g/l boric acid.

Comparison 1

[0067] After washing ring-shaped bonded magnets obtained with the same method as in Embodiment 1, non-electrolytic copper plating was performed to a plating thickness of 5 μm . After the non-electrolytic copper plating, nickel plating was performed under the same conditions as in Embodiment 1. The ring-shaped bonded magnets obtained were subjected to an environment test for 500 hours at 80°C and 90% relative humidity. The results are noted in Tables 1 to 3.

[0068] The non-electrolytic copper plating conditions were a plating time of 20 minutes, pH of 11.5, and bath temperature of 20°C, with a plating solution composition of 29 g/l copper sulfate, 25 g/l sodium carbonate, 140 g/l tartrate, 40 g/l sodium hydroxide, and 150 ml 37% formaldehyde.

Comparison 2

[0069] After washing ring-shaped bonded magnets obtained by the same method as in Embodiment 1, nickel powder was mixed into a phenol resin and a 10 μm electrically conductive film was formed. After this process, nickel plating was performed under the same conditions as in Embodiment 1. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and 90% relative humidity. The results are indicated in Tables 1 to 3.

[0070] The conditions for the electrically conductive film-coating process were a process time of 30 minutes using a treatment solution composition of 5 wt.% phenol resin, 5 wt.% nickel powder (particle size 0.7 μm or smaller), and 90 wt.% of MEK (methylethyl ketone).

Comparison 3

[0071] After washing ring bonded magnets obtained by the same method as in Embodiment 1, a phenol resin layer was pre-formed as a bonding layer using an immersion procedure, after which silver powder (particle size 0.7 μm or smaller) was made to adhere to the surface, after which a 7 μm electrically conductive coating layer was formed with a vibrating barrel. After the vibrating barrel treatment, nickel plating was performed under the same conditions as in Embodiment 1. The ring bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and 90% relative humidity. The results are indicated in Tables 1 to 3.

[0072] The conditions for the vibrating barrel treatment were the use of a vibrating barrel having a capacity of 3.5 liters into which 50 bonded magnets were loaded, and performing the treatment for 3 hours using steel balls having an apparent volume of 2 liters and diameter of 2.5 mm for the medium.

[0073] As is evident from Tables 1 and 2, spot rusting was found in Comparison 1 after 100 hours, in Comparison 2 after 300 hours, and in Comparison 3 after approximately 350 hours. In Embodiment 1, on the other hand, no spot rusting could be found under a 30-power microscope even after 500 hours.

Table 1

	Before humidity resistance test			After humidity resistance test			Magnetic property deterioration ratio (%)		
	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)	Br (kG)	iHc	(BH) _{max} (MGOe)
Embodiment 1	6.6	8.9	9.0	6.5	8.7	8.8	3.0	2.2	2.2
Comparison 1	6.4	8.7	8.8	5.7	7.7	7.6	14.9	15.6	15.5
Comparison 2	6.4	8.9	9.0	6.3	8.5	8.5	6.3	4.4	5.5
Comparison 3	6.4	8.9	9.0	6.3	8.5	8.5	6.3	4.4	5.5

Rate of deterioration in magnetic properties (%) =

$$\frac{[(\text{new material magnetic properties}) - (\text{magnetic properties after humidity-resistance test})] / (\text{new material magnetic properties}) \times 100}{}$$

Table 2

	Surface condition at humidity resistance test time	Film thickness dimensional precision (μm)	Manufacturing method
Embodiment 1	No change (no rusting)	20±1	Cu film layer + Ni plating
Comparison 1	Spot rusting after 100 hours	25±2	Non-electrolytic Cu plating + Ni plating
Comparison 2	Minute rust spots after 300 hours	30±10	Electrically conductive resin layer + Ni plating
Comparison 3	Minute rust spots after 350 hours	27 ± 10	Electrically conductive coating layer + Ni plating

Embodiment 2

[0074] To an alloy powder having an average particle size of 150 μm and a composition of 12 at.% Nd, 77 at.% Fe, 6 at.% B, and 5 at.% Co, made in a super-quick-cooling method, 2 wt.% of an epoxy resin were added. This was kneaded and subjected to compression molding under a pressure of 7 ton/cm², and then cured at 170°C for 1 hour to yield ring-shaped bonded magnets having an external diameter of 26 mm, an internal diameter of 24 mm, and a height of 5 mm. The properties of the bonded magnets so obtained were Br = 6.8 kG, iHc = 9.1 kOe, and (BH)_{max} = 9.2 MGOe.

[0075] 100 magnets (200 g) so obtained were placed together with Al₂O₃-based spherical barrel stones having an average diameter of 3 mm in a vibrating barrel having a capacity of 20 liters. Then a vegetable medium consisting of

walnut meat having diameters of approximately 1 mm the surface whereof had been modified by Al_2O_3 powder having particle diameters of approximately $1\text{ }\mu\text{m}$ was loaded in the amount of 50% of the barrel capacity and surface polishing was performed in a dry process for 120 minutes with an amplitude of 20 mm, thereby implementing pore sealing and smoothing processing.

5 **[0076]** Next, the bonded magnets were placed in the vibrating barrel and dry-process barrel polishing was performed with a vibration frequency of 70 Mz and vibration amplitude of 3 mm, in an atmosphere of argon gas, using short rod-shaped copper pieces having diameters of 1 mm and lengths of 1 mm to form an electrically conductive coating layer with fine copper pieces. The fine copper pieces were press-fitted into the resin surface and porous portions to a depth of approximately $0.7\text{ }\mu\text{m}$ and the thickness of the coating on the magnetic powder surfaces was $0.1\text{ }\mu\text{m}$. The conditions for the barrel polishing process were that 50 bonded magnets (having an apparent volume of 0.15 liters and weight of 100 g) and copper pieces having the dimensions noted earlier (having an apparent volume of 2 liters and weight of 10 kg) were loaded into a vibrating barrel having a capacity of 3.5 liters, and the treatment was performed for 3 hours with an amplitude of 20 mm and the total loaded volume being 60% of the barrel capacity.

10 **[0077]** Washing was then performed, and nickel electroplating was conducted in a rack plating apparatus. The film thickness after plating was $21\text{ }\mu\text{m}$ on the inner diameter side and $23\text{ }\mu\text{m}$ on the outer diameter side. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 800 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 3. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are noted in Table 4.

20 **[0078]** The nickel electroplating conditions were a current density of 2 A/dm^2 , plating time 60 minutes, pH 4.2, and bath temperature 55°C , with a plating solution composition of 240 g/l nickel sulfate, 45 g/l nickel chloride, titrated nickel carbonate (for pH adjustment), and 30 g/l boric acid.

Comparison 4

25 **[0079]** Ring-shaped bonded magnets obtained by the same method as in Embodiment 2 were washed, subjected to a sealing and surface smoothing treatment as in Embodiment 2, again washed, and subjected to non-electrolytic copper plating. The plating thickness was $5\text{ }\mu\text{m}$. After non-electrolytic copper plating, nickel plating was performed under the same conditions as in Embodiment 2. The ring-shaped bonded magnets obtained were subjected to an environmental test (humidity resistance test) under the same conditions as in Embodiment 2. The results and film thickness dimensional precision (humidity resistance test) were conducted. The results are noted in Tables 3 and 4.

30 **[0080]** The non-electrolytic copper plating conditions were a plating time of 20 minutes, pH of 11.5, and bath temperature of 20°C , with a plating solution composition of 29 g/l copper sulfate, 25 g/l sodium carbonate, 140 g/l tartrate, 40 g/l sodium hydroxide, and 150 ml 37% formaldehyde.

Comparison 5

[0081] Ring-shaped bonded magnets obtained by the same method as in Embodiment 2 were washed, then coated with a mixture of a phenol resin and nickel powder under the conditions noted below to form a $10\text{ }\mu\text{m}$ electrically conductive resin film. The magnets and 5 mm copper balls were then loaded to 60% barrel capacity in a vibrating barrel, and smoothing and polishing were performed by barrel polishing for 60 minutes with an amplitude of 20 mm.

40 **[0082]** Nickel plating was then performed under the same conditions as in Embodiment 2. The ring-shaped bonded magnets obtained were subjected to an environmental test (humidity resistance test) under the same conditions as in Embodiment 2. The results and film thickness dimensional precision (humidity resistance test) were performed. The results are given in Tables 3 and 4.

45 **[0083]** The electrically conductive coating process conditions were a process time of 30 minutes using a treatment solution composition of 5 wt.% phenol resin, 5 wt.% nickel powder (particle size $0.7\text{ }\mu\text{m}$ or smaller), and 90 wt.% MEK (methylene ketone).

50 **[0084]** As may be seen from Table 4, spot rusting was found in Comparison 4 after 700 hours and in Comparison 5 after 600 hours. In Embodiment 2, on the other hand, no spot rusting could be found under a 30-power microscope even after 800 hours.

Table 3

	Before humidity resistance test			After humidity resistance test			Magnetic property deterioration ratio (%)		
	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)
Embodiment 2	6.7	9.0	9.1	6.5	8.7	8.7	4.4	4.4	5.4
Comparison 4	6.7	8.9	9.1	6.3	8.5	8.3	7.4	6.6	9.8
Comparison 5	6.7	9.0	9.1	6.3	8.7	8.2	7.4	7.7	10.9

Rate of deterioration in magnetic properties (%) =

$$\frac{[(\text{new material magnetic properties}) - (\text{magnetic properties after humidity-resistance test})] / (\text{new material magnetic properties}) \times 100}{}$$

Table 4

	Surface condition at humidity resistance test time	Film thickness dimensional precision (μm)	Manufacturing method
Embodiment 2	No change (no rusting)	22±1	Sealing process + Cu film layer + Ni plating
Comparison 4	Spot rusting after 700 hours	25±2	Sealing process + non-electrolytic Cu plating + Ni plating
Comparison 5	Spot rusting after 600 hours	28±5	Electrically conductive resin layer + smoothing Ni plating

Embodiment 3

[0085] Ring-shaped bonded magnets measuring 25 mm (outer diameter) × 23 mm (inner diameter) × 3 mm (height) were manufactured by the same method as in Embodiment 1. The properties of the bonded magnets obtained were Br = 6.9 kG, iHc = 9.1 kOe, and (BH)_{max} = 9.3 MGOe.

[0086] The bonded magnets obtained were placed in a vibrating barrel and subjected to dry-process barrel polishing, using short rod-shaped tin pieces having diameters of 2 mm and lengths of 1 mm, to form an electrically conductive coating layer of fine tin pieces. The press-fitting depth of the fine pieces in the resin surface was approximately 0.9 μm and the coating thickness on the magnetic powder surfaces was 0.4 μm. The barrel polishing treatment conditions were the same as in Embodiment 1.

[0087] Washing was then performed, and copper electroplating was conducted in a rack plating apparatus, after which nickel electroplating was performed. The film thickness after plating was 22 μm on the inner diameter side and 23 μm on the outer diameter side. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 5. The surface condition results and film thickness dimensional precision at

the time of the humidity resistance test are noted in Table 6.

[0088] The copper electroplating conditions were a current density of 2.5 A/dm^2 , plating time 5 hours, pH 10, and bath temperature 40°C , with a plating solution composition of 20 g/l copper and 10 g/l free cyanogen. The nickel electroplating conditions were the same as in Embodiment 1.

Embodiment 4

[0089] Ring-shaped bonded magnets obtained by the same method as in Embodiment 3 were placed in a vibrating barrel and a dry-process barrel treatment was conducted, using rod-shaped zinc pieces having diameters of 1 mm and lengths of 2 mm, to form an electrically conductive coating layer of fine zinc pieces. The press-fitting depth of the fine zinc pieces in the resin surface was approximately $0.8 \mu\text{m}$ and the coating thickness on the magnet powder surfaces was $0.2 \mu\text{m}$. The barrel polishing treatment conditions were the same as in Embodiment 1.

[0090] Then copper and nickel plating were conducted under the same conditions as in Embodiment 3. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 5. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are given in Table 6.

Embodiment 5

[0091] Ring-shaped bonded magnets obtained by the same method as in Embodiment 3 were placed in a vibrating barrel and a dry-process barrel treatment was conducted, using rod-shaped lead pieces having diameters of 1 mm and lengths of 1 mm, to form an electrically conductive coating layer of fine lead pieces. The press-fitting depth of the fine lead pieces in the resin surface was approximately $0.9 \mu\text{m}$ and the coating thickness on the magnet powder surfaces was $0.6 \mu\text{m}$. The barrel polishing treatment conditions were the same as in Embodiment 1.

[0092] Then copper and nickel plating were conducted under the same conditions as in Embodiment 3. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 5. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are given in Table 6.

Comparison 6

[0093] Ring-shaped bonded magnets obtained by the same method as that in Embodiment 3 were washed and subjected to non-electrolytic copper plating. The plating thickness was $5 \mu\text{m}$. After the non-electrolytic copper plating, copper and nickel plating were conducted under the same conditions as in Embodiment 3. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 5. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are given in Table 6. The non-electrolytic copper plating conditions were the same as in Comparison 1.

Comparison 7

[0094] Ring-shaped bonded magnets obtained by the same method as that in Embodiment 3 were washed, and then a $10 \mu\text{m}$ electrically conductive coating film was formed with a mixture of a phenol resin and nickel powder. After this treatment copper and nickel plating were performed under the same conditions as in Embodiment 3. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 5. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are given in Table 6. The non-electrolytic copper plating conditions were the same as in Comparison 2.

Comparison 8

[0095] Ring-shaped bonded magnets obtained by the same method as that in Embodiment 3 were washed, a phenol resin layer was preformed as a bonding layer by an immersion method, silver powder (particle size $0.7 \mu\text{m}$ or smaller) was made to adhere to the surface thereof, and a $7 \mu\text{m}$ electrically conductive coating layer was formed in a vibrating barrel. After the vibrating barrel treatment, copper and nickel plating were conducted under the same conditions as in Embodiment 3. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity

resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 5. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are given in Table 6. The non-electrolytic copper plating conditions were the same as in Comparison 3.

Table 5

	Before humidity resistance test			After humidity resistance test			Magnetic property deterioration ratio (%)		
	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)
Embodiment 3	6.7	9.0	9.0	6.7	8.9	9.0	2.8	2.2	3.2
Embodiment 4	6.7	9.0	9.0	6.7	8.8	9.0	2.8	3.2	3.2
Embodiment 5	6.7	9.0	9.0	6.6	8.8	8.9	4.4	3.3	4.3
Comparison 6	6.5	8.7	8.8	5.8	7.6	7.7	15.9	16.5	17.2
Comparison 7	6.5	8.9	8.9	6.2	8.4	8.5	10.1	7.7	8.6
Comparison 8	6.5	8.9	9.0	6.2	8.5	8.5	10.1	6.6	8.6

Rate of deterioration in magnetic properties (%) =

$$\frac{[(\text{new material magnetic properties}) - (\text{magnetic properties after humidity-resistance test})] / (\text{new material magnetic properties}) \times 100}{}$$

Table 6

	Surface condition at humidity resistance test time	Film thickness dimensional precision (μm)	Manufacturing method
Embodiment 3	No change (no rusting)	22±1	Sn film layer + Cu, Ni plating
Embodiment 4	No change (no rusting)	22±1	Zn coating layer + Cu, Ni plating
Embodiment 5	No change (no rusting)	22±1	Pb coating layer + Cu, Ni plating
Comparison 6	Spot rusting after 130 hours	26±2	Non-electrolytic Cu plating + Cu, Ni plating
Comparison 7	Minute rusting after 250 hours	32±9	Electrically conductive resin layer + Cu, Ni plating
Comparison 8	Minute rusting after 330 hours	28±10	Electrically conductive film layer + Cu, Ni plating

[0096] As is evident from Tables 5 and 6, spot rusting was found in Comparison 6 after approximately 130 hours, in Comparison 7 after 250 hours, and Comparison 8 after approximately 330 hours. In Embodiment 3, on the other hand, no spot rusting could be found under a 30-power microscope even after 500 hours.

5 Embodiment 6

[0097] Ring-shaped bonded magnets measuring 34 mm (outer diameter) \times 31 mm (inner diameter) \times 8 mm (height) were manufactured by the same method as in Embodiment 1. The properties of the bonded magnets obtained were $B_r = 6.7$ kG, $iH_c = 9.1$ kOe, and $(BH)_{max} = 9.1$ MGOe.

10 **[0098]** The obtained magnets were subjected to a sealing and smoothing treatment with Al_2O_3 spherical barrel stones having an average diameter of 3 mm, using a vibrating barrel, under the same conditions and using the same method as in Embodiment 2.

[0099] The bonded magnets were next placed in a vibrating barrel and subjected to dry-process barrel polishing, using short rod-shaped pieces of tin, zinc, and lead having diameters of 1 mm and lengths of 1 mm to form an electrically conductive coating layer of fine metal pieces. The press-fitting depths of the fine metal pieces in the resin surface and porous portions, and the coating thickness on the magnetic powder surfaces, are indicated in Table 7. The barrel polishing treatment conditions were the same as in Embodiment 2.

15 **[0100]** Washing was then performed, and nickel electroplating was conducted in a rack plating apparatus, after which nickel plating was performed. The film thickness after plating was 21 μm on the inner diameter side and 22 μm on the outer diameter side. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 1000 hours at 80°C and relative humidity of 90%. The results thereof and the film thickness dimensional precision are noted in Tables 8 and 9. The copper and nickel electroplating conditions were the same as in Embodiment 2.

25 Comparison 9

[0101] Ring-shaped bonded magnets obtained by the same method as in Embodiment 6 were washed, subjected to a sealing and surface smoothing treatment as in Embodiment 6, again washed, and subjected to non-electrolytic copper plating. The plating thickness was 5 μm . After non-electrolytic copper plating, copper plating and nickel plating were performed under the same conditions as in Embodiment 6.

30 **[0102]** The ring-shaped bonded magnets obtained were subjected to an environmental test (humidity resistance test) under the same conditions as in Embodiment 6. The magnet properties before and after the humidity resistance test are noted in Table 8. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are noted in Table 9. The non-electrolytic copper plating conditions were the same as in Comparison 4.

Comparison 10

40 **[0103]** Ring-shaped bonded magnets obtained by the same method as that in Embodiment 6 were washed, a mixture of phenol resin and nickel powder was coated on to form a 10 μm electrically conductive resin coating film, and the magnets were loaded together with 5 mm steel balls into a vibrating barrel, to 60% of barrel capacity, and smoothing and polishing were performed by barrel polishing for 60 minutes at an amplitude of 20 mm.

45 **[0104]** Then copper plating and nickel plating were performed under the same conditions as in Embodiment 6. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) under the same conditions as in Embodiment 6. The results thereof and the film thickness dimensional precision are noted in Tables 8 and 9. The electrically conductive coating film treatment conditions were the same as in Comparison 5.

Table 7

Metal pieces	Press-fitting depth (μm) in resin surface and porous portion	Coating thickness (μm) on magnetic powder sur- faces
Sn	0.9	0.4
Zn	0.7	0.3
Pb	0.9	0.5

Table 8

	Before humidity resistance test			After humidity resistance test			Magnetic property deterioration ratio (%)		
	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)
Embodiment 6 Sn	6.6	9.0	9.0	6.4	8.6	8.6	4.5	5.5	5.5
Embodiment 6 Zn	6.6	9.0	9.0	6.3	8.6	8.6	6.0	5.5	5.5
Embodiment 6 Pb	6.6	9.0	9.0	6.3	8.5	8.5	6.0	6.6	6.6
Comparison 9	6.6	8.9	9.0	6.2	8.4	8.3	7.5	7.7	8.8
Comparison 10	6.6	9.0	9.0	6.0	8.2	8.1	10.4	9.9	11.0

Rate of deterioration in magnetic properties (%) =

$$\frac{\{(\text{new material magnetic properties}) - (\text{magnetic properties after humidity-resistance test})\}}{(\text{new material magnetic properties})} \times 100$$

Table 9

	Surface condition at humidity resistance test time	Film thickness dimensional precision (μm)	Manufacturing method
Embodiment 6 Sn	No change (no rusting)	22±1	Sealing treatment + Sn film layer + Cu, Ni plating
Embodiment 6 Zn	No change (no rusting)	22±1	Sealing treatment + Zn coating layer + Cu, Ni plating
Embodiment 6 Pb	No change (no rusting)	22±1	Sealing treatment + Pb coating layer + Cu, Ni plating
Comparison 9	Spot rusting after 800 hours	27±2	Sealing treatment + non-electrolytic Cu plating + Cu, Ni plating
Comparison 10	Spot rusting after 600 hours	30±5	Electrically conductive resin layer + smoothing and polishing + Cu, Ni plating

[0105] As may be seen from Table 9, spot rusting was found in Comparison 9 after approximately 800 hours, and in Comparison 10 after 600 hours. In Embodiment 6, on the other hand, no spot rusting could be found under a 30-power microscope even after 1000 hours.

Embodiment 7

[0106] Ring-shaped bonded magnets measuring 21 mm (outer diameter) \times 18 mm (inner diameter) \times 4 mm (height) were manufactured by the same method as in Embodiment 1. The properties of the bonded magnets obtained were $B_r = 6.8$ kG, $iH_c = 9.1$ kOe, and $(BH)_{max} = 9.2$ MGOe, as noted in Table 11.

[0107] The bonded magnets obtained were placed in a vibrating barrel and dry-process barrel polishing was performed, using short rod-shaped Fe, Ni, Co, and Cr pieces having diameters of 0.7 mm and lengths of 0.5 mm to form an electrically conductive coating layer of fine pieces of those metals. The press-fitting depths of the fine metal pieces in the resin surface and the coating thickness on the magnetic powder surfaces are noted in Table 10. The barrel polishing treatment conditions were the same as in Embodiment 1.

[0108] Washing was then performed, copper electroplating was performed in a rack apparatus, and nickel electroplating was then performed. After plating, the film thickness was 18 μm on the inner diameter side and 21 μm on the outer diameter side. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The magnet properties after the humidity resistance test are noted in Table 12. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are noted in Table 13. The conditions for the copper electroplating and nickel electroplating were the same as in Embodiment 1.

Comparison 11

[0109] Ring-shaped bonded magnets obtained by the same method as that in Embodiment 7 were washed and subjected to non-electrolytic copper plating. The plating thickness was 6 μm . After the non-electrolytic copper plating, copper and nickel plating were conducted under the same conditions as in Embodiment 3. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 12. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are given in Table 13. The non-electrolytic copper plating conditions were the same as in Comparison 1.

Comparison 12

[0110] Ring-shaped bonded magnets obtained by the same method as that in Embodiment 7 were washed, and then a 10 μm electrically conductive coating film was formed with a mixture of a phenol resin and nickel powder. After this treatment copper and nickel plating were performed under the same conditions as in Embodiment 7. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 12. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are given in Table 13. The non-electrolytic copper plating conditions were the same as in Comparison 2.

Comparison 13

[0111] Ring-shaped bonded magnets obtained by the same method as that in Embodiment 7 were washed, a phenol resin layer was preformed as a bonding layer by an immersion method, silver powder (particle size 0.7 μm or smaller) was made to adhere to the surface thereof, and a 7 μm electrically conductive coating layer was formed in a vibrating barrel. After the vibrating barrel treatment, copper and nickel plating were conducted under the same conditions as in Embodiment 7. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 12. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are given in Table 13. The non-electrolytic copper plating conditions were the same as in Comparison 3.

Table 10

Metal pieces	Press-fitting depth (μm) in resin surface and porous portion	Coating thickness (μm) on magnetic powder sur- faces
Fe	0.5	0.1

Table 10 (continued)

Metal pieces	Press-fitting depth (μm) in resin surface and porous portion	Coating thickness (μm) on magnetic powder sur- faces
Ni	0.4	0.1
Co	0.3	0.1
Cr	0.3	0.1

Table 11

	New material magnetic properties		
	Br(kG)	iHc(kOe)	(BH)max MGOe
Embodiment 7 Fe	6.8	9.1	9.2
Embodiment 7 Ni	6.8	9.1	9.2
Embodiment 7 Co	6.8	9.1	9.2
Embodiment 7 Cr	6.8	9.1	9.2
Comparison 11	6.8	9.1	9.2
Comparison 12	6.8	9.1	9.2
Comparison 13	6.8	9.1	9.2

Table 12

	Before humidity resistance test			After humidity resistance test			Magnetic property deterioration ratio (%)		
	Br (kG)	iHc (kOe)	(BH)max (MGOe)	Br (kG)	iHc (kOe)	(BH)max (MGOe)	Br (kG)	iHc	(BH)max (MGOe)
Embodiment 7 Fe	6.7	9.0	9.0	6.4	8.7	8.7	5.9	4.4	5.5
Embodiment 7 Ni	6.7	9.0	9.0	6.4	8.7	8.7	5.9	4.4	5.5
Embodiment 7 Co	6.7	9.0	9.0	6.4	8.6	8.7	5.9	5.5	5.5
Embodiment 7 Cr	6.7	9.0	9.0	6.4	8.6	8.6	5.9	5.5	6.6
Comparison 11	6.4	8.7	8.7	5.7	7.7	7.7	16.2	15.4	16.3
Comparison 12	6.6	8.9	9.0	6.3	8.5	8.5	7.4	6.6	7.6
Comparison 13	6.6	9.0	9.0	6.3	8.4	8.5	7.4	7.7	7.6

Rate of deterioration in magnetic properties (%) =

$$\frac{\{(\text{new material magnetic properties}) - (\text{magnetic properties after humidity-resistance test})\}}{(\text{new material magnetic properties})} \times 100$$

Table 13

	Surface condition at humidity resistance test time	Film thickness dimensional precision (μm)	Manufacturing method
Embodiment 7 Fe	No change (no rusting)	18±2	Fe coating layer + Ni plating
Embodiment 7 Ni	No change (no rusting)	18±2	Ni coating layer + Ni plating
Embodiment 7 Co	No change (no rusting)	18±2	Co coating layer + Ni plating
Embodiment 7 Cr	No change (no rusting)	18±2	Pb coating layer + Ni plating
Comparison 11	Spot rusting after 130 hours	24±2	Non-electrolytic Cu plating + Ni plating
Comparison 12	Spot rusting after 350 hours	28±10	Electrically conductive resin layer + Ni plating

Table 13 (continued)

	Surface condition at humidity resistance test time	Film thickness dimensional precision (μm)	Manufacturing method
Comparison 13	Spot rusting after 370 hours	25 \pm 10	electrically conductive resin layer + Ni plating

[0112] As is evident from Tables 10 to 13, spot rusting was found in Comparison 11 after approximately 130 hours, in Comparison 12 after 350 hours, and in Comparison 13 after approximately 370 hours. In Embodiment 7, on the other hand, no spot rusting was found under a 30-power microscope even after 500 hours.

Embodiment 8

[0113] Ring-shaped bonded magnets measuring 29 mm (outer diameter) \times 25 mm (inner diameter) \times 5 mm (height) were manufactured by the same method as in Embodiment 1. The properties of the bonded magnets obtained were Br = 6.7 kG, iHc = 9.3 kOe, and (BH)_{max} = 9.5 MGOe, as noted in Table 15.

[0114] The obtained magnets were subjected to a sealing and smoothing treatment with Al₂O₃ spherical barrel stones having an average diameter of 3 mm, using a vibrating barrel, under the same conditions and using the same method as in Embodiment 2.

[0115] The bonded magnets were next placed in a vibrating barrel and subjected to dry-process barrel polishing, using short rod-shaped pieces of Fe, Ni, Co, and Cr, having diameters of 0.5 mm and lengths of 0.4 mm to form an electrically conductive coating layer of fine metal pieces. The press-fitting depths of the fine metal pieces in the resin surface and porous portions, and the coating thickness on the magnetic powder surfaces, are indicated in Table 14. The barrel polishing treatment conditions were the same as in Embodiment 2.

[0116] Washing was then performed, and nickel electroplating was conducted in a rack plating apparatus, after which nickel plating was performed. The film thickness after plating was 20 μm on the inner diameter side and 22 μm on the outer diameter side. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 1000 hours at 80°C and relative humidity of 90%. The results thereof and the film thickness dimensional precision are noted in Tables 16 and 17.

[0117] The copper and nickel electroplating conditions were the same as in Embodiment 2. The zinc substitution treatment conditions were a process time of 40 seconds, bath temperature of 22°C, and solution composition of 300 g/l sodium hydroxide, 40 g/l zinc oxide, 1 g/l ferric chloride, and 30 g/l Rossel salts. The film thickness was 0.01 μm .

Comparison 14

[0118] Ring-shaped bonded magnets obtained by the same method as in Embodiment 8 were washed, subjected to a sealing and surface smoothing treatment as in Embodiment 6, again washed, and subjected to non-electrolytic copper plating. The plating thickness was 5 μm . After non-electrolytic copper plating, copper plating and nickel plating were performed under the same conditions as in Embodiment 8.

[0119] The ring-shaped bonded magnets obtained were subjected to an environmental test (humidity resistance test) under the same conditions as in Embodiment 8. The results thereof and film thickness dimensional precision are noted in Tables 16 and 17. The non-electrolytic copper plating conditions were the same as in Comparison 4.

Comparison 15

[0120] Ring-shaped bonded magnets obtained by the same method as that in Embodiment 6 were washed, a mixture of phenol resin and nickel powder was coated on to form a 10 μm electrically conductive resin coating film, and the magnets were loaded together with 5 mm steel balls into a vibrating barrel, to 60% of barrel capacity, and smoothed and polished by barrel polishing for 60 minutes at an amplitude of 20 mm.

[0121] Then copper plating and nickel plating were performed under the same conditions as in Embodiment 8. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) under the same conditions as in Embodiment 6. The results thereof and the film thickness dimensional precision are noted in Tables 16 and 17. The electrically conductive coating film treatment conditions were the same as in Comparison 5.

Table 14

Metal pieces	Press-fitting depth (μm) in resin surface and porous portion	Coating thickness (μm) on magnetic powder sur- faces
Fe	0.5	0.1
Ni	0.5	0.1
Co	0.4	0.1
Cr	0.4	0.1

Table 15

	New material magnetic properties		
	Br (kG)	iHc (kOe)	(BH)max (MGOe)
Embodiment 8 Fe	6.9	9.3	9.5
Embodiment 8 Ni	6.9	9.3	9.5
Embodiment 8 Co	6.9	9.3	9.5
Embodiment 8 Cr	6.9	9.3	9.5
Comparison 14	6.9	9.3	9.5
Comparison 15	6.9	9.3	9.5

Table 16

	Before humidity resistance test			After humidity resistance test			Magnetic property deterioration ratio (%)		
	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)	Br (kG)	iHc (kOe)	(BH) _{max} (MGOe)
Embodiment 8 Fe	6.7	9.2	9.4	6.6	8.9	9.0	4.3	4.3	5.3
Embodiment 8 Ni	6.7	9.2	9.4	6.5	8.9	8.9	5.8	4.3	6.3
Embodiment 8 Co	6.6	9.2	9.4	6.4	8.8	8.8	7.2	5.4	7.4
Embodiment 8 Cr	6.7	9.2	9.4	6.5	8.7	8.8	5.8	6.5	7.4
Comparison 14	6.6	9.1	9.3	6.2	8.5	8.5	10.1	8.6	10.5
Comparison 15	6.7	9.1	9.3	6.2	8.3	8.4	10.1	10.8	11.6

Rate of deterioration in magnetic properties (%) =

$$\frac{[(\text{new material magnetic properties}) - (\text{magnetic properties after humidity-resistance test})] / (\text{new material magnetic properties}) \times 100}{}$$

Table 17

	Surface condition at humidity resistance test time	Film thickness dimensional precision (μm)	Manufacturing method
Embodiment 8 Fe	No change (no rusting)	20±2	Sealing process + Fe coating layer + Ni plating
Embodiment 8 Ni	No change (no rusting)	20±2	Sealing process + Ni coating layer + Ni plating
Embodiment 8 Co	No change (no rusting)	20±2	Sealing process + Co coating layer + Ni plating
Embodiment 8 Cr	No change (no rusting)	20±2	Sealing process + Cr coating layer + Ni plating
Comparison 14	Spot rusting after 700 hours	25±2	Sealing process + non-electrolytic Cu plating + Ni plating

Table 17 (continued)

	Surface condition at humidity resistance test time	Film thickness dimensional precision (μm)	Manufacturing method
Comparison 15	Spot rusting after 550 hours	26 \pm 5	Electrically conductive resin layer + smoothing and polishing + Ni plating

[0122] As is seen from Table 17, spot rusting was found in Comparison 14 after 700 hours, and in Comparison 15 after 550 hours. By comparison therewith, in Embodiment 8, no spot rusting was found under a 30-power microscope even after 800 hours.

Embodiment 9

[0123] Ring-shaped bonded magnets measuring 20 mm (outer diameter) \times 17 mm (inner diameter) \times 6 mm (height) were manufactured by the same method as in Embodiment 1. The properties of the bonded magnets obtained were Br = 6.9 kG, iHc = 9.4 kOe, and (BH)_{max} = 9.6 MGOe.

[0124] The bonded magnets obtained were placed in a vibrating barrel and subjected to dry-process barrel polishing, using short rod-shaped aluminum pieces having diameters of 0.8 mm and lengths of 1 mm, to form an electrically conductive coating layer of fine aluminum pieces. The press-fitting depth of the fine pieces in the resin surface was approximately 0.9 μm and the coating thickness on the magnetic powder surfaces was 0.5 μm . The barrel polishing treatment conditions were the same as in Embodiment 1.

[0125] Washing was then performed, a zinc substitution treatment was administered, and then nickel electroplating was conducted in a rack plating apparatus, after which nickel electroplating was performed. The film thickness after plating was 19 μm on the inner diameter side and 21 μm on the outer diameter side. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 18. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are noted in Table 19. The nickel electroplating conditions were the same as in Embodiment 1.

Comparison 16

[0126] Ring-shaped bonded magnets obtained by the same method as that in Embodiment 9 were washed and subjected to non-electrolytic copper plating. The plating thickness was 6 μm . After the non-electrolytic copper plating, copper and nickel plating were conducted under the same conditions as in Embodiment 3. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 18. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are given in Table 19. The non-electrolytic copper plating conditions were the same as in Comparison 1.

Comparison 17

[0127] Ring-shaped bonded magnets obtained by the same method as that in Embodiment 9 were washed, and then a 10 μm electrically conductive coating film was formed with a mixture of a phenol resin and nickel powder. After this treatment, nickel plating was performed under the same conditions as in Embodiment 9. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 18. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are given in Table 19. The non-electrolytic copper plating conditions were the same as in Comparison 2.

Comparison 18

[0128] Ring-shaped bonded magnets obtained by the same method as that in Embodiment 9 were washed, a phenol resin layer was preformed as a bonding layer by an immersion method, silver powder (particle size 0.7 μm or smaller) was made to adhere to the surface thereof, and a 7 μm electrically conductive coating layer was formed in a vibrating barrel. After the vibrating barrel treatment, nickel plating was conducted under the same conditions as in Embodiment 9. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance

test are noted in Table 18. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are given in Table 19. The non-electrolytic copper plating conditions were the same as in Comparison 3.

Table 18

	Before humidity resistance test			After humidity resistance test			Magnetic property deterioration ratio (%)		
	Br (kG)	iHc (kOe)	(BH) _{max} (MGoe)	Br (kG)	iHc (kOe)	(BH) _{max} (MGoe)	Br (kG)	iHc (kOe)	(BH) _{max} (MGoe)
Embodiment 9	6.7	9.0	9.2	6.4	8.8	9.0	7.2	6.4	6.3
Comparison 16	6.4	8.7	8.9	5.7	7.9	8.0	17.4	16.0	16.7
Comparison 17	6.6	8.9	9.3	6.2	8.6	8.7	10.1	8.5	9.4
Comparison 18	6.6	9.0	9.2	6.2	8.6	8.7	10.1	8.5	9.4

Rate of deterioration in magnetic properties (%) =

$$\frac{[(\text{new material magnetic properties}) - (\text{magnetic properties after humidity-resistance test})] / (\text{new material magnetic properties}) \times 100}{}$$

Table 19

	Surface condition at humidity resistance test time	Film thickness dimensional precision (μm)	Manufacturing method
Embodiment 9	No change (no rusting)	20±2	Al coating layer (zinc substitution) + Ni plating
Comparison 16	Spot rusting after 120 hours	27±2	Non-electrolytic Cu plating + Ni plating
Comparison 17	Slight rusting after 270 hours	28±10	Electrically conductive resin layer + Ni plating
Comparison 18	Slight rusting after 300 hours	26±10	Electrically conductive coating layer + Ni plating

[0129] As is evident from Tables 18 and 19, spot rusting was found in Comparison 16 after approximately 120 hours, in Comparison 17 after 270 hours, and in Comparison 18 after approximately 300 hours. In Embodiment 9, on the other hand, no spot rusting was found under a 30-power microscope even after 500 hours.

[0130] Ring-shaped bonded magnets measuring 36 mm (outer diameter) × 33 mm (inner diameter) × 3 mm (height) were manufactured by the same method as in Embodiment 1. The properties of the bonded magnets obtained were Br = 6.7 kG, iHc = 9.2 kOe, and (BH)_{max} = 9.5 MGoe.

5 [0131] 220 magnets so obtained were placed together with spherical Al_2O_3 barrel stones having an average diameter of 4 mm in a vibrating barrel having a capacity of 20 liters. Then a vegetable medium consisting of walnut meat having a diameter of 2 mm or so the surface whereof had been modified with Al_2O_3 having a particle size of 2 μm or so was loaded to 50% of barrel capacity and surface polishing was performed in a dry process for 150 minutes, thus performing a treatment for both sealing and smoothing.

10 [0132] The bonded magnets obtained were placed in a vibrating barrel and subjected to dry-process barrel polishing, using short rod-shaped aluminum pieces having diameters of 0.5 mm and lengths of 0.7 mm, to form an electrically conductive coating layer of fine aluminum pieces. The press-fitting depth of the fine pieces in the resin surface was approximately 1.1 μm and the coating thickness on the magnetic powder surfaces was 0.6 μm . The barrel polishing treatment conditions were the same as in Embodiment 1.

15 [0133] Washing was then performed, a zinc substitution treatment was administered, and then nickel electroplating was conducted in a rack plating apparatus, after which nickel electroplating was performed. The film thickness after plating was 17 μm on the inner diameter side and 19 μm on the outer diameter side. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 500 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 20. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are noted in Table 21.

20 [0134] The copper and nickel electroplating conditions were the same as in Embodiment 2. The zinc substitution treatment conditions were a process time of 40 seconds, bath temperature of 22°C, and solution composition of 300 g/l sodium hydroxide, 40 g/l zinc oxide, 1 g/l ferric chloride, and 30 g/l Rossel salts. The film thickness was 0.01 μm .

Comparison 19

25 [0135] Ring-shaped bonded magnets obtained by the same method as in Embodiment 10 were washed, subjected to a sealing and surface smoothing treatment as in Embodiment 10, again washed, and subjected to non-electrolytic copper plating. The plating thickness was 6 μm . After non-electrolytic copper plating, copper plating and nickel plating were performed under the same conditions as in Embodiment 10. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 1000 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 20. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are given in Table 21. The non-electrolytic copper plating conditions were the same as in Comparison 4.

Comparison 20

35 [0136] Ring-shaped bonded magnets obtained by the same method as that in Embodiment 10 were washed, and then a 12 μm electrically conductive coating film was formed with a mixture of a phenol resin and nickel powder, under the conditions noted below. These magnets were loaded together with 2 mm steel balls in a vibrating barrel to 70% of barrel capacity and smoothing and polishing were performed by barrel polishing for 90 minutes.

40 [0137] Then nickel plating was performed under the same conditions as in Embodiment 10. The ring-shaped bonded magnets obtained were subjected to an environment test (humidity resistance test) for 1000 hours at 80°C and relative humidity of 90%. The properties of the magnets after the humidity resistance test are noted in Table 20. The surface condition results and film thickness dimensional precision at the time of the humidity resistance test are given in Table 21. The non-electrolytic copper plating conditions were the same as in Comparison 5.

45

50

55

Table 20

	Before humidity resistance test			After humidity resistance test			Magnetic property deterioration ratio (%)		
	Br (kG)	iHc (kOe)	(BH)max (MGOe)	Br (kG)	iHc (kOe)	(BH)max (MGOe)	Br (kG)	iHc (kOe)	(BH)max (MGOe)
Embodiment 10	6.5	9.0	9.2	6.4	8.7	9.0	4.5	5.4	5.3
Comparison 19	6.4	8.7	8.9	6.0	8.3	8.5	10.5	9.8	10.5
Comparison 20	6.4	8.9	9.3	6.1	8.4	8.5	9.0	8.7	10.5

Rate of deterioration in magnetic properties (%) =

$$\frac{[(\text{new material magnetic properties}) - (\text{magnetic properties after humidity-resistance test})] / (\text{new material magnetic properties}) \times 100}{}$$

Table 21

	Surface condition at humidity resistance test time	Film thickness dimensional precision (μm)	Manufacturing method
Embodiment 10	No change (no rusting)	18±2	Sealing process + Al coating layer (zinc substitution) + Ni plating
Comparison 19	Spot rusting after 750 hours	24±2	Sealing process + non-electrolytic Cu plating + Ni plating
Comparison 20	Spot rusting after 680 hours	28±6	Electrically conductive resin layer + smoothing and polishing + Ni plating

[0138] As is evident from Tables 20 and 21, spot rusting was found in Comparison 19 after approximately 750 hours, and in Comparison 20 after 680 hours. In Embodiment 10, on the other hand, no spot rusting was found under a 30-power microscope even after 1000 hours.

INDUSTRIAL APPLICABILITY

[0139] In the present invention, porous R-Fe-B-base bonded magnets are subjected to barrel polishing in a dry process, using as a polishing medium either a mixture of a polishing agent and a vegetable medium, or a polishing agent and a vegetable medium modified with inorganic powder. This makes it possible to seal the porous portions of the R-Fe-B-base bonded magnets with the polishing powder, inorganic powder, and polishing chips, bonding those thereto with the fatty component in the vegetable medium. The bonded magnets can also be modified, it being possible to perform a surface smoothing treatment simultaneously. Furthermore, the R-Fe-B-base bonded magnets are barrel polished in a barrel apparatus, in a dry process, using aluminum of undefined shape such as spherical, massive, or aricular (wire-form), and of required dimensions, press-fitting pulverized fine aluminum pieces into the resin surface and porous portions of the bonded magnet surface and coating the same therewith, or coating the magnetic powder surfaces with fine aluminum pieces, thereby forming an aluminum coating film on the surface of the R-Fe-B-base bonded

magnets, then subjecting the surface of that aluminum coating layer to a zinc substitution treatment, thus making it possible to form an electrolytic plating layer that is tight and which has no pin holes, and to obtain R-Fe-B-base bonded magnets exhibiting extremely outstanding corrosion resistance.

5 Claims

1. A high corrosion-resistant R-Fe-B-base bonded magnet wherein fine metal pieces are pressed into a resin surface and porous portions constituting a surface of said R-Fe-B-base bonded magnet, and covering same, and wherein said R-Fe-B-base bonded magnet comprises a metal coating surface formed by coating surfaces of magnetic powder constituting the surface with the metal fine pieces, and an electrolytic plating layer formed on outermost surface of the magnet with said metal coating surface interposed therebetween.
2. A high corrosion-resistant R-Fe-B-base bonded magnet wherein porous portions formed in surface of said R-Fe-B bonded magnet are sealed with polishing agent powder and bonded magnet polished chips, or also with inorganic powder bonded thereto with fatty component of a vegetable medium, fine metal pieces are pressed into resin surface and said porous portions constituting a magnet surface, covering same, and wherein said R-Fe-B-base bonded magnet comprises a metal coating surface formed by coating surfaces of magnetic powder constituting the surface of the magnet with the metal fine pieces, and an electrolytic plating layer formed on outermost surface of the magnet with said metal coating surface interposed therebetween.
3. The high corrosion-resistant R-Fe-B-base bonded magnet according to claim 1 or claim 2, wherein said fine metal pieces are Cu, Sn, Zn, Pb, Cd, In, Au, Ag, Fe, Ni, Co, Cr, or Al, or alloy thereof.
4. The high corrosion-resistant R-Fe-B-base bonded magnet according to claim 1 or claim 2, wherein thickness of press-fit coating layer of fine metal pieces formed in the resin surface and porous portions is 0.1 μm to 2 μm .
5. The high corrosion-resistant R-Fe-B-base bonded magnet according to claim 1 or claim 2, wherein thickness of coating layer of fine metal pieces coated on magnetic powder surfaces is 1.0 μm or less.
6. The high corrosion-resistant R-Fe-B-base bonded magnet according to claim 5, wherein thickness of coating layer of Cu, Fe, Ni, Co, or Cr, or alloy thereof, coated on magnetic powder surfaces is 0.2 μm or less.
7. The high corrosion-resistant R-Fe-B-base bonded magnet according to claim 1 or claim 2, having an electrolytic plating layer with an intervening zinc layer formed on surface of aluminum or aluminum alloy coating surface on said magnet surface, when said fine metal pieces are aluminum or alloy thereof.
8. A method of manufacturing high corrosion-resistant R-Fe-B-base bonded magnets comprising the steps of:

loading R-Fe-B-base bonded magnets and fine metal pieces of undefined shape into a barrel apparatus, where barrel polishing is performed by a dry process, so that pulverized fine metal pieces are pressed into resin surface and porous portions constituting surface of the R-Fe-B bonded magnets, covering same, and surfaces of magnet powder constituting said magnet surface are covered with said fine metal pieces, whereby a metal coating layer is formed on said magnet surfaces; and

electrolytic plating outermost surface for forming an electrolytic plating layer over the electrically conductive metal coating layer thus provided.
9. A method of manufacturing high corrosion-resistant R-Fe-B-base bonded magnets comprising the steps of:

barrel polishing R-Fe-B-base bonded magnets by a dry process, using as a medium a mixture of a polishing agent and a vegetable medium or a vegetable medium having surface thereof modified with an inorganic powder, so that porous portions formed in surface of said R-Fe-B bonded magnet are sealed with polishing agent powder and bonded magnet polished chips, or also with inorganic powder bonded thereto with fatty component of a vegetable medium, and the surface is smoothed and modified;

loading said bonded magnets and fine metal pieces of undefined shape into a barrel apparatus where barrel polishing is done, in a dry process, so that pulverized fine metal pieces are pressed into resin surface and said porous portions of said magnets, covering same, and surfaces of magnet powder on the surface are covered with fine metal pieces, whereby imparting electrical conductivity to the surface of said R-Fe-B-base bonded magnets; and then forming an electrolytic plating layer on outermost surface of the magnet.

10. The method of manufacturing high corrosion-resistant R-Fe-B-base bonded magnets according to claim 8 or claim 9, wherein said fine metal pieces are Cu, Sn, Zn, Pb, Cd, In, Au, Ag, Fe, Ni, Co, Cr, or Al, or alloy thereof.
- 5 11. The method of manufacturing high corrosion-resistant R-Fe-B-base bonded magnets according to claim 8 or claim 9, wherein an electrolytic plating layer is formed with an intervening zinc layer formed by a zinc substitution process on surface of aluminum coating on said magnet surfaces, when said fine metal pieces are aluminum.
12. The method of manufacturing high corrosion-resistant R-Fe-B-base bonded magnets according to claim 8 or claim 9, wherein said fine metal pieces of undefined shape are spherical, massive, or aricular in shape and 0.1 mm to 10
10 mm in size.
13. The method of manufacturing high corrosion-resistant R-Fe-B-base bonded magnets according to claim 12, wherein said fine Cu, Fe, Ni, Co, or Cr pieces of undefined shape are spherical, massive, or aricular in shape and 0.1 mm to 5 mm in size.
15
14. The method of manufacturing high corrosion-resistant R-Fe-B-base bonded magnets according to claim 8 or claim 9, wherein size of fine metal pieces pulverized by barrel polishing is 5 μ m or less in length.
15. The method of manufacturing high corrosion-resistant R-Fe-B-base bonded magnets according to claim 8 or claim 9, wherein barrel polishing is done by using a revolving, vibrating, or centrifugal barrel, with a volumetric ratio
20 between said magnets and said fine metal pieces (magnets/fine metal pieces) of 3 or less.
16. The method of manufacturing high corrosion-resistant R-Fe-B-base bonded magnets according to claim 9, wherein a polishing agent is metal balls or polishing stones of baked and hardened inorganic powder.
25
17. The method of manufacturing high corrosion-resistant R-Fe-B-base bonded magnets according to claim 9, wherein said vegetable medium is vegetable husks, sawdust, fruit rind, or corncobs.
18. The method of manufacturing high corrosion-resistant R-Fe-B-base bonded magnets according to claim 8 or claim 9, wherein said R-Fe-B-base bonded magnets and said fine metal pieces are barrel polished by dry process in an
30 atmosphere of inert gas.

35

40

45

50

55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/04829

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁶ H01F7/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁶ H01F7/02		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1998 Kokai Jitsuyo Shinan Koho 1971-1998 Jitsuyo Shinan Toroku Koho 1996-1998		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 62-290107, A (Seiko Instruments Inc.), 17 December, 1987 (17. 12. 87), Claims (Family: none)	1-7
A	JP, 8-250356, A (Daido Steel Co., Ltd.), 27 September, 1996 (27. 09. 96), Claims (Family: none)	8-18
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 17 November, 1998 (17. 11. 98)		Date of mailing of the international search report 1 December, 1998 (01. 12. 98)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No. --		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)