

## (11) EP 2 123 794 A1

(12)

## **EUROPEAN PATENT APPLICATION** published in accordance with Art. 153(4) EPC

(43) Date of publication: **25.11.2009 Bulletin 2009/48** 

(21) Application number: 07831582.7

(22) Date of filing: 10.11.2007

(51) Int Cl.: C23C 24/04 (2006.01) C23C 26/00 (2006.01)

(86) International application number: **PCT/JP2007/071851** 

(87) International publication number: WO 2008/090662 (31.07.2008 Gazette 2008/31)

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE
SI SK TR

(30) Priority: 26.01.2007 JP 2007017145

(71) Applicants:

 LTT Bio-Pharma Co., Ltd. Minato-ku Tokyo 105-0022 (JP) Sawaguchi, Kazuo
 Higashinakatomi, Aizumi-cho
 Itano-gun Tokushima, 7711222 (JP)

(72) Inventor: SAWAGUCHI, Kazuo Itano-gun Tokushima 771-1222 (JP)

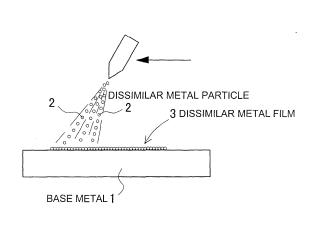
 (74) Representative: Hart-Davis, Jason et al Cabinet Beau de Loménie,
 158, rue de l'Université
 75340 Paris Cedex 07 (FR)

#### (54) METAL SURFACE TREATMENT METHOD

(57) To reliably bond in an alloyed state various kinds of metals on a surface of various base metals in a simple, easy and efficient manner. A metal surface treatment method includes: a shot-peening step of shot-peening a dissimilar metal particle (2) on a surface of a base metal (1), the dissimilar metal particle (2) being a metal particle different from the base metal (1), to provide a dissimilar

metal film (3) on the surface of the base metal (1); and an electron beam irradiation step of irradiating the surface of the base metal (1) with an electron beam (4), the surface of the base metal (1) having been provided with the dissimilar metal film (3) in the shot-peening step, to bond the dissimilar metal film (3) and the base metal (1) together.

FIG. 1



EP 2 123 794 A1

#### Description

Technical Field

5 [0001] The present invention relates to a metal surface treatment method in which a dissimilar metal is bonded on a surface of a base metal.

Background Art

[0002] When a metal undergoes a surface treatment, a surface of the metal is processed into a state best suited for a specified use. For example, the surface is hardened, resistance to wear is improved by a reduced coefficient of friction, or the metal surface is insulated by provision of an insulation layer over the surface. As a metal surface treatment method, there has been developed a method such as a metal plating, a metal spraying, and a carburization. The plating process suffers the disadvantage that a use of various chemicals involves a cumbersome waste liquid treatment. In the spraying process as well, a surface treatment is prone to become difficult in that large-scaled equipment is required for heating metal powder into a molten state to be sprayed on a base metal. Also in the case of the carburization, this method suffers the disadvantage that only a specific kind of chemical element can penetrate into the base metal and the treatment is cumbersome. As a method of overcoming the drawbacks faced by the above-mentioned surface treatment methods, there has been developed a method in which a powdered metal is supplied on the surface of the base metal and then the powdered metal is irradiated with an electron beam to alloy the base metal with the powdered metal. (Refer to Patent Document 1.)

Patent Document 1 JP 2000-216310A

25 Disclosure of the Invention

30

35

40

45

55

Problem To Be Solved by the Invention

[0003] Disclosed in Patent Document 1 is a method in which a layer of powdered metal being composed mainly of molybdenum is provided on the surface of the base metal, the layer of powdered metal is irradiated with a laser or electron beam, and such powder layer is heated above its melting point. According to this method, a good interface layer is formed in the vicinity of the interface bonded with a metal composed mainly of molybdenum, and a metal of the powdered metal layer is bonded on the surface of the base metal. In this method, however, it is difficult that the layer of powdered metal including molybdenum is provided on the surface of the base metal uniformly in a specified thickness. When the layer of powdered metal is not uniformly provided, a surface layer cannot be provided in an ideal state by being irradiated with the electron beam. When the thickness is uneven in the layer of powdered metal, it is difficult to adjust an electron beam in terms of its irradiation energy. This is because the thickness of the layer of powdered metal is determinant in differentiating an energy density of the electron beam required for bonding the layer onto the base metal. Patent Document 1 further describes a technique of spraying the powdered metal mainly composed of molybdenum to be blasted on the surface of the base metal. In the method, a particle whose surface portion is heated above its melting point is impinged upon the surface of the base metal so that the metal mainly composed of the molybdenum is welded on the surface of the base metal. In the surface treatment by a spraying process, however, it is difficult to strongly bond the metal such as the molybdenum on the surface of the base metal.

**[0004]** The present invention has been made to remedy the above-mentioned drawbacks. It is an object of the present invention to provide a metal surface treatment method in which a variety of metals can be reliably bonded on a surface of various kinds of base metals in a simple, easy and efficient manner.

Means for Solving Problems

50 [0005] The metal surface treatment method in accordance with a first aspect of the present invention includes:

a shot-peening step of shot-peening a dissimilar metal particle 2 on a surface of a base metal 1, the dissimilar metal particle 2 being a metal particle different from the base metal 1, to provide a dissimilar metal film 3 on the surface of the base metal 1; and

an electron beam irradiation step of irradiating the surface of the base metal 1 with an electron beam 4, the surface of the base metal 1 having been provided with the dissimilar metal film 3 in the shot-peening step, to bond the dissimilar metal film 3 and the base metal 1 together.

**[0006]** In the metal surface treatment method in accordance with a second aspect of the present invention, the dissimilar metal film 3 and the base metal 1 are bonded together in an alloyed state by means of an electron beam irradiation. The "alloyed state" meant in the present specification is used to include a state that the base metal and the dissimilar metal become alloyed and also a state that the base metal and the dissimilar metal are bonded together in a molten state by means of energy of the electron beam.

**[0007]** The metal surface treatment method in accordance with a third aspect of the present invention is **characterized in that**, in the shot-peening step, the dissimilar metal particle 2 is shot-peened on the surface of the base metal 1, the dissimilar particle 2 being a metal particle with a low melting point as compared with the base metal 1, and such step is followed by the electron beam irradiation step where the surface is irradiated with the electron beam 4 to melt the dissimilar metal particle 2 and bond the dissimilar metal film 3 to the base metal 1.

**[0008]** The metal surface treatment method in accordance with a fourth aspect of the present invention is **characterized in that**, in the shot-peening step, the dissimilar metal particle 2 is shot-peened on the surface of the base metal 1, the dissimilar particle 2 being a metal particle with a high melting point as compared with the base metal 1, and such step is followed by the electron beam irradiation step where the surface is irradiated with the electron beam 4 to melt the base metal 1 and bond the dissimilar metal film 3 to the base metal 1.

**[0009]** The metal surface treatment method in accordance with a fifth aspect of the present invention is **characterized** in **that**, in the shot-peening step, a plurality of dissimilar metal particles 2 composed of different metals are jetted on the surface of the base metal 1.

[0010] The metal surface treatment method in accordance with a sixth aspect of the present invention is **characterized** in **that**, in the shot-peening step, the metal particles with different average particle sizes are jetted on the surface of the base metal 1.

20

30

35

40

45

50

55

**[0011]** The metal surface treatment method in accordance with a seventh aspect of the present invention is **characterized in that** the surface of the base metal 1 having been provided with the dissimilar metal film 3 in the shot-peening step is irradiated with the electron beam 4 in the electron beam irradiation step so as to bond the dissimilar metal film 3 and the base metal 1 together and a surface layer 5 is provided on the surface of the base metal 1, and that the shot-peening step and the electron beam irradiation step are repeated a plurality of times to laminate a plurality of surface layers 5 on the surface of the base metal 1.

[0012] The metal surface treatment method in accordance with an eighth aspect of the present invention is **characterized in that**, in the shot-peening step, the dissimilar metal particle 2 used for the shot-peening operation includes at least either of W, C, B, Ti, Ni, Cr, Si, Mo, Ag, Au, Ba, Be, Ca, Co, Cu, Fe, F, fluoride, Mg, Mn, Nb, Pt, S, a sulfide, Ta, or V. [0013] The metal surface treatment method in accordance with a ninth aspect of the present invention is **characterized in that**, in the shot-peening step, the dissimilar metal particle 2 used for the shot-peening operation is an alloy of a plurality of metals and a compound containing a metal.

[0014] The metal surface treatment method in accordance with a tenth aspect of the present invention is **characterized** in that, in the shot-peening step, the dissimilar metal particle 2 used for the shot-peening operation is 0.03  $\mu$ m or more in an average particle size.

[0015] The metal surface treatment method in accordance with an eleventh aspect of the present invention is **characterized in that**, in the shot-peening step, the dissimilar metal particle 2 used for the shot-peening operation is 500  $\mu$ m or less in an average particle size.

**[0016]** The metal surface treatment method in accordance with a twelfth aspect of the present invention is **characterized in that** the base metal 1 is either of: a metal including Fe, Al, Cu, an iron base alloy, an aluminum base alloy, a copper base alloy, a metal including Ag, Au, Ba, Ca, Co, F, fluoride, Mg, Mn, Ni, Nb, Pt, S, a sulfide, Ta, Ti, and V; a silver base alloy; a gold base alloy; a calcium base alloy; a cobalt base alloy; a chromium base alloy; a magnesium base alloy; a manganese base alloy; a nickel base alloy; a niobium base alloy; a tantalum base alloy; a titanium base alloy; a vanadium base alloy; or a sintered metal.

**[0017]** The metal surface treatment method in accordance with a thirteenth aspect of the present invention is **characterized in that**, in the electron beam irradiation step, the base metal 1 having been provided with the dissimilar metal film 3 is irradiated with the electron beam 4 in a vacuum or in a gas.

**[0018]** Further, the metal surface treatment method in accordance with a fourteenth aspect of the present invention is **characterized in that**, in the electron beam irradiation step, the surface is irradiated with the electron beam 4 to bond the dissimilar metal film 3 and the base metal 1 together to provide the surface layer 5 on the surface of the base metal 1, and then the surface of the surface layer 5 is polished in a polishing step.

[0019] Further, the metal surface treatment method in accordance with a fifteenth aspect of the present invention includes:

a temporary filming step where a dissimilar metal particle 2 being a metal particle different from a base metal 1 is accelerated toward and impinged upon the base metal 1 and attached to a surface of the base metal 1 via a binder 6 becoming lost by energy of an energy beam so as to provide a powdered metal layer 9 on the surface of the base

metal 1, and

5

20

30

35

40

45

50

55

a beam irradiation step where the surface of the base metal 1 having the powdered metal layer 9 provided thereon in a temporary filming step is irradiated with an energy beam of an electron beam or a laser beam 4, the binder 6 becomes lost, and the powdered metal layer 9 and the base metal 1 are bonded together to provide a surface layer 5 on the surface of the base metal 1.

**[0020]** The metal surface treatment method in accordance with a sixteenth aspect of the present invention is **characterized in that** the surface of the surface layer 5 is polished in a polishing step after the beam irradiation step,

[0021] Further, the metal surface treatment method in accordance with a seventeenth aspect of the present invention is **characterized in that**, in the polishing step, the surface layer 5 is polished by shot-blasting an abrasive particle thereon.

[0022] The metal surface treatment method in accordance with an eighteenth aspect of the present invention is **characterized in that**, in the temporary filming step, the dissimilar metal particle 2 is accelerated by energy of a pressurized fluid.

**[0023]** The metal surface treatment method in accordance with a nineteenth aspect of the present invention is **characterized in that**, in the temporary filming step, the dissimilar metal particle 2 is accelerated by the effect of an electric field and/or a magnetic field.

**[0024]** The metal surface treatment method in accordance with a twentieth aspect of the present invention is **characterized in that**, in the temporary filming step, the dissimilar metal particle 2 with a low melting point as compared with the base metal 1 is impinged upon the surface of the base metal 1.

**[0025]** The metal surface treatment method in accordance with a twenty-first aspect of the present invention is **characterized in that**, in the temporary filming step, the dissimilar metal particle 2 with a high melting point as compared with the base metal 1 is impinged upon the surface of the base metal 1.

**[0026]** The metal surface treatment method in accordance with a twenty-second aspect of the present invention is **characterized in that**, in the temporary filming step, a plurality of kinds of dissimilar metal particles 2 composed of different metals are impinged upon the surface of the base metal 1.

**[0027]** The metal surface treatment method in accordance with a twenty-third aspect of the present invention is **characterized in that**, in the temporary filming step, the dissimilar metal particles 2 with different average particle sizes are impinged upon the surface of the base metal 1.

[0028] The metal surface treatment method in accordance with a twenty-fourth aspect of the present invention is characterized in that, in the beam irradiation step, the powdered metal layer 9 and the base metal 1 are bonded together into an alloyed state.

**[0029]** The metal surface treatment method in accordance with a twenty-fifth aspect of the present invention is **characterized in that** the temporary filming step and the beam irradiation step are repeated a plurality of times to laminate a plurality of surface layers 5 on the surface of the base metal 1.

**[0030]** The metal surface treatment method in accordance with a twenty-sixth aspect of the present invention is **characterized in that**, in the temporary filming step, the dissimilar metal particle 2 accelerated toward and impinged upon the surface of the base metal 1 includes at least either of: W, C, B, Ti, Ni, Cr, Si, Mo, Ag, Au, Ba, Be, Ca, Co, Cu, Fe, Mg, Mn, Nb, Pt, Ta, V, F, S; or fluoride, a sulfide, nitride, a carbide, or boride of such metals.

**[0031]** The metal surface treatment method in accordance with a twenty-seventh aspect of the present invention is **characterized in that**, in the temporary filming step, the dissimilar metal particle 2 including either of molybdenum disulfide, tungsten sulfide, or boron nitride is accelerated toward and impinged upon the surface of the base metal 1.

**[0032]** The metal surface treatment method in accordance with a twenty-eighth aspect of the present invention is **characterized in that**, in the temporary filming step, the dissimilar metal particle 2 being an alloy of a plurality of metals and a compound containing a metal is accelerated toward and impinged upon the surface of the base metal 1.

[0033] The metal surface treatment method in accordance with a twenty-ninth aspect of the present invention is characterized in that, in the temporary filming step, the dissimilar metal particle 2 with its average particle size being  $0.03~\mu m$  or more is accelerated toward and impinged upon the surface of the base metal 1.

[0034] The metal surface treatment method in accordance with a thirtieth aspect of the present invention is **characterized in that**, in the temporary filming step, the dissimilar metal particle 2 with its average particle size being 500  $\mu$ m or less is accelerated toward and impinged upon the surface of the base metal 1.

[0035] The metal surface treatment method in accordance with a thirty-first aspect of the present invention is **characterized in that** the base metal 1 is either of: a metal including Fe, Al, Cu, an iron base alloy, an aluminum base alloy, and a copper base alloy; a metal including Ag, Au, Ba, Ca, Co, Mg, Mn, Ni, Nb, Pt, Ta, Ti, and V; a silver base alloy; a gold base alloy; a calcium base alloy; a cobalt base alloy; a chromium base alloy; a magnesium base alloy; a manganese base alloy; a nickel base alloy; a niobium base alloy; a tantalum base alloy; a titanium base alloy; a vanadium base alloy; a sintered metal; F, S; or fluoride, sulfide, nitride, a carbide or boride of such metals.

[0036] The metal surface treatment method in accordance with a thirty-second aspect of the present invention is characterized in that, in the beam irradiation step, the base metal 1 provided, on its surface, with the powdered metal

layer 9 is irradiated with the energy beam in a vacuum or in a gas.

**[0037]** The metal surface treatment method in accordance with a thirty-third aspect of the present invention is **characterized in that**, in the temporary filming step, a binder 6 being water-soluble or organic solvent-soluble is used as the binder 6 allowing for attachment of the dissimilar metal particle 2.

[0038] The metal surface treatment method in accordance with a thirty-fourth aspect of the present invention is **characterized in that**, in the temporary filming step, an oil is used as the binder 6 for attaching the dissimilar metal particle 2 to the base metal 1.

**[0039]** The metal surface treatment method in accordance with a thirty-fifth aspect of the present invention is **characterized in that**, in the temporary filming step, saccharides or celluloses are used as the binder 6 for attaching the dissimilar metal particle 2 to the base metal 1.

**[0040]** The metal surface treatment method in accordance with a thirty-sixth aspect of the present invention is **characterized in that**, in the temporary filming step, a substance used as the binder 6, alone or in a mixture of a plurality of kinds, to attach the dissimilar metal particle 2 to the base metal 1 is either of:

a material such as gum Arabic, tragacanth, gum karaya, caramel, starch, soluble starch, dextrin, a starch, sodium alginate, gelatin, locust bean gum, and casein;

a semi-synthetic material derived from a natural product, the material being either of lignosulfonate, carboxymethyl cellulose sodium salt, methyl cellulose, hydroxyethyl cellulose, sodium salt of carboxymethylated starch, hydroxyethylated starch, sodium salt of starch phosphate, hydroxypropyl cellulose, hydroxypropyl methyl cellulose, ethyl cellulose, acetyl cellulose, or ester gum; or

a composite being either of polyvinyl alcohol, polyvinyl methyl ether, polyacrylamide, sodium salt of polyacrylic acid, water-soluble copolymer, copolymer of partially saponificated vinyl acetate and vinyl ether, acrylic acid, methacrylic acid, maleic acid and polymer or copolymer of maleic acid ester or salt, polyethylene glycol, polyethylene oxide, polyvinyl pyrrolidone, vinylpyrrolidone-vinyl acetate copolymer, polyvinyl acetate, coumarone resin, petroleum resin, or phenolic resin.

**[0041]** The metal surface treatment method in accordance with a thirty-seventh aspect of the present invention is **characterized in that**, in the temporary filming step, a radiation hardening-type resin cured by ultraviolet irradiation is used as the binder 6 for attaching the dissimilar metal particle 2 to the base metal 1.

**[0042]** The metal surface treatment method in accordance with a thirty-eighth aspect of the present invention is **characterized in that**, in the temporary filming step, the powdered metal layer 9 is provided through a process that the binder 6 is coated on the surface of the base metal 1 and the dissimilar metal particle 2 is accelerated toward and impinged upon the surface of the base metal 1 having been coated with the binder 6.

**[0043]** The metal surface treatment method in accordance with a thirty-ninth aspect of the present invention is **characterized in that**, in the temporary filming step, the dissimilar metal particle 2 is accelerated toward and impinged upon the surface of the base metal 1 and, in particular, both of the binder 6 and the dissimilar metal particle 2 are accelerated toward and impinged upon the surface of the base metal 1 to provide the powdered metal layer 9.

**[0044]** The metal surface treatment method in accordance with a fortieth aspect of the present invention is **characterized in that**, in the temporary filming step, the powdery binder 6 and the dissimilar metal particle 2 are electrostatically attached to the surface of the base metal 1 and subsequently heated to bond the dissimilar metal particle 2 to the base metal 1 by means of the heated binder 6 to provide the powdered metal layer 9.

**[0045]** The metal surface treatment method in accordance with a forty-first aspect of the present invention is **characterized in that**, in the temporary filming step, the powdered metal layer 9 is provided on the surface of the base metal 1 through a process that the dissimilar metal particle 2 is attached to the surface of the base metal 1 via the binder 6 of an ultraviolet hardening type, and the binder 6 of the ultraviolet hardening type is cured by ultraviolet irradiation.

**[0046]** The metal surface treatment method in accordance with a forty-second aspect of the present invention is **characterized in that**, in the temporary filming step, a coating material is sprayed on the surface of the powdered metal layer 9.

50 Effect of the Invention

15

20

25

30

35

40

45

55

[0047] The metal surface treatment method in accordance with a first aspect of the present invention carries the advantage that a variety of metals can be reliably bonded on a surface of various kinds of base metals in a simple, easy and efficient manner. This becomes possible because the surface treatment method of the present invention is so designed that a dissimilar metal particle is shot-peened on the surface of the base metal to provide a dissimilar metal film on the surface and that such surface of the base metal provided with the dissimilar metal film is irradiated with an electron beam to bond the dissimilar metal film and the base metal together. Particularly, the surface treatment method of the present invention is distinctive in that the dissimilar metal film is provided on the surface of the base metal by the

shot-peening operation and that such surface is irradiated with the electron beam. Unlike in a method of providing a dissimilar metal film by a metal plating process, a waster liquid treatment is not required in the shot-peening process. In addition, the dissimilar metal film can be provided efficiently by using a simple system when compared with a metal spraying process. Further, in the case of the dissimilar metal film provided by shot-peening the dissimilar metal particle, a film thickness can be controlled by a choice of a particle size of the dissimilar metal particle to be shot-peened. This is because when a large particle size of dissimilar metal particle is shot-peened, the film thickness of the dissimilar metal film becomes larger with the large particle size of dissimilar metal particle being attached to the surface of the base metal. Therefore, in the surface treatment method of the present invention, the film thickness of the dissimilar metal film can be freely controlled by the choice of the particle size of the dissimilar metal particle to provide a surface treatment film being best suited for a specified use. Further, in the method of shot-peening the dissimilar metal particle, the dissimilar metal film can be provided in a uniform film thickness on the surface of the base metal. This is because in the case of the dissimilar metal film formed by the shot-peening operation, the dissimilar metal particle is attached in a monolayer on the surface of the base metal. The dissimilar metal particle jetted on the surface of the base metal by the shot-peening operation is attached to the base metal but is not attached to the dissimilar metal particle having previously been attached on the surface. In view of this aspect, even when the dissimilar metal particle is jetted unevenly on the surface of the base metal, the dissimilar metal particle is attached in a monolayer on the surface of the base metal and the dissimilar metal film can be provided in a uniform film thickness. This factor is especially important in a method of bonding the dissimilar metal film and the base metal together by means of an electron beam irradiation. This is possible because the electron beam scanning with a constant energy density over the surface of the base metal enables a uniform film thickness of the dissimilar metal film to be bonded to the base metal in a uniform condition. When the surface of the base metal is irradiated with the electron beam, such electron beam varies in its energy density in accordance with a film thickness of the dissimilar metal film. An ideally bonded state is obtained when the energy density of the electron beam irradiation is set to be high for a thick dissimilar metal film and when the energy density of the electron beam irradiation is set to be low for a thin dissimilar metal film. When a thick dissimilar metal film is irradiated with an electron beam having a low energy density, the metal constituent in the dissimilar metal film is not bonded to the base metal in a perfect state. Conversely, when a thin dissimilar metal film is irradiated with an electron beam having a high energy density, the dissimilar metal film becomes lost due to the heat. Since the surface treatment method of the present invention is so designed as to provide the dissimilar metal film on the surface of the base metal by the shot-peening process, the dissimilar metal film can be provided in a uniform manner and in a film thickness being best suited for a specified use; and when the dissimilar metal film having such uniform film thickness is irradiated with the electron beam, the dissimilar metal and the base metal can be bonded together in an ideal state to obtain a reliable junction.

20

30

35

40

45

50

55

**[0048]** Further, since the metal surface treatment method of the present invention is capable of obtaining a metal surface having a variety of properties such as lubricating ability, resistance to wear, resistance to corrosion, and releasability, this method can be applied to a metal surface of a product corresponding with an intended property as enumerated above.

**[0049]** Furthermore, the metal surface treatment method in accordance with a fifteenth aspect of the present invention carries the advantage that a variety of metals can be reliably bonded on the surface of various kinds of base metals in a simple, easy and efficient manner. This is possible because the surface treatment method of the present invention is so designed that the dissimilar metal particle being a metal particle different from the base metal is accelerated toward and impinged upon the surface of the base metal; the powdered metal layer is provided on the surface of the base metal via a binder becoming lost by the effect of the energy of the energy beam; the surface of the base metal provided with the powdered metal layer is irradiated with the energy beam of an electron beam or a laser beam; and the binder is lost for allowing the powdered metal layer and the base metal to be bonded together.

[0050] Particularly, in the surface treatment method in accordance with a fifteenth aspect of the present invention, the dissimilar metal particle is attached to the surface of the base metal by means the binder which becomes lost by the effect of the energy beam and the dissimilar metal particle is accelerated toward and impinged upon the surface of the base metal to obtain the powdered metal layer. The dissimilar metal particle impinged upon the surface of the base metal is placed tightly and densely in contact with the surface of the base metal. The powdered metal layer having the dissimilar metal particle attached in such state can reduce the amount of the binder between the dissimilar metal particles, with each individual dissimilar metal particle being mutually in proximity, and the binder can also be reduced between the dissimilar metal particle and the surface of the base metal. The dissimilar metal particle accelerated toward and impinged upon the surface of the base metal penetrates into the unhardened or hardened binder by the effect of kinetic energy. The depth of penetration by the dissimilar metal particle into the binder is determined by the kinetic energy of the dissimilar metal particle. The kinetic energy of the dissimilar metal particle is proportional to a product of a squared speed of impingement upon the base metal and a mass of the particle. The mass is determined by a product of a volume and a specific gravity of the particle. The dissimilar metal particle made of a metal has a large specific gravity, and the mass is large even when the particle size is small, and thus the kinetic energy becomes large. The dissimilar metal particle impinged upon the surface of the base metal by the effect of the large kinetic energy penetrates deeply into the

binder resident on the surface of the base metal. The dissimilar metal particle penetrating deeply into the binder contacts the surface of the base metal and is collected densely in a configuration on the surface to thus form the powdered metal layer in a closely coupled state.

[0051] Aside from the method of the present invention, it is also possible that the dissimilar metal particle is mixed with the binder and such mixture is stirred, and the mixture is coated on the surface of the base metal to provide the dissimilar metal film. However, as shown in FIG. 19, in the case of the dissimilar metal film provided in such method, the powered metal particles 92 are clumped to form a particulate aggregate 90 varying in size from small to large, and such particulate aggregate 90 is uneven and in a state of coarse density, and is further attached to the base metal 91 via the binder 96 without being in close contact with the surface of the base metal 91. When the dissimilar metal film 93 in such state is irradiated with the energy beam, the surface condition is in a remarkably different state by the effect of the energy of the energy beam and in accordance with the size and location of the particulate aggregate having been clumped. That is, in the portion that is approached by the particulate aggregate having been clumped on the surface of the base metal, the particulate aggregate is melted by the effect of the energy beam to form an alloyed layer in a convex state; and in the portion that is not resided by the particulate aggregate closely on the surface, the surface of the base metal is irradiated with the energy beam, the base metal is melted and jabbed out, and debris are flown in the air, thus defining a convexity on the surface. Therefore, the surface of the base metal having been irradiated with the energy beam becomes uneven, so that a sparse alloyed layer is formed, hampering a uniform, good surface treatment. When the base metal in such surface state is used as a friction surface, there occurs an evil effect that an opposite material in contact is to be subjected to aggression and is seriously damaged.

15

20

30

35

40

45

50

55

[0052] On the other hand, the dissimilar metal film provided in the temporary filming step in the surface treatment method in accordance with a fifteenth aspect of the present invention is provided in a state that the dissimilar metal particles are collected on the surface of the base metal in a high density. This is possible because the present invention is so designed that the dissimilar metal particle is accelerated toward and impinged upon the surface of the base metal to obtain the powdered metal layer. The dissimilar metal particle impinged upon the surface of the base metal is tightly bonded on the surface of the base metal without being scattered and clumped under the shock of the impingement. The dissimilar metal particle accelerated toward and impinged upon the surface of the base metal penetrates into the unhardened binder to be tightly bonded on the surface of the base metal. Further, even when the dissimilar metal particle is impinged upon a surface of hardened binder, the particle penetrates into the binder by the effect of the kinetic energy and is tightly bonded on the surface of the base metal. This is because the hardened binder is sufficiently small when compared with the base metal.

**[0053]** In the above-described state, namely when the powdered metal layer having the dissimilar metal particle bonded tightly on the surface of the base metal is irradiated with the energy beam, such energy beam melts the dissimilar metal particle to form a surface layer which is thermally coupled with the surface of the base metal.

**[0054]** Further, the surface treatment method in accordance with a fifteenth aspect of the present invention carries the advantage that since the powdered metal layer composed of the dissimilar metal particle is provided on the surface of the base metal with the aid of the binder, the powdered metal layer can be thickly provided on the surface of the base metal, and further since in the step of the powdered metal layer being irradiated with the energy beam the amount of powdered metal layer being flown in the air can be reduced to minimum, the surface treatment film in a film thickness as desired can be provided on the surface of the base metal.

[0055] Further, unlike in the metal plating process, the surface treatment method in accordance with a fifteenth aspect of the present invention does not require a waste liquid treatment, and also carries the advantage that the surface treatment method can be efficiently carried out with a simple system as compared with a surface treatment method by a metal spraying operation. In addition, in the case of the powdered metal layer which is provided by the acceleration and impingement of the dissimilar metal particle, the film thickness can also be controlled by a choice of the particle size of the dissimilar metal particle. When the powdered metal layer is provided via the binder by a large particle size of the dissimilar metal particle being accelerated toward and impinged upon the surface of the base metal, the film thickness of the powdered metal layer can be made large by a large particle size of the dissimilar metal particle. As such, in the surface treatment method of the present invention, the film thickness of the powdered metal layer can be freely controlled by a choice of the particle size of the dissimilar metal particle to obtain a surface treatment film best suited for a specified use. Further, in the method of the dissimilar metal particle being accelerated toward and impinged upon the surface of the base metal and being attached by the binder, the powdered metal layer in a uniform film thickness can be provided even on a sterically irregular surface of the base metal.

**[0056]** To mention in particular, in the metal surface treatment method respectively in accordance with a fourteenth aspect and a sixteenth aspect of the present invention, the dissimilar metal film and the base metal are bonded together or the powdered metal layer and the base metal are bonded together, and then the surface of the surface layer is polished in the polishing step; and further in the surface treatment method in accordance with a seventeenth aspect of the present invention, an abrasive particle is shot-blasted on the surface layer in the polishing step. The surface layer having been polished by the shot-blasting operation becomes a smooth surface, resulting in smaller friction resistance. Owing to the

smooth surface, an abrasive wear of an opposite contacted surface can also be reduced. Especially, according to this method, a beam irradiation mark caused by the energy beam being scanned can be smoothed to obtain a beautiful surface finish by tidying up into proper plane roughness. Particularly in this method, the irradiation mark caused by the energy beam irradiation can be polished and controlled to obtain given smoothness, and thus achieving ideal flatness. It is not necessarily ideal that sliding surfaces contacting in a state of sliding over each other have a perfectly smooth surface. For example, when the sliding surfaces with smoothness of 0.01  $\mu$ m respectively are contacted with each other, the contact surfaces cannot almost be slid due to a vacuum state produced in between. In view of this fact, in order to control a coefficient of friction to the minimal value, the coefficient of friction owned by the base metal surface and its surface roughness become vital. As such, in the method of the present invention in which the energy beam irradiation mark is caused by scanning the beam, the surface roughness can be controlled in the subsequent polishing step to adjust the surface to have optimal roughness. Therefore, the surface treatment method of the present invention carries the advantage that the polishing step is carried out after the beam irradiation step and that the surface roughness to be finished in the polishing step can be controlled to obtain an ideal sliding surface.

15 Mode for Carrying Out the Embodiment(s)

**[0057]** Embodiments in accordance with the present invention shall be described hereinafter in conjunction with the accompanying drawings. It should be noted, however, that the ensuing description of embodiments is merely illustrative of the metal surface treatment method to embody technical ideas conceived in the present invention and that the invention shall in no way be limited to the surface treatment method described below.

**[0058]** Further, in the present specification, reference numerals corresponding to members shown in the embodiments are affixed to members shown in the "CLAIMS" and "MEANS FOR SOLVING PROBLEMS" in order to facilitate a better appreciation of the claims. However, those members shown in the claims shall in no way be specified to those members shown in the embodiments.

**[0059]** The metal surface treatment method of the present invention is so designed that in a shot-peening step shown in FIG. 1 a dissimilar metal particle 2 being a metal particle different from a base metal 1 is shot-peened on a surface of the base metal 1 to provide a dissimilar metal film 3 on the surface of the base metal 1 and that in an electron beam irradiation step shown in FIG. 2 the surface of the base metal 1 having been provided with the dissimilar metal film 3 in the shot-peening process is irradiated with an electron beam 4 to bond the dissimilar metal film 3 and the base metal 1 together.

(Shot-Peening Step)

20

30

35

40

45

50

55

[0060] In the shot-peening step shown in FIG. 1, the dissimilar metal particle 2 being a metal particle different from the base metal 1 is shot-peened on the surface of the base metal 1 to provide the dissimilar metal film 3 on the surface of the base metal 1. Used as the base metal 1 is a metal best suited for a specified purpose, such as a metal including Fe, Al, Cu, an iron base alloy, an aluminum base alloy, a copper base alloy, Ag, Au, Ba, Ca, Co, F, fluoride, Mg, Mn, Ni, Nb, Pt, S, a sulfide, Ta, Ti, and V; a silver base alloy; a gold base alloy; a calcium base alloy; a cobalt base alloy; a chromium base alloy; a magnesium base alloy; a manganese base alloy; a nickel base alloy; a niobium base alloy; a tantalum base alloy; a titanium base alloy; a vanadium base alloy; and a sintered metal. Used as the dissimilar metal particle 2 for the shot-peening operation is at least either of W, C, B, Ti, Ni, Cr, Si, Mo, Ag, Au, Ba, Be, Ca, Co, Cu, Fe, F, fluoride, Mg, Mn, Nb, Pt, S, a sulfide, Ta, or V. For the shot-peening operation, it is also possible to use a mixture of a plurality of kinds of dissimilar metal particles. Further, used as the dissimilar metal particle 2 for the shot-peening operation is a metal particle with a low melting point as compared with the base metal 1; and conversely, a metal particle with a low melting point as compared with the base metal 1 is used.

**[0061]** In the method of shot-peening the dissimilar metal particle 2 to be bonded to the base metal 1, the dissimilar metal particle 2 is vigorously impinged upon the base metal 1 and physically bonded to the base metal 1 by the effect of kinetic energy of the dissimilar metal particle 2. Therefore, a variety of metals can be used as the base metal 1 and the dissimilar metal particle 2.

[0062] In the shot-peening step, the dissimilar metal particle 2 with its average particle size of 0.03  $\mu$ m through 500  $\mu$ m is jetted toward the surface of the base metal 1 at injection pressure of 0.3 MPa or more, and preferably of 0.5 MPa or more. The average particle size of the dissimilar metal particle 2 jetted toward the base metal 1 determines a film thickness of the dissimilar metal film 3. Therefore, used as the dissimilar metal particle 2 jetted toward the base metal 1 is a particle with an optimal value in view of the film thickness of the dissimilar metal film 3, and such value is preferably 0.1  $\mu$ m through 50  $\mu$ m, and more preferably 0.3  $\mu$ m through 10  $\mu$ m. Also usable as the dissimilar metal particle 2 is a particle of substance in which a metal fine particle of dissimilar metal intended to serve as the dissimilar metal film. In the case of such

dissimilar metal particle 2, the average particle size of the transport carrier particle is 100  $\mu$ m through 1 mm, while the metal fine particle is 0.03  $\mu$ m through 30  $\mu$ m. When the metal fine particle in such dissimilar metal particle 2 is sufficiently small, a thin dissimilar metal film can be efficiently attached on the surface of the base metal 1. This is because the kinetic energy of a large transport carrier particle is large, which enables the metal fine particle to be vigorously impinged upon the surface of the base metal 1.

(Electron Beam Irradiation Step)

10

20

30

35

40

45

50

55

[0063] In this step, the surface of the base metal 1 provided with the dissimilar metal film 3 is irradiated with the electron beam 4, and the dissimilar metal film 3 is locally heated by the effect of energy of the electron beam 4 so as to be bonded to the base metal 1. FIG. 2 shows an electron beam irradiator 10 used in the electron beam irradiation step. The electron beam irradiator 10 is so constructed and arranged that the base metal 1 provided with the dissimilar metal film 3 is placed inside a sealed chamber 11, the sealed chamber 11 is evacuated, and the surface is irradiated with the electron beam 4. It should be noted that the sealed chamber 11 may be in an atmosphere of being filled with a gas such as nitrogen gas, depending on a specified purpose. The electron beam 4 is tuned to be in an energy density best suited for enabling the dissimilar metal film 3 to be bonded to the base metal 1, and the surface of the base metal 1 is subjected to irradiation. The electron beam irradiator 10 includes an electron gun 12 for emitting an electron by heating a heater 18, a focusing coil 13 for focusing an electron ray, emitted by the electron gun 12, into the electron beam 4 by the effect of a magnetic field, and a deflecting coil 14 for scanning the focused electron beam 4 over the surface of the base metal 1 by the effect of the magnetic field.

[0064] The electron gun 12 includes a cathode 15 for emitting a thermoelectron when the heater 18 is heated, a bias electrode 16 for controlling the number of electron emitted by the cathode 15, namely, a current value of the electron beam 4, and an anode 17 for accelerating the electron beam 4. The cathode 15 and the bias electrode 16 receive a negative going voltage and the anode 17 receives a high-tension, positive going voltage, both of the voltages being supplied from a power source 19. The electron beam 4 emitted by the electron gun 12 is focused by means of the focusing coil 13 onto a spot having a given area on the surface of the base metal 1. Further, the electron beam 4 is scanned by the deflecting coil 14 to irradiate an entire area of the base metal 1 with the electron beam 4.

**[0065]** The energy of the electron beam 4 is controllable by adjusting an acceleration voltage of the anode 17, a current value of the electron beam 4 provided by the negative going voltage of the bias electrode 16, and a scanning speed provided by the deflecting coil 14. The energy density in the irradiation range can be increased by increasing the acceleration voltage, decreasing the negative going voltage of the bias electrode 16, decreasing the spot area of focusing the electron beam 4, and further slowing down the scanning speed.

[0066] The energy of the electron beam 4 with which the surface of the base metal 1 is irradiated by the electron beam irradiator 10 is set at an optimal value, depending on the material and film thickness of the dissimilar film 3 and on the kind of the base metal 1. The energy of the electron beam is preferably of an amount such that the dissimilar metal film 3 and the base metal 1 are bonded together in an alloyed state. In this method, a surface layer 5 with the dissimilar metal film 3 and the base metal 1 having been bonded together in an alloyed state is formed on the surface of the base metal 1 as shown in FIG. 3.

[0067] However, the energy of the electron beam is also controllable to be of an amount such that the dissimilar metal particle 2 being a metal particle with a low melting point as compared with the base metal 1 is shot-peened on the surface of the base metal 1, such surface is irradiated with the electron beam 4 to melt the dissimilar metal film 3, and the dissimilar metal film 3 is bonded to the base metal 1. In such method, the dissimilar metal film 3 having been melted is bonded on the surface of the base metal 1 to form the surface layer 5 as shown in FIG. 4.

[0068] Further, the energy of the electron beam is also controllable to be of an amount such that the dissimilar metal particle 2 being a metal particle with a high melting point as compared with the base metal 1 is shot-peened on the surface of the base metal 1, such surface is irradiated with the electron beam 4 to melt the base metal 1, and the dissimilar metal film 3 is bonded to the base metal 1. In such method, the surface layer 5 with the dissimilar metal film 3 being bonded in a buried state on the surface of the base metal 1 having been melted is formed on the surface of the base metal 1 as shown in FIG. 5.

**[0069]** Further, in the shot-peening step, the dissimilar metal particles 2 with different average particle sizes can be jetted toward the surface of the base metal 1 to provide the dissimilar metal film 3 having a surface irregularity as shown in FIG. 6. When such dissimilar metal film 3 is irradiated with the electron beam, the dissimilar metal film 3 is bonded in a state of the surface irregularity to the base metal 1 and the surface layer 5 is formed with such surface irregularity as shown in the drawing.

**[0070]** Further, although not shown, in the shot-peening step, a plurality of dissimilar metal particles composed of different metals can also be jetted toward the surface of the base metal to provide the dissimilar metal film composed of the different metals. When the dissimilar metal film is irradiated with the electron beam, the surface layer composed of a plurality kinds of metal particles can be formed on the surface of the base metal.

[0071] Further, in the surface treatment method of the present invention, when the shot-peening step and the electron beam irradiation step are repeated a plurality of times, a plurality of surface layers 5 can also be laminated on the surface of the base metal 1. As shown in FIG. 7, in this method, the dissimilar metal film 3 provided on the surface of the base metal 1 in the shot-peening step is irradiated with the electron beam in the electron beam irradiation step, the dissimilar metal film 3 and the base metal 1 are bonded together, and the surface layer 5 is provided on the surface of the base metal 1; subsequently, the dissimilar metal particle 2 is shot-peened on the surface of the surface layer 5 to obtain the dissimilar metal film 3; further the dissimilar metal film 3 is irradiated with the electron beam to bond the dissimilar metal film 3 on the surface layer 5; and the surface layers 5 in two layers are laminated on the surface of the base metal 1. When these steps are further repeated, the surface layer in multiple layers can be laminated on the surface of the base metal. Thus, in the method of laminating a plurality of surface layers 5 on the surface of the base metal 1, a thick film can be formed on the surface of the base metal 1. Further, the plurality of surface layers 5 laminated on the surface of the base metal 1 may be composed of the metals of the same kind or of the metals of different kinds. The method of laminating the surface layers composed of the metals of the same kind on the surface of the base metal enables the surface layer in a thick film composed of metals of the same kind to be formed on the surface of the base metal. Further, the method of laminating the surface layer composed of the metals of different kinds on the surface of the base metal enables the plurality of metal films with different properties to be formed in a laminated state on the surface of the base

**[0072]** Since the above-described shot-peening step and electron beam irradiation step in the metal surface treatment method of the present invention can be repeated a plurality of times, the film thickness of the entire surface layer formed on the surface of the base metal can be made thick. Therefore, by adjusting such film thickness, a metal surface on a broad variety of products can be processed to be suitable for a specified purpose.

(Example 1)

20

30

35

40

#### 25 (1) Shot-Peening Step

[0073] The dissimilar metal particle 2 composed of molybdenum disulfide was shot-peened on the surface of pure copper or a copper base alloy being the base metal 1. The average particle size of the dissimilar metal particle 2 was 10  $\mu$ m, and the injection pressure for shot-peening operation was 1 MPa. In this shot-peening operation, the dissimilar metal film 3 of molybdenum disulfide was provided on the surface of the base metal 1.

#### (2) Electron Beam Irradiation Step

**[0074]** The base metal 1 whose surface was provided with the dissimilar film 3 of molybdenum disulfide was placed inside the sealed chamber 11, the sealed chamber 11 was evacuated into a vacuum state, and the surface of the base metal 1 was irradiated with the electron beam 4. Conditions for the electron beam irradiation were set as follows. The degree of vacuum in the sealed chamber was 7 Pa or less.

 $\begin{array}{lll} \mbox{Diameter of the Area Spotted by the Electron Beam} & 0.3 \mbox{ mm} \\ \mbox{Acceleration Voltage} & 30 \mbox{ kV} \\ \mbox{Beam Current} & 100 \mbox{ mA} \\ \mbox{Scanning Area of the Electron Beam} & 30 \mbox{ mm} \times 30 \mbox{ mm} \\ \mbox{Scanning Time Period over the Entire Area} & 2 \mbox{ sec.} \end{array}$ 

45

50

**[0075]** When the electron beam 4 is scanned in a parallel direction and the entire scanning area is uniformly subjected to the electron beam irradiation, the surface layer with an excellent lubricating ability is provided on the surface of the base metal 1, with copper and molybdenum disulfide being in an alloyed state. When compared with the surface treatment in which molybdenum disulfide is merely shot-peened to and attached on the surface of the base metal 1, the above-mentioned surface layer realizes a very good lubricating ability and resistance to wear, with iron and molybdenum disulfide being strongly bonded together in an alloyed state.

**[0076]** Further, when such shot-peening step and electron beam irradiation step are repeated a plurality of times, the surface of the base metal 1 can be provided with a thick surface layer of molybdenum disulfide having been strongly bonded in an alloyed state with iron of the base metal.

#### (Example 2)

15

20

25

30

40

45

50

55

- (1) Shot-Peening Step
- The dissimilar metal particle 2 composed of tungsten was shot-peened on the surface of Ti being the base metal 1. The average particle size of tungsten being the dissimilar metal particle 2 was 20 μm, and the injection pressure for shot-peening operation was 1 MPa. In this shot-peening operation, the dissimilar metal film 3 of tungsten was provided on the surface of the base metal 1.
- (2) Electron Beam Irradiation Step

**[0078]** The base metal 1 whose surface was provided with the dissimilar metal film 3 of tungsten was placed inside the sealed chamber 11, the sealed chamber 11 was evacuated into a vacuum state, and the surface of the base metal 1 was irradiated with the electron beam 4. Conditions for the electron beam irradiation were set as follows. The degree of vacuum in the sealed chamber was 7 Pa or less.

Diameter of the Area Spotted by the Electron Beam 30 kVAcceleration Voltage 30 kVBeam Current 110 mAScanning Area of the Electron Beam  $30 \text{ mm} \times 30 \text{ mm} \times 30 \text{ mm}$ Scanning Time Period over the Entire Area 1 sec.

[0079] When the electron beam 4 is scanned in a parallel direction and the entire scanning area is uniformly subjected to the electron beam irradiation, the surface layer with excellent resistance to wear is provided on the surface of the base metal 1, with titanium and tungsten being in an alloyed state. When compared with the surface treatment in which tungsten is merely shot-peened to and attached on the surface of the base metal 1, the above-mentioned surface layer realizes a very good resistance to wear, with tungsten and titanium being strongly bonded together in the alloyed state.

[0080] Further, when such shot-peening step and electron beam irradiation step are repeated a plurality of times, the surface of the base metal can be provided with a thick surface layer of tungsten being strongly bonded in an alloyed state with titanium of the base metal.

(Example 3)

35 (1) Shot-Peening Step

[0081] SKD-11 was used as the base metal 1, and the dissimilar metal particle 2 composed of SiC was shot-peened on the surface of the base metal 1. The average particle size of the dissimilar metal particle 2 was 3  $\mu$ m, and the injection pressure for shot-peening operation was 1 MPa. In this shot-peening operation, the dissimilar metal film 3 of SiC was provided on the surface of the base metal 1.

(2) Electron Beam Irradiation Step

**[0082]** The base metal 1 whose surface was provided with the dissimilar metal film 3 of SiC was placed inside the sealed chamber 11, the sealed chamber 11 was evacuated into a vacuum state, and the surface of the base metal 1 was irradiated with the electron beam 4. Conditions for the electron beam irradiation were set as follows. The degree of vacuum in the sealed chamber was 7 Pa or less.

 $\begin{array}{lll} \mbox{Diameter of the Area Spotted by the Electron Beam} & 0.3 \mbox{ mm} \\ \mbox{Acceleration Voltage} & 30 \mbox{ kV} \\ \mbox{Beam Current} & 100 \mbox{ mA} \\ \mbox{Scanning Area of the Electron Beam} & 30 \mbox{ mm} \times 30 \mbox{ mm} \\ \mbox{Scanning Time Period over the Entire Area} & 2 \mbox{ sec.} \\ \end{array}$ 

[0083] When the electron beam 4 is scanned in a parallel direction and the entire scanning area is uniformly subjected to the electron beam irradiation, the surface layer with SKD-11 and SiC being in an alloyed state is provided on the surface of the base metal 1. When a coefficient of friction respectively of the surface layer and the SKD-11 being the

base metal was measured in a ball-on-disk testing method, the ratio of the base metal and the obtained surface layer was 1:0.2. In view of this result, it can be seen that a surface layer with a low coefficient of friction is obtained.

[0084] Further as can be seen in FIG. 8, the metal surface treatment method of the present invention is so designed that in the temporary filming step the dissimilar metal particle 2 being a metal particle different from the base metal 1 is accelerated toward, impinged upon, and attached to the base metal 1 via a binder 6 which becomes lost by the effect of the energy of the energy beam, and thus the powdered metal layer 9 is provided on the surface of the base metal 1; and that in the beam irradiation step shown in FIG. 2 the surface of the base metal 1 having been provided with the powdered metal layer 9 in the temporary filming step is irradiated with the energy beam of the electron beam 4 or the laser beam, and thus the powdered metal layer 9 and the base metal 1 can be bonded together.

(Temporary Filming Step)

10

20

30

35

40

45

50

55

**[0085]** In the temporary filming step shown in FIG. 8, the powdered metal layer 9 is provided on the surface of the base metal 1 by attaching via the binder 6 the dissimilar metal particle 2 being a metal particle different from the base metal 1. The dissimilar metal particle 2 is accelerated toward and impinged upon the surface of the base metal 1 to be attached on the surface of the base metal 1 with the aid of the binder 6.

**[0086]** Used as the base metal 1 is a metal best suited for a specified purpose, such as a metal including Fe, Al, Cu, an iron base alloy, an aluminum base alloy, a copper base alloy, Ag, Au, Ba, Ca, Co, Mg, Mn, Ni, Nb, Pt, Ta, Ti, and V; a silver base alloy; a gold base alloy; a calcium base alloy; a cobalt base alloy; a chromium base alloy; a manganese base alloy; a nickel base alloy; a niobium base alloy; a tantalum base alloy; a titanium base alloy; a vanadium base alloy; a sintered metal; F, S; or fluoride, a sulfide, nitride, a carbide, or boride of such metals.

[0087] Used as the dissimilar metal particle 2 is at least either of W, C, B, Ti, Ni, Cr, Si, Mo, Ag, Au, Ba, Be, Ca, Co, Cu, Fe, Mg, Mn, Nb, Pt, Ta, V, F, S, or fluoride, a sulfide, nitride, a carbide, or boride of such metals. Also usable as the dissimilar metal particle 2 for the powdered metal layer 9 is a mixture of plurality of kinds of dissimilar metal particles. Further, usable as the dissimilar metal particle 2 for the powdered metal layer 9 is a metal particle with a low melting point as compared with the base metal 1; and conversely, a metal particle with a high melting point as compared with the base metal 1 is also usable. Further, a mixture of both the metal particles with a low melting point and a high melting point as compared with the base metal 1 is also usable. In order to reduce frictional resistance of the base metal surface and further improve resistance to wear, either of molybdenum disulfide or tungsten sulfide or boron nitride is used as the dissimilar metal particle, or a mixture of such substances is used.

**[0088]** In order to provide the powdered metal layer 9 composed of the dissimilar metal particle 2, the binder 6 is coated on the surface of the base metal 1, and the dissimilar metal particle 2 is accelerated toward and impinged upon the surface of the base metal 1 having been provided with the binder 6. The dissimilar metal particle 2 impinged upon the surface of the base metal 1 penetrates into the binder 6 by the effect of the kinetic energy and is tightly bonded on the surface of the base metal 1 to become the powdered metal layer.

[0089] The dissimilar metal particle 2 is accelerated by the effect of the energy of a pressurized fluid or accelerated by the effect of an electric field toward and impinged upon the surface of the base metal 1. The pressurized fluid accelerating the dissimilar metal particle 2 is either pressurized air or a pressurized liquid. The shot-peening operation is suited for accelerating the dissimilar metal particle 2 by means of the pressurized air. In the shot-peening operation, the dissimilar metal particle 2 is accelerated by the pressurized air toward and impinged upon the surface of the base metal 1. In the shot-peening operation, the dissimilar metal particle 2 is accelerated toward and impinged upon the surface of the base metal 1 which has been pre-coated with the binder 6. The dissimilar metal particle 2, accelerated by the short-peening operation toward and impinged upon the base metal 1, penetrates into the unhardened binder 6 or penetrates into the hardened binder and is tightly bonded on the surface of the base metal 1 to thus form the powdered metal layer 9 on the surface. In this method, pressure of the air is set to be 0.3 MPa or more, and preferably 0.5 MPa or more, and the dissimilar metal particle 2 is accelerated toward the surface of the base metal 1. Such air pressure is varied, depending on whether the binder is in an unhardened state or in a hardened state. The air pressure accelerating the dissimilar metal particle toward the unhardened binder can be set to be lower than the air pressure accelerating the dissimilar metal particle toward the hardened binder. This is because the unhardened binder allows the dissimilar metal particle to smoothly penetrate inside, while the hardened binder requires large kinetic energy to allow the dissimilar metal particle to penetrate inside. Even if the binder is hardened, the binder is lower in hardness than the base metal, and the dissimilar metal particle accelerated by the fluid is allowed to penetrate inside so as to be tightly bonded on the surface of the base metal.

**[0090]** As can be seen in FIG. 9, in order to accelerate the dissimilar metal particle by means of the pressurized liquid, the dissimilar metal particle 2 is mixed with the binder 6 in a liquid or paste form, such binder 6 mixed with the dissimilar metal particle 2 is pressurized and jetted out of a nozzle 7, and the dissimilar metal particle 2 is impinged upon the surface of the base metal 1. The dissimilar metal particle 2 accelerated together with the binder 6 toward the base metal 1 has large specific gravity as compared with the binder 6 itself, penetrates into the binder 6 by the effect of large kinetic

energy as compared with the binder 6, and is attached on the surface of the base metal 1 to become the powdered metal layer 9.

[0091] FIG. 10 and FIG. 11 show that the dissimilar metal particle 2 is accelerated by the effect of the electric field toward and impinged upon the surface of the base metal 1. In the method shown in FIG. 10, high voltage is applied to both of the dissimilar metal particle 2 and the base metal 1. The dissimilar metal particle 2, being electrostatically charged, is jetted out of the nozzle 7. Such charged dissimilar metal particle 2 is accelerated by the effect of an electrostatic field toward and impinged upon the base metal 1. To describe this method, with the binder 6 being in an unhardened state, the dissimilar metal particle 2 accelerated by the effect of the electric field is impinged upon the surface of the base metal 1 having been coated with the binder 6, and thus the powdered metal layer 9 is provided on the surface. In this method, it is also possible to provide the powdered metal layer when both of the binder and the dissimilar metal particle are accelerated by the effect of the electric field toward and impinged upon the surface of the base metal.

**[0092]** In the method shown in FIG. 11, the base metal 1 is immersed in the binder 6 mixed with the dissimilar metal particle 2, and voltage is applied to both of an electro-conductive vessel 8 filled with the binder 6 and the base metal 1. The dissimilar metal particle 2 mixed with the binder 6, being electrostatically charged, is accelerated by electrostatic force toward the surface of the base metal 1.

[0093] Further, FIG. 12 shows a method in which the dissimilar metal particle 2 is accelerated by the effect of a magnetic field toward and impinged upon the surface of the base metal 1. In the illustrated method, the dissimilar metal particle 2 is accelerated by the effect of both the electric field and magnetic field toward and impinged upon the surface of the base metal 1. In this method, the dissimilar metal particle 2, being electrostatically charged, is jetted out of the nozzle 7. The jetted dissimilar metal particle 2 is accelerated by the effect of the magnetic field toward, focused by the magnetic field on, and impinged upon the surface of the base metal 1. This method enables the dissimilar metal particle 2 jetted out of the nozzle 7 to be focused in a beam state by the effect of the magnetic field and impinged upon the surface of the base metal 1. Therefore, such beam of dissimilar metal particle 2 is scanned over the surface of the base metal 1, and the accelerated dissimilar metal particle 2 can be impinged upon the entire surface area of the base metal 1. [0094] The binder 6 becomes lost when subjected to the energy beam irradiation. That is to say, the binder 6 serves to temporarily bond the dissimilar metal particle 2 to the base metal 1 before the dissimilar metal particle 2 is bonded in a molten state to the base metal 1 by the effect of the energy of the electron beam or the laser beam. Therefore, it suffices that the binder 6 allows the dissimilar metal particle 2 to remain bonded to the base metal 1 until the dissimilar metal particle 2 is melted and bonded to the base metal 1 by the irradiation of the electron beam or the laser beam. The binder 6 becomes lost by the energy beam, but all components in the binder do not necessarily have to be fully lost. As an exemplary part of the components contained in the binder, when silicone is contained in the binder, such silicone can also be contained as an alloy ingredient constituted by the dissimilar metal particle and the base metal.

20

30

35

40

45

50

55

**[0095]** Used as the binder 6 is a substance that is water soluble or organic solvent soluble; for example, saccharides or celluloses. More specifically, the substance used as the binder 6, alone or in a mixture of a plurality of kinds, is either of:

a material such as gum Arabic, tragacanth, gum karaya, caramel, starch, soluble starch, dextrin, a starch, sodium alginate, gelatin, locust bean gum, and casein;

a semi-synthetic material derived from a natural product, the material being either of lignosulfonate, carboxymethyl cellulose sodium salt, methyl cellulose, hydroxyethyl cellulose, sodium salt of carboxymethylated starch, hydroxyethylated starch, sodium salt of starch phosphate, hydroxypropyl cellulose, hydroxypropyl methyl cellulose, ethyl cellulose, acetyl cellulose, or ester gum; or

a composite being either of polyvinyl alcohol, polyvinyl methyl ether, polyacrylamide, sodium salt of polyacrylic acid, water-soluble copolymer, copolymer of partially saponificated vinyl acetate and vinyl ether, acrylic acid, methacrylic acid, maleic acid and polymer or copolymer of maleic acid ester or salt, polyethylene glycol, polyethylene oxide, polyvinyl pyrrolidone, vinylpyrrolidone-vinyl acetate copolymer, polyvinyl acetate, coumarone resin, petroleum resin, or phenolic resin.

Also usable as the binder 6 is an irradiation-curing resin which is hardened by UV irradiation, and liquid such as an oil is also usable which has an effect of attaching the dissimilar metal particle. In the case of the oil like a lubricating oil, when its viscosity is set to be high, the powdered metal layer can be made thick, and when the viscosity is set to be low, the powdered metal layer can be made thin. Unlike an adhesive or glue, the oil is not hardened but its adhesive strength serves to attach the dissimilar metal particle to the surface of the base metal.

[0096] In the temporary filming step, it is also possible that the binder 6 in a power state and the dissimilar metal particle 2 are electrostatically attached to the surface of the base metal 1 and subsequently heated to bond the dissimilar metal particle 2 on the surface of the base metal 1 by means of such heated binder 6, and thus the powdered metal layer 9 is provided on the surface. Used as such binder 6 is a hot-melt type of binder which is melted when heated. The hot-melt type binder, after being heated and melted, cools down to bond the dissimilar metal particle 2 on the surface of the base metal 1. When the powdered binder 6 and dissimilar metal particle 2 are accelerated by the electrostatic

force toward the surface of the base metal 1, the kinetic energy of the dissimilar metal particle 2 becomes larger because the specific gravity of the dissimilar metal particle is large as compared with the binder 6. Therefore, when the binder 6 and the dissimilar metal particle 2 both in a powder state is electrostatically accelerated toward and attached on the surface of the base metal 1, the heavier dissimilar metal particle 2 penetrates into the lighter binder 6 and is tightly bonded on the surface of the base metal 1 to become the powdered metal layer 9.

[0097] In the case of the powdered metal layer 9 bonded via the binder 6 on the surface of the base metal 1, the film thickness of the powdered metal layer 9 is controllable by adjusting the viscosity of the binder 6 and the film thickness of coating the binder 6. When the viscosity of the binder 6 is set to be high, the film thickness of the powdered metal layer 9 can be made thick. And, when the film thickness of the binder 6 coated on the surface of the base metal 1 is set to be thick, the film thickness of the powdered metal layer 9 can also be made thick. The viscosity of the binder 6 is controllable by adjusting the amount of dilution by the solvent. The viscosity of the binder 6, being thinly diluted by an increased amount of solvent, can be made low.

[0098] In the temporary filming step, the dissimilar metal particle 2 with its average particle size being 0.03  $\mu$ m through 500  $\mu$ m is accelerated toward and impinged upon the surface of the base metal 1. The average particle size of the dissimilar metal particle 2 is influential on the film thickness of the powdered metal layer 9. Used as the dissimilar metal particle 2 jetted toward the base metal 1 is a particle with an optimal value in view of the film thickness of the powdered metal layer 9, with such value being preferably 0.1  $\mu$ m or more, and more preferably 0.3  $\mu$ m or more; preferably 50  $\mu$ m or less, and more preferably 10  $\mu$ m or less.

[0099] Further, also usable as the dissimilar metal particle is a substance in which a metal fine particle of the dissimilar metal becoming the powdered metal layer is attached on the surface of the transport carrier particle not becoming the powdered metal layer. In such dissimilar metal particle, the average particle size of the transport carrier particle is set to be 100  $\mu$ m through 1 mm, while the metal fine particle is set to be 0.03  $\mu$ m through 30  $\mu$ m. In such dissimilar metal particle, when the metal fine particle is small, a thin powdered metal layer can be efficiently attached on the surface of the base metal. This is because the kinetic energy of the large transport carrier particle enables the metal fine particle to be vigorously impinged upon the surface of the base metal.

(Beam Irradiation Step)

20

25

30

35

40

45

50

55

[0100] In this step, the surface of the base metal 1 provided with the powdered metal layer 9 is irradiated with the energy beam of the electron beam or the laser beam, and the powdered metal layer 9 is locally heated by the effect of the energy of the energy beam so as to be bonded to the base metal 1. FIG. 2 shows the electron beam irradiator 10 used in the beam irradiation step. The electron beam irradiator 10 is so constructed and arranged that the base metal 1 provided with the powdered metal layer 9 is placed inside a sealed chamber 11, the sealed chamber 11 is evacuated, and the surface is irradiated with the electron beam 4. It should be noted that the sealed chamber 11 may be in an atmosphere of being filled with a gas such as nitrogen gas, depending on a specified purpose. The electron beam 4 is tuned to be in an energy density best suited for enabling the powdered metal layer 9 to be bonded to the base metal 1, and the surface of the base metal 1 is subjected to irradiation. The electron beam irradiator 10 includes an electron gun 12 for emitting an electron by heating a heater 18, a focusing coil for focusing an electron ray, emitted by the electron gun 12, into the electron beam 4 by the effect of a magnetic field, and a deflecting coil 14 for scanning the focused electron beam 4 over the surface of the base metal 1 by the effect of the magnetic field.

**[0101]** The electron gun 12 includes a cathode 15 for emitting a thermoelectron when the heater 18 is heated, a bias electrode 16 for controlling the number of electron emitted by the cathode 15, namely, a current value of the electron beam 4, and an anode 17 for accelerating the electron beam 4. The cathode 15 and the bias electrode 16 receive a negative going voltage and the anode 17 receives a high-tension, positive going voltage, both of the voltages being supplied from a power source 19. The electron beam 4 emitted by the electron gun 12 is focused by means of the focusing coil 13 onto a spot having a given area on the surface of the base metal 1. Further, the electron beam 4 is scanned by the deflecting coil 14 to irradiate an entire area of the base metal 1 with the electron beam 4.

**[0102]** The energy of the electron beam 4 is controllable by adjusting an acceleration voltage of the anode 17, a current value of the electron beam 4 provided by the negative going voltage of the bias electrode 16, and a scanning speed provided by the deflecting coil 14. The energy density in the irradiation range can be increased by increasing the acceleration voltage, decreasing the negative going voltage of the bias electrode 16, decreasing the spot area of focusing the electron beam 4, and further slowing down the scanning speed.

**[0103]** The energy of the electron beam 4 with which the surface of the base metal 1 is irradiated by the electron beam irradiator 10 is set at an optimal value, depending on the material and film thickness of the powdered metal layer 9 and on the kind of the base metal 1. The energy of the electron beam is preferably of an amount such that the powdered metal layer 9 and the base metal 1 are bonded together in an alloyed state. In this method, a surface layer 5 with the powdered metal layer 9 and the base metal 1 having been bonded together in an alloyed state is formed on the surface of the base metal 1 as shown in FIG. 13.

**[0104]** However, the energy of the electron beam 4 is also controllable to be of an amount such that the dissimilar metal particle 2 being a metal particle with a low melting point as compared with the base metal 1 is shot-peened on the surface of the base metal 1, such surface is irradiated with the electron beam 4 to melt the powdered metal layer 9, and the powdered metal layer 9 is bonded to the base metal 1. In such method, the powdered metal layer 9 having been melted is bonded on the surface of the base metal 1 to form the surface layer 5 as shown in FIG. 14.

**[0105]** Further, the energy of the electron beam irradiation is also controllable to be of an amount such that the dissimilar metal particle 2 being a metal particle with a high melting point as compared with the base metal 1 is shot-peened on the surface of the base metal 1, such surface is irradiated with the electron beam 4 to melt the base metal 1, and the powdered metal layer 9 is bonded to the base metal 1. In such method, the surface layer 5 with the powdered metal layer 9 being bonded in a buried state on the surface of the base metal 1 having been melted is formed on the surface of the base metal 1 as shown in FIG. 15.

**[0106]** Further, in the temporary filming step, the dissimilar metal particles 2 with different average particle sizes can be jetted toward the surface of the base metal 1 to provide the powdered metal layer 9 having a surface irregularity as shown in FIG. 16. When such powdered metal layer 9 is irradiated with the electron beam, the powdered metal layer 9 is bonded in a state of the surface irregularity to the base metal 1 and the surface layer 5 is formed with such surface irregularity as shown in the drawing.

**[0107]** Further, although not shown, in the temporary filming step, a plurality of dissimilar metal particles composed of different metals can also be jetted toward the surface of the base metal to provide the powdered metal layer composed of the different metals. When the powdered metal layer is irradiated with the electron beam, the surface layer composed of a plurality kinds of metal particles can be formed on the surface of the base metal.

[0108] Further, in the surface treatment method of the present invention, when the shot-peening step and the electron beam irradiation step are repeated a plurality of times, a plurality of surface layers 5 can also be laminated on the surface of the base metal 1. As shown in FIG. 17, in this method, the powdered metal layer 9 provided on the surface of the base metal 1 in the temporary filming step is irradiated with the electron beam in the electron beam irradiation step, the powdered metal layer 9 and the base metal 1 are bonded together, and the surface layer 5 is provided on the surface of the base metal 1; subsequently, the powdered metal layer 9 is provided via the binder 6 on the surface of the surface layer 5; further the powdered metal layer 9 is irradiated with the energy beam to bond the powdered metal layer 9 on the surface layer 5; and the surface layers 5 in two layers are laminated on the surface of the base metal 1. When these steps are further repeated, the surface layer in multiple layers can be laminated on the surface of the base metal. Thus, in the method of laminating a plurality of surface layers 5 on the surface of the base metal 1, a thick film can be formed on the surface of the base metal 1. Further, the plurality of surface layers 5 laminated on the surface of the base metal 1 may be composed of the metals of the same kind or of the metals of different kinds. The method of laminating the surface layers composed of the metals of the same kind on the surface of the base metal enables the surface layer in a thick film composed of metals of the same kind to be formed on the surface of the base metal. Further, the method of laminating the surface layer composed of the metals of different kinds on the surface of the base metal enables the plurality of metal films with different properties to be formed in a laminated state on the surface of the base metal.

**[0109]** Since the above-described shot-peening step and electron beam irradiation step in the metal surface treatment method of the present invention can be repeated a plurality of times, the film thickness of the entire surface layer formed on the surface of the base metal can be made thick. Therefore, by adjusting such film thickness, a metal surface on a broad variety of products can be processed to be suitable for a specified purpose.

**[0110]** In the above-described method, the powdered metal layer 9 is irradiated with the electron beam 4 and bonded on the surface of the base metal 1, but the powdered metal layer can also be bonded on the surface of the base metal when irradiated with the laser beam instead of the electron beam. That is, the powdered metal layer can also be bonded on the surface of the base metal by the effect of the energy of the laser beam instead of the energy of the electron beam. The laser beam melts both or one of the dissimilar metal particle and the base metal by the energy of an electromagnetic wave instead of the energy of the electron.

(Polishing Step)

20

30

35

40

45

[0111] In the polishing step, the surface of the surface layer provided by bonding the powdered metal layer to the base metal is polished to be smoothed. This polishing step is not an essential step to the present invention, but when the surface layer is polished, the surface can be controlled for given surface smoothness so as to reduce its friction resistance to a further extent. Further, the wear of the opposite contact surface being in contact with the surface layer can also be reduced. The polishing step is performed by shot-blasting an abrasive particle on the surface layer of the base metal. Usable as the abrasive particle is an organic fine powder being silicon carbide, silica, alumina, or a mixture of such substances, and a metal particle is also usable, including at least either of W, C, B, Ti, Ni, Cr, Si, Mo, Ag, Au, Ba, Be, Ca, Co, Cu, Fe, F, fluoride, Mg, Mn, Nb, Pt, S, a sulfide, Ta, or V. The abrasive particle used for the shot-blasting operation in the polishing step is set to have its average particle size being larger than 1 μm and smaller than 50 μm.

#### (Example 4)

- (1) Temporary Filming Step
- [0112] The binder in a paste state was coated on the surface of the base metal composed of a tool steel (SKD-11). Gum Arabic was used as the binder. With the binder being in an unhardened state, the power of molybdenum disulfide as the dissimilar metal particle was shot-peened. The shot-peened power of molybdenum disulfide was accelerated by the pressurized air toward the surface of the base metal and impinged on the surface of the ferrous tool steel being the base metal so as to become the powdered metal layer. The molybdenum disulfide being the dissimilar metal particle was set to have its average particle size of 10 µm, and the air pressure for shot-peening operation was set to be 0.1 MPa. Subsequently, the binder was hardened. In this temporary filming step, the powdered metal layer of molybdenum disulfide with its film thickness of 200 µm was provided on the surface of the base metal.
  - (2) Beam Irradiation Step

[0113] After the binder had been hardened, the base metal provided with the powdered metal layer of molybdenum disulfide was placed inside the sealed chamber. The sealed chamber was evacuated into a vacuum state, and the surface of the base metal was irradiated with the electron beam. Conditions for the electron beam irradiation were set as follows. The degree of vacuum in the sealed chamber was 7 Pa or less.

> Diameter of the Area Spotted by the Electron Beam  $0.3 \, \text{mm}$ Acceleration Voltage 30 kV **Beam Current** 100 mA Scanning Area of the Electron Beam  $30 \, \text{mm} \times 30 \, \text{mm}$ Scanning Time Period over the Entire Area 87 sec.

[0114] When the electron beam is scanned in a parallel direction and the entire scanning area is uniformly subjected to the electron beam irradiation, molybdenum disulfide and tool steel (SKD-11) are melted and bonded together, and the surface layer of molybdenum disulfide with its excellent lubricating ability is provided on the surface of the base metal. Subsequently, the dissimilar metal particle flying and being attached on the surface while being irradiated with the electron beam is scraped away for adjustment of the surface roughness.

[0115] In the above-described step, the surface layer of molybdenum disulfide sized about 10  $\mu$ m is obtained. With the SKD-11 metal and the molybdenum disulfide being strongly bonded together in an alloyed state, the surface layer can have a very small coefficient of friction, and very good resistance to wear is also realized. In the case of the tool steel having been surface-treated in the above-described method, the surface layer can be bonded very strongly as compared with the method of merely shot-peening the molybdenum disulfide.

[0116] In the case of the tool steel having been surface-treated in the above method, a very small value is obtained in terms of the coefficient of friction of the surface.

(Example 5)

[0117] Except that the surface layer being surface-treated in Example 4 was polished in the below-mentioned polishing step to obtain best-suited smoothness, the base metal was subjected to the same surface treatment as in Example 4. The energy beam irradiation mark on the surface layer was smoothed in the polishing step. The polishing step was carried out by shot-blasting the abrasive particle upon the surface layer to smoothly polish the surface. The polishing step by the shot-blasting operation was carried out by jetting the silicon carbide of its average diameter of 50 µm by means of the pressurized air of 0.5 MPa in the first shot-blasting operation, and by jetting the silicon carbide of its average diameter of 20 µm by means of the pressurized air of 1.2 MPa in the second shot-blasting operation. Further in the third shot-blasting operation, a particle witch diamond dust being attached on a surface of a plastic particle was jetted by means of the air of 1 MPa.

[0118] Such polished surface layer has a very small value of 0.27 in terms of the surface coefficient of friction according to the ball-on-disk wear test, the value being a match with a level of 0.2 exhibited by DLC which is deemed to have the smallest coefficient of friction.

[0119] However, the ball-on-disk wear test was performed in the following conditions, as shown in FIG. 18.

16

20

15

25

30

40

35

45

50

(Measurement Condition)

[0120]

5

10

15

20

25

30

35

40

45

50

55

Sliding Speed 0.1 m/sec.

Load 5 N

Measurement Time 900 sec.

Opposite Steel Ball SUJ2 (3/8 in.)

(Example 6)

[0121] Except that the dissimilar metal particle was changed from the molybdenum disulfide to the tungsten disulfide, the surface layer of tungsten sulfide sized about 10  $\mu$ m was provided on the surface of the base metal in the same manner as in Example 4. With the SKD-11 metal and the tungsten disulfide being strongly bonded together in an alloyed state, the surface layer was able to have a very small coefficient of friction, and very good resistance to wear was also realized. In the case of the tool steel having been surface-treated in the above method, the surface layer was able to be bonded very strongly on the surface as compared with the method of merely shot-peening the tungsten disulfide.

[0122] In the case of the tool steel having been surface-treated in the above method as well, a very small value is obtained in terms of the coefficient of friction of the surface.

(Example 7)

**[0123]** Except that the surface layer being surface-treated in Example 6 was polished in the same polishing step as in Example 5 to obtain best-suited smoothness, the base metal was subjected to the same surface treatment as in Example 6. The energy beam irradiation mark on the surface layer was smoothed in the polishing step, and such polished surface layer had a very small value of 0.3 in terms of the surface coefficient of friction, the value being a match with a level of 0.2 exhibited by DLC which is deemed to have the smallest coefficient of friction.

(Example 8)

[0124] Except that the dissimilar metal particle was changed from the molybdenum disulfide to the boron nitride, the surface layer of boron nitride sized about 10  $\mu$ m was provided on the surface of the tool steel in the same manner as in Example 4. With the SKD-11 metal and the boron nitride being strongly bonded together in an alloyed state, the surface layer was able to have a very small coefficient of friction, and very good resistance to wear was also realized. In the case of the tool steel having been surface-treated in the above method, the surface layer was able to be bonded very strongly as compared with the method of merely shot-peening the boron nitride.

[0125] In the case of the tool steel having been surface-treated in the above method as well, a very small value is obtained in terms of the coefficient of friction of the surface.

(Example 9)

**[0126]** Except that the surface layer being surface-treated in Example 8 was polished in the same polishing step as in Example 5, the base metal was subjected to the same surface treatment as in Example 8. The energy beam irradiation mark on the surface layer was smoothed in the polishing step, and such polished surface layer had a very small value of 0.3 in terms of the surface coefficient of friction, the value being close to a level of 0.2 exhibited by DLC which is deemed to have the smallest coefficient of friction.

(Example 10)

[0127] Except that the laser beam was irradiated instead of the electron beam, the surface layer of boron nitride sized about 10  $\mu$ m was provided on the base metal in the same manner as in Example 8. With the SKD-11 metal and the boron nitride being melted and strongly bonded together in an alloyed state, the surface layer was able to have a very small coefficient of friction, and very good resistance to wear was also realized, as compared with the surface treatment in which the boron nitride was merely shot-peened and attached on the surface of the base metal.

**[0128]** In the above-described Examples, the dissimilar metal particle was attached via the binder on the surface of the base metal, the powdered metal layer was provided on the surface of the base metal, the surface layer was provided when the powdered metal layer was irradiated with the energy beam to obtain the surface layer, and subsequently the

surface layer was polished in the polishing step. In the present invention, however, it is also possible that, without using the binder, the dissimilar metal particle is shot-peened to be attached on the surface of the base metal, the surface is irradiated with the energy beam of the electron beam or the laser beam so as to provide the surface layer, and subsequently the irradiation mark caused by the energy beam irradiation is polished to control for obtaining an optimal value of smoothness on the surface layer.

Industrial Applicability

**[0129]** The present invention, in which the base metal is surface-treated, realizes the good friction resistance and the small coefficient of friction which might not be realized by the base metal alone or by other surface treatment operation such as a metal plating operation, and the present invention is usable in an ideal state for various applications, particularly for a variety of applications where good resistance to wear and a smaller friction resistance are required.

Brief Description of the Drawings

#### [0130]

10

15

20

25

35

40

45

50

55

- FIG. 1 is a schematic view showing the shot-peening step in the metal surface treatment method in accordance with an embodiment of the present invention;
- FIG. 2 is a schematic view showing the electron beam irradiation step in the metal surface treatment method in accordance with an embodiment of the present invention;
  - FIG. 3 is a schematic, cross-sectional view showing the metal surface treatment method in accordance with an embodiment of the present invention;
  - FIG. 4 is a schematic, cross-sectional view showing the metal surface treatment method in accordance with another embodiment of the present invention;
  - FIG. 5 is a schematic, cross-sectional view showing the metal surface treatment method in accordance with even another embodiment of the present invention;
  - FIG. 6 is a schematic, cross-sectional view showing the metal surface treatment method in accordance with yet another embodiment of the present invention;
- FIG. 7 is a schematic, cross-sectional view showing the metal surface treatment method in accordance with a further embodiment of the present invention;
  - FIG. 8 is a schematic view showing the temporary filming step in the metal surface treatment method in accordance with another embodiment of the present invention;
  - FIG. 9 is a schematic, cross-sectional view showing the temporary filming step in the metal surface treatment method in accordance with yet another embodiment of the present invention;
  - FIG. 10 is a schematic, cross-sectional view showing the temporary filming step in the metal surface treatment method in accordance with a further embodiment of the present invention;
  - FIG. 11 is a schematic, cross-sectional view showing the temporary filming step in the metal surface treatment method in accordance with an even further embodiment of the present invention;
  - FIG. 12 is a schematic, cross-sectional view showing the temporary filming step in the metal surface treatment method in accordance with a yet further embodiment of the present invention;
  - FIG. 13 is a schematic, cross-sectional view showing the metal surface treatment method in accordance with another embodiment of the present invention;
  - FIG. 14 is a schematic, cross-sectional view showing the metal surface treatment method in accordance with yet another embodiment of the present invention;
  - FIG. 15 is a schematic, cross-sectional view showing the metal surface treatment method in accordance with even another embodiment of the present invention;
  - FIG. 16 is a schematic, cross-sectional view showing the metal surface treatment method in accordance with a further embodiment of the present invention;
  - FIG. 17 is a schematic, cross-sectional view showing the metal surface treatment method in accordance with an even further embodiment of the present invention;
    - FIG. 18 is a schematic, perspective view showing an example of the ball-on-disk wear test; and
    - FIG. 19 is an enlarged, cross-sectional view showing an example in which the dissimilar metal film is provided on the base metal in a conventional surface treatment method.

**Description of Reference Numerals** 

[0131]

1... Base Metal

55

		2Dissimilar Metal Particle
5		3Dissimilar Metal Film
		4Electron Beam
10	0	5Surface Layer
70		6Binder
		7 Nozzle
15		8 Electro-Conductive Vessel
		9 Powdered Metal Layer
20		10Electron Beam Irradiator
		11 Sealed Chamber
		12Electron Gun
25		13 Focusing Coil
		14 Deflecting Coil
30		15 Cathode
		16Bias Electrode
		17Anode
35		18 Heater
		19 Power Source
40		90Particulate Aggregate
		91 Base Metal
		92 Powdered Metal Particle
45		93Dissimilar Metal Film
		96Binder
50	Cla	ims
		A metal surface treatment method comprising:
	•	The second of th

on the surface of the base metal (1); and

a shot-peening step of shot-peening a dissimilar metal particle (2) on a surface of a base metal (1), the dissimilar

metal particle (2) being a metal particle different from the base metal (1), to provide a dissimilar metal film (3)

an electron beam irradiation step of irradiating the surface of the base metal (1) with an electron beam (4), the surface of the base metal (1) having been provided with the dissimilar metal film (3) in the shot-peening step,

to bond the dissimilar metal film (3) and the base metal (1) together.

5

10

15

25

40

- 2. The metal surface treatment method as recited in claim 1, **characterized in that** the dissimilar metal film (3) and the base metal (1) are bonded together in an alloyed state by means of an electron beam irradiation.
- 3. The metal surface treatment method as recited in claim 1, wherein said electron beam irradiation step includes melting the dissimilar metal particle (2) and bonding the dissimilar metal film (3) to the base metal (1) by being irradiated with the electron beam (4), after the dissimilar metal particle (2) has been shot-peened on the surface of the base metal (1), the dissimilar metal particle (2) being a metal particle with a low melting point as compared with the base metal (1).
- 4. The metal surface treatment method as recited in claim 1, wherein said electron beam irradiation step includes melting the base metal (1) and bonding the dissimilar metal film (3) to the base metal (1) by being irradiated with the electron beam (4), after the dissimilar metal particle (2) has been shot-peened on the surface of the base metal (1), the dissimilar metal particle (2) being a metal particle with a high melting point as compared with the base metal (1).
- **5.** The metal surface treatment method as recited in claim 1, **characterized in that**, in the shot-peening step, a plurality of dissimilar metal particles (2) composed of different metals are jetted on the surface of the base metal (1).
- 20 **6.** The metal surface treatment method as recited in claim 1, **characterized in that**, in the shot-peening step, the metal particles with different average particle sizes are jetted on the surface of the base metal (1).
  - 7. The metal surface treatment method as recited in claim 1, **characterized in that** the surface of the base metal (1) having been provided with the dissimilar metal film (3) in the shot-peening step is further irradiated with the electron beam (4) in the second electron beam irradiation step so as to bond the dissimilar metal film (3) and the base metal (1) together and a surface layer (5) is provided on the surface of the base metal (1), and that the shot-peening step and the electron beam irradiation step are repeated a plurality of times to laminate a plurality of surface layers (5) on the surface of the base metal (1).
- 30 **8.** The metal surface treatment method as recited in claim 1, **characterized in that**, in the shot-peening step, the dissimilar metal particle (2) used for the shot-peening operation includes at least either of W, C, B, Ti, Ni, Cr, Si, Mo, Ag, Au, Ba, Be, Ca, Co, Cu, Fe, F, fluoride, Mg, Mn, Nb, Pt, S, a sulfide, Ta, or V.
- 9. The metal surface treatment method as recited in claim 1 or claim 7, **characterized in that**, in the shot-peening step, the dissimilar metal particle (2) used for the shot-peening operation is an alloy of a plurality of metals and a compound containing a metal.
  - **10.** The metal surface treatment method as recited in claim 1, **characterized in that**, in the shot-peening step, the dissimilar metal particle (2) used for the shot-peening operation is 0.03 μm or more in an average particle size.
  - **11.** The metal surface treatment method as recited in claim 1, **characterized in that**, in the shot-peening step, the dissimilar metal particle (2) used for the shot-peening operation is 500 μm or less in an average particle size.
- 12. The metal surface treatment method as recited in claim 1, **characterized in that** the base metal (1) is either of: a metal including Fe, Al, Cu, an iron base alloy, an aluminum base alloy, and a copper base alloy; a metal including Ag, Au, Ba, Ca, Co, F, fluoride, Mg, Mn, Ni, Nb, Pt, S, a sulfide, Ta, Ti, and V; a silver base alloy; a gold base alloy; a calcium base alloy; a cobalt base alloy; a chromium base alloy; a magnesium base alloy; a manganese base alloy; a nickel base alloy; a niobium base alloy; a tantalum base alloy; a titanium base alloy; a vanadium base alloy; or a sintered metal.
  - 13. The metal surface treatment method as recited in claim 1, **characterized in that**, in the electron beam irradiation step, the base metal (1) having been provided with the dissimilar metal film (3) is irradiated with the electron beam (4) in a vacuum or in a gas.
- 14. The metal surface treatment method as recited in claim 1, **characterized in that**, in the electron beam irradiation step, the surface is irradiated with the electron beam (4) to bond the dissimilar metal film (3) and the base metal (1) together to provide the surface layer (5) on the surface of the base metal (1), and then the surface of the surface layer (5) is polished in a polishing step.

**15.** A metal surface treatment method comprising:

a temporary filming step where a dissimilar metal particle (2) being a metal particle different from a base metal (1) is accelerated toward and impinged upon the base metal (1) and attached to a surface of the base metal (1) via a binder (6) becoming lost by energy of an energy beam so as to provide a powdered metal layer (9) on the surface of the base metal (1), and a beam irradiation step where the surface of the base metal (1) having the powdered metal layer (9) provided

a beam irradiation step where the surface of the base metal (1) having the powdered metal layer (9) provided thereon in a temporary filming step is irradiated with an energy beam of an electron beam or a laser beam (4), the binder (6) becomes lost, and the powdered metal layer (9) and the base metal (1) are bonded together to provide a surface layer (5) on the surface of the base metal (1).

- **16.** The metal surface treatment method as recited in claim 15, further comprising a polishing step in which the surface of the surface layer (5) is polished after the beam irradiation step.
- 17. The metal surface treatment method as recited in claim 14 or claim 16, **characterized in that**, in the polishing step, the surface layer (5) is polished by shot-blasting an abrasive particle thereon.
  - **18.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, the dissimilar metal particle (2) is accelerated by energy of a pressurized fluid.
  - **19.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, the dissimilar metal particle (2) is accelerated by the effect of an electric field and/or a magnetic field.
  - 20. The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, the dissimilar metal particle (2) with a low melting point as compared with the base metal (1) is impinged upon the surface of the base metal (1).
  - **21.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, the dissimilar metal particle (2) with a high melting point as compared with the base metal (1) is impinged upon the surface of the base metal (1).
  - 22. The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, a plurality of kinds of dissimilar metal particles (2) being different metals are impinged upon the surface of the base metal (1).
  - 23. The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, the dissimilar metal particles (2) with different average particle sizes are impinged upon the surface of the base metal (1).
- **24.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the beam irradiation step, the powdered metal layer (9) and the base metal (1) are bonded together into an alloyed state.
  - **25.** The metal surface treatment method as recited in claim 15, **characterized in that** the temporary filming step and the beam irradiation step are repeated a plurality of times to laminate a plurality of surface layers (5) on the surface of the base metal (1).
  - 26. The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, the dissimilar metal particle (2) accelerated toward and impinged upon the surface of the base metal (1) includes at least either of: W, C, B, Ti, Ni, Cr, Si, Mo, Ag, Au, Ba, Be, Ca, Co, Cu, Fe, Mg, Mn, Nb, Pt, Ta, V, F, S; or fluoride, a sulfide, nitride, a carbide, or boride of such metals.
  - 27. The metal surface treatment method as recited in claim 26, **characterized in that**, in the temporary filming step, the dissimilar metal particle (2) including either of molybdenum disulfide, tungsten sulfide, or boron nitride is accelerated toward and impinged upon the surface of the base metal (1).
  - 28. The metal surface treatment method as recited in claim 15 or claim 25, **characterized in that**, in the temporary filming step, the dissimilar metal particle (2) being an alloy of a plurality of metals and a compound containing a metal is accelerated toward and impinged upon the surface of the base metal (1).

25

5

10

35

30

55

45

- **29.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, the dissimilar metal particle (2) with an average particle size thereof being 0.03  $\mu$ m or more is accelerated toward and impinged upon the surface of the base metal (1).
- 5 **30.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, the dissimilar metal particle (2) with an average particle size thereof being 500 μm or less is accelerated toward and impinged upon the surface of the base metal (1).
- 31. The metal surface treatment method as recited in claim 15, **characterized in that** the base metal (1) is either of: a metal including Fe, Al, Cu, an iron base alloy, an aluminum base alloy, and a copper base alloy; a metal including Ag, Au, Ba, Ca, Co, Mg, Mn, Ni, Nb, Pt, Ta, Ti, and V; a silver base alloy; a gold base alloy; a calcium base alloy; a cobalt base alloy; a chromium base alloy; a magnesium base alloy; a manganese base alloy; a nickel base alloy; a niobium base alloy; a tantalum base alloy; a titanium base alloy; a vanadium base alloy; a sintered metal; F, S; or fluoride, a sulfide, nitride, a carbide or boride of such metals.

15

25

35

40

45

**32.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the beam irradiation step, the base metal (1) provided with the powdered metal layer (9) thereon is irradiated with the energy beam in a vacuum or in a gas.

- 33. The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, a binder (6) being water-soluble or organic solvent-soluble is used as the binder (6) allowing for attachment of the dissimilar metal particle (2).
  - **34.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, an oil is used as the binder (6) for attaching the dissimilar metal particle (2) to the base metal (1).
  - **35.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, saccharides or celluloses are used as the binder (6) for attaching the dissimilar metal particle (2) to the base metal (1).
- **36.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, a substance used as the binder 6, alone or in a mixture of a plurality of kinds, to attach the dissimilar metal particle 2 to the base metal 1 is either of:
  - a material such as gum Arabic, tragacanth, gum karaya, caramel, starch, soluble starch, dextrin, a starch, sodium alginate, gelatin, locust bean gum, and casein;
  - a semi-synthetic material derived from a natural product, the material being either of lignosulfonate, carboxymethyl cellulose sodium salt, methyl cellulose, hydroxyethyl cellulose, sodium salt of carboxymethylated starch, hydroxy-ethylated starch, sodium salt of starch phosphate, hydroxypropyl cellulose, hydroxypropyl methyl cellulose, ethyl cellulose, acetyl cellulose, or ester gum; or
  - a composite being either of polyvinyl alcohol, polyvinyl methyl ether, polyacrylamide, sodium salt of polyacrylic acid, water-soluble copolymer, copolymer of partially saponificated vinyl acetate and vinyl ether, acrylic acid, methacrylic acid, maleic acid and polymer or copolymer of maleic acid ester or salt, polyethylene glycol, polyethylene oxide, polyvinyl pyrrolidone, vinylpyrrolidone-vinyl acetate copolymer, polyvinyl acetate, coumarone resin, petroleum resin, or phenolic resin.
  - **37.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, a radiation hardening-type resin cured by ultraviolet irradiation is used as the binder (6) for attaching the dissimilar metal particle (2) to the base metal (1).
- 38. The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, the powdered metal layer (9) is provided through a process that the binder (6) is coated on the surface of the base metal (1) and the dissimilar metal particle (2) is accelerated toward and impinged upon the surface of the base metal (1) having been coated with the binder (6).
- 39. The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, both of the binder (6) and the dissimilar metal particle (2) are accelerated toward and impinged upon the surface of the base metal (1) to provide the powdered metal layer (9).

**40.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, the powdery binder (6) and the dissimilar metal particle (2) are electrostatically attached to the surface of the base metal (1) and subsequently heated to bond the dissimilar metal particle (2) to the base metal (1) by means of the binder (6) to provide the powdered metal layer (9).

- **41.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, the powdered metal layer (9) is provided on the surface of the base metal (1) through a process that the dissimilar metal particle (2) is attached to the surface of the base metal (1) via the binder (6) of an ultraviolet hardening type, and the binder (6) of the ultraviolet hardening type is cured by ultraviolet irradiation.
- **42.** The metal surface treatment method as recited in claim 15, **characterized in that**, in the temporary filming step, a coating material is sprayed on the surface of the powdered metal layer (9).

# FIG. 1

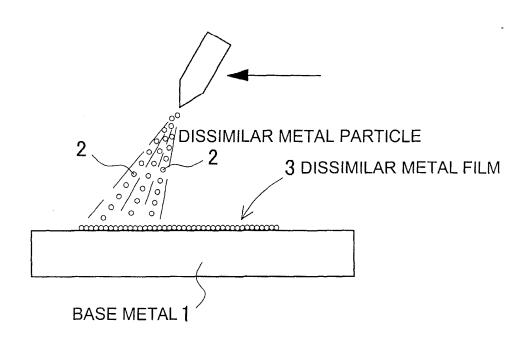


FIG. 2

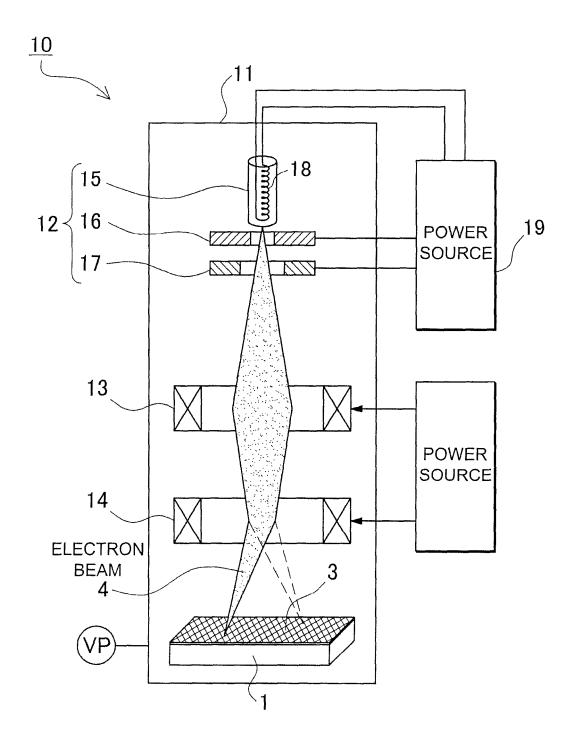


FIG. 3

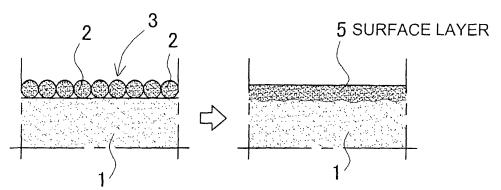


FIG. 4

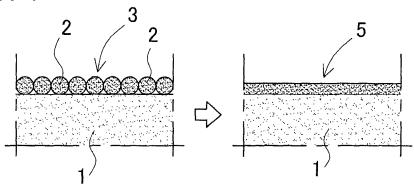


FIG. 5

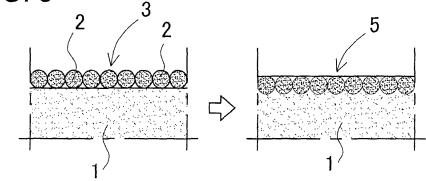
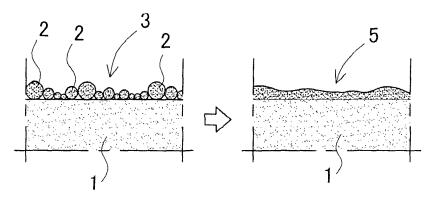


FIG. 6





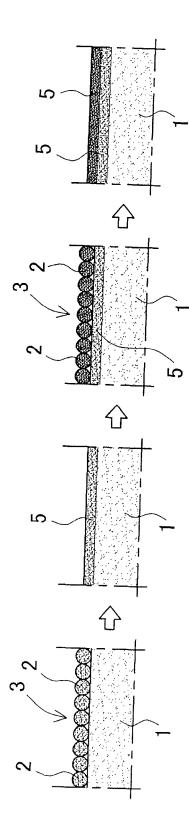


FIG. 8

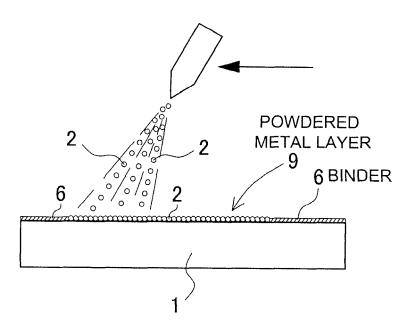


FIG. 9

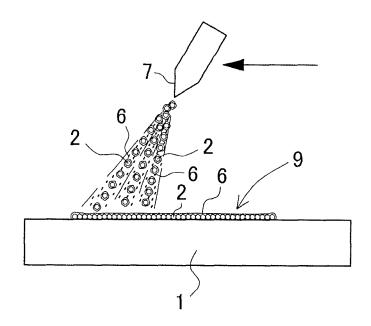


FIG. 10

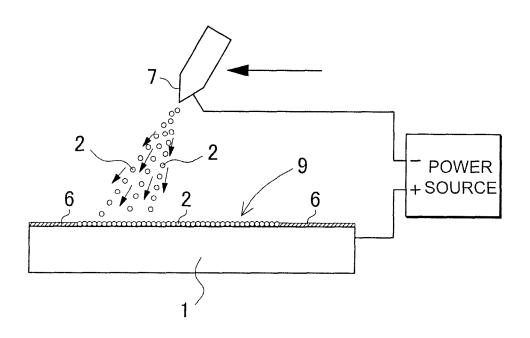


FIG. 11

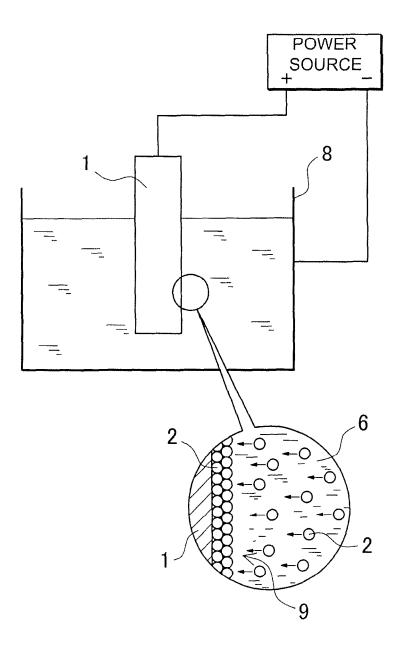


FIG. 12

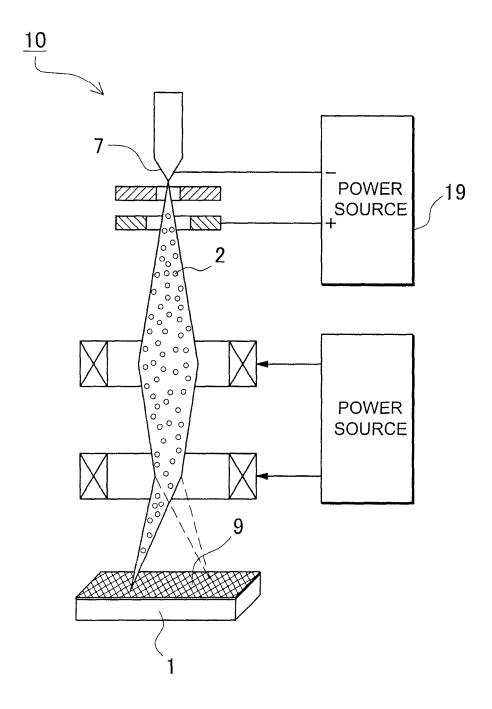


FIG. 13

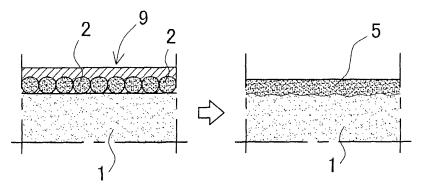


FIG. 14

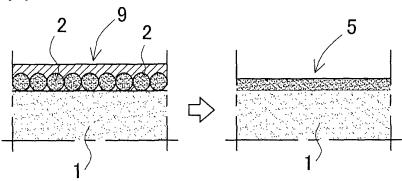


FIG. 15

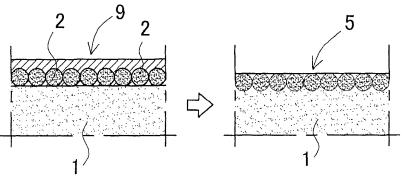
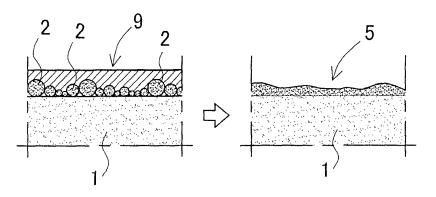


FIG. 16



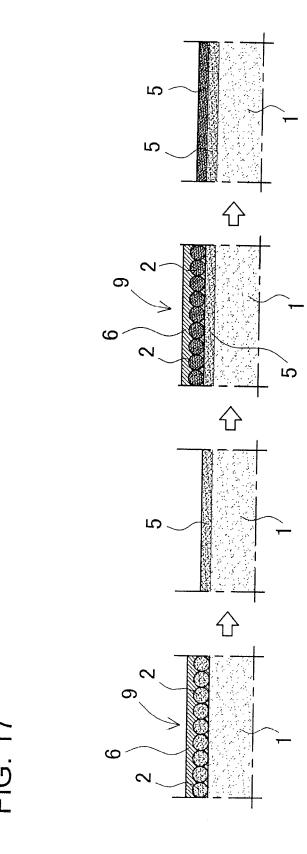


FIG. 18

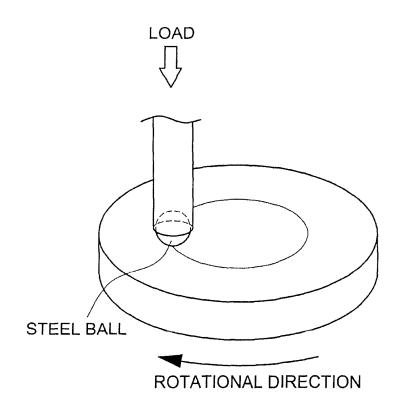
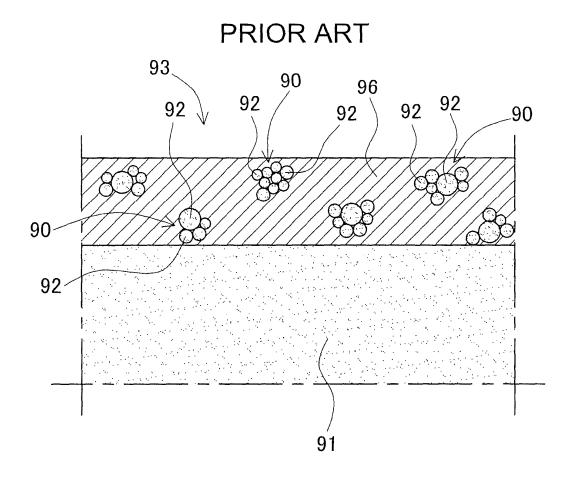


FIG. 19



#### INTERNATIONAL SEARCH REPORT

International application No.

		PCT/JP2	1007/071851							
	ATION OF SUBJECT MATTER (2006.01) i, C23C26/00(2006.01)	i								
According to Inte	ernational Patent Classification (IPC) or to both national	al classification and IPC								
B. FIELDS SE	B. FIELDS SEARCHED									
Minimum docum C23C24/00	nentation searched (classification system followed by cl $-30/00$	assification symbols)								
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2008 Kokai Jitsuyo Shinan Koho 1971-2008 Toroku Jitsuyo Shinan Koho 1994-2008										
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)										
C. DOCUMEN	ITS CONSIDERED TO BE RELEVANT									
Category*	Citation of document, with indication, where ap	<u> </u>	Relevant to claim No.							
Х <u>Ч</u>	JP 2003-106265 A (Aisin AW C 09 April, 2003 (09.04.03), Claims; Par. Nos. [0015] to (Family: none)		1-2,4,8, 12-13 <u>3,5-7,9-11,</u> <u>14-42</u>							
Y	JP 2000-273653 A (Toyota Cer. Development Laboratories, Inc. 03 October, 2000 (03.10.00), Claims; Par. Nos. [0012] to (Family: none)	3,5-7,9-11, 14-42								
Y	JP 2000-216310 A (Toyota Cen Development Laboratories, Ind 04 August, 2000 (04.08.00), Claims; Par. Nos. [0005] to (Family: none)	c.),	3,5-7,9-11, 14-42							
× Further do	cuments are listed in the continuation of Box C.	See patent family annex.								
	ories of cited documents:  fining the general state of the art which is not considered to lar relevance	"T" later document published after the inter date and not in conflict with the applicat the principle or theory underlying the in	ion but cited to understand							
•	eation or patent but published on or after the international filing	"X" document of particular relevance; the cl considered novel or cannot be considered.								
cited to esta	thich may throw doubts on priority claim(s) or which is blish the publication date of another citation or other n (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is								
"O" document re	ferring to an oral disclosure, use, exhibition or other means blished prior to the international filing date but later than the	considered to involve an investment step when the adocument 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								
15 Janı	ll completion of the international search uary, 2008 (15.01.08)	Date of mailing of the international sea 29 January, 2008 (								
	ng address of the ISA/ se Patent Office	Authorized officer								
Facsimile No.		Telephone No.								

Facsimile No.
Form PCT/ISA/210 (second sheet) (April 2007)

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/071851

		PCT/JP2	P2007/071851	
C (Continuation	a). DOCUMENTS CONSIDERED TO BE RELEVANT			
Category*	Citation of document, with indication, where appropriate, of the relevant	ant passages	Relevant to claim No.	
Y	JP 2001-527601 A (The University of Tenr Research Corp.), 25 December, 2001 (25.12.01), Claims; page 5, line 26 to page 16, line & US 6350326 B1 & WO 97/26388 A2	24	15-42	
Y	JP 2004-176086 A (Nippon Steel Corp.), 24 June, 2004 (24.06.04), Claims & US 2006/0166029 A1 & EP 1580288 A1 & WO 2004/046406 A1		15-42	
Y	JP 11-291028 A (The Furukawa Electric Contd.), 26 October, 1999 (26.10.99), Claims; Par. Nos. [0004] to [0013] (Family: none)	o.,	15-42	

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

#### REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

## Patent documents cited in the description

• JP 2000216310 A [0002]