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54 Boride-dispersed alloy material and process for manufacturing same.

57 A process for manufacturing a boride-dispersed alloy material having high electrical and thermal conductivity comprises preparing a metallic matrix containing 0.5 to 40 atom % of at least one boride-forming metal element, such as beryllium, magnesium, aluminum, titanium, cobalt or nickel, the balance being gold, silver or an alloy of gold or silver, and diffusing boron into the matrix to form therein a surface layer in which fine particles of a boride are uniformly dispersed, and which has a thickness of 0.01 to 0.25 mm.

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TITLE OF THE INVENTION

BORIDE-DISPERSED ALLOY MATERIAL AND PROCESS FOR
MANUFACTURING SAME

BACKGROUND OF THE INVENTION

5 Field of the Invention:

This invention relates to a boride-dispersed alloy material, i.e., an alloy material containing a boride distributed in the surface portion of a metallic material and a process for manufacturing same. Such alloy is useful
10 as a material for electrical contacts, sliding parts, or the like.

Description of the Prior Art:

It is known that a composite material composed of a metal and a boride can be produced by sintering or melting.
15 The former method comprises preparing an appropriate mixture of a fine boride powder and, for example, copper powder, and sintering it at an appropriate temperature in an appropriate gas atmosphere. This method, however, involves difficulty in the uniform distribution of the boride, and is
20 expensive. The latter method comprises preparing a mixture of copper and a boride, heating it to a high temperature to melt it, and cooling the molten mixture to solidify it. This method has the disadvantage of the boride being crystallized when the molten alloy is solidified. The
25 boride forms too coarse particles to be satisfactorily finely divided even by forging. Moreover, both of these methods fail to have a boride distributed exclusively in the surface portion of a metallic material, and therefore, produces an alloy having low electrical conductivity.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a boride-dispersed alloy material having high electrical and thermal conductivity and having a surface portion being excellent in wear, adhesion and arc resistance.

It is another object of this invention to provide a boride-dispersed alloy material containing a boride dispersed only in the surface portion of a substrate of gold, silver, a gold alloy or a silver alloy.

It is a further object of this invention to provide a process for manufacturing the aforementioned alloy material.

The boride-dispersed alloy material of this invention comprises a substrate mainly composed of gold or silver and a surface layer formed in a surface portion of the substrate and having a diffusion structure in which fine particles of a boride are uniformly dispersed.

The process of this invention comprises: preparing a metallic matrix containing 0.5 to 40 atom % of at least one boride-forming metal element, the balance being selected from gold, silver, a gold alloy and a silver alloy; and diffusing boron into the matrix to form therein a surface layer in which fine particles of a boride of the boride-forming metal element are uniformly dispersed.

The boride-forming metal element is selected from the group consisting of beryllium (Be), magnesium (Mg), aluminum (Al), silicon (Si), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), gallium (Ga), arsenic (As), zirconium (Zr), niobium (Nb), molybdenum (Mo), palladium (Pd), cadmium (Cd), tantalum (Ta), tungsten (W) and platinum (Pt).

BRIEF DESCRIPTION OF THE DRAWING

FIGURE 1 is a microphotograph showing a cross section, along the thickness, of a boride-dispersed alloy manufactured from an alloy composed of 85 atom % of gold and 15 atom % of cobalt by a process embodying this invention as will hereinafter be described in EXAMPLE 1;

FIGURE 2 is a microphotograph showing a cross section, along the thickness, of a boride-dispersed alloy manufactured from an alloy composed of 70 atom % of gold and 30 atom % of vanadium in EXAMPLE 2 of this invention; and

FIGURE 3 is a microphotograph showing a cross section, along the thickness, of a boride-dispersed alloy manufactured from an alloy composed of 93 atom % of silver and 7 atom % of titanium in EXAMPLE 5.

DETAILED DESCRIPTION

The boride-dispersed alloy material of this invention comprises a substrate mainly composed of gold or silver. This composition is favorable since gold and silver have high electrical and thermal conductivity. Further, they have excellent corrosion resistance against every kind of acidic solution such as hydrochloric acid or sulfuric acid and alkaline solution such as sodium hydroxide or calcium hydroxide. Gold and silver also exhibit high resistance against oxidation when, for example, heated in the air.

The substrate of the boride-dispersed alloy material of this invention is composed of one of the following compositions:

(1) gold or silver;

(2) a gold alloy, a silver alloy or a gold-silver

alloy;

(3) an alloy composed of gold and/or silver and at least one boride-forming element selected from the group consisting of beryllium, magnesium, aluminum, silicon, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, gallium, arsenic, zirconium, niobium, molybdenum, palladium, cadmium, tantalum, tungsten and platinum;

(4) an alloy composed of gold and/or silver and at least one boride-nonforming element selected from the group consisting of copper, zinc, tin, lead, etc.; and

10 (5) an alloy composed of gold and/or silver, at least one boride-forming element selected from the group consisting of beryllium, magnesium, aluminum, silicon, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, gallium, arsenic, zirconium, niobium, molybdenum, palladium, cadmium, tantalum, tungsten and platinum, and at
15 least one boride-nonforming element selected from the group consisting of copper, zinc, tin, lead, etc.

As described above, the substrate composed of gold and silver has excellent corrosion resistance and oxidation
20 resistance. Further, the substrate composed of gold and/or silver alloyed with a boride forming element and/or a boride-non-forming element possesses improved mechanical characteristics, e.g. high mechanical strength.

In the boride-dispersed alloy material of this
25 invention, the surface layer has the diffusion structure wherein fine boride particles resulted from boron and at least one boride-forming element are uniformly dispersed in the surface portion of the substrate.

The boride-forming element is selected from the group
30 consisting of beryllium, magnesium, aluminum, silicon, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, gallium, arsenic, zirconium, niobium, molybdenum,

palladium, cadmium, tantalum, tungsten, platinum, etc. These elements have relatively high hardness, a low specific resistance and a high melting point. All of these elements are capable of forming a solid solution or being dispersed in gold, silver, a gold alloy, a silver alloy or a gold-silver alloy, and combining with boron to form fine and uniformly dispersed particles of a boride.

The surface layer of the boride-dispersed alloy material of this invention includes fine and uniformly dispersed particles of at least one boride selected from the group consisting of AlB_2 , AlB_{10} , AsB , AsB_6 , CdB_6 , Co_2B , CoB , CrB , CrB_2 , FeB , Fe_2B , MgB_2 , MgB_4 , MoB_2 , Mo_2B , NbB , NbB_2 , Ni_2B , PtB , Pt_2B_3 , TaB , TaB_2 , TiB_2 , VB , VB_2 , W_2B_5 , ZrB_2 .

Accordingly, the surface portion of the substrate includes a surface layer having a diffusion structure in which fine particles of these borides are uniformly dispersed and thus having high resistance to wear, adhesion and arc. Further, since the substrate is mainly formed of gold or silver, the surface layer formed thereon also possesses excellent corrosion and oxidation resistance. This composition serves to prevent the formation of oxides on the surface.

According to the process of this invention, the surface portion of the metallic material has a surface layer which is 0.01 to 0.25 mm in depth, and which contains 0.5 to 40 atom % of at least one element selected from Be, Mg, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Ga, As, Zr, Nb, Mo, Pd, Cd, Ta, W and Pt, the balance being gold, silver or an alloy of gold or silver, since it is important to form a boride in the surface layer alone. The rest of the metallic material may be added with any metal, depending on the purpose for which the alloy is used.

At least one of the metal elements hereinabove listed

is used, since they are all capable of forming a solid solution or being dispersed in gold, silver, or an alloy of gold or silver, and combining with the boron diffused in the surface portion of the metallic material to form fine boride particles therein. Moreover, the boride of any such element has a relatively high degree of hardness, a low specific resistance and a high melting point which are important properties for electrical contacts or sliding parts for which the material produced by the process of this invention can advantageously be used. TABLE 1 compares the physical properties of various borides with those of conventional electrical contact materials. All of these borides have a specific resistance of 14 to $100 \times 10^{-6} \Omega \text{ cm}$, a melting point of $1,220^{\circ}\text{C}$ to $3,100^{\circ}\text{C}$ and a hardness of Hv 1,500 to 3,300, and are superior to the conventional materials in melting point and hardness.

The proportion of the boride-forming element is in the range of 0.5 to 40 atom %. If it is less than 0.5 atom %, it is impossible to form the boride in a sufficient quantity to ensure the effect expected from the resulting boride. If it exceeds 40 %, the formation of too much boride disables its proper mixing with gold, silver or a gold or silver alloy in the material produced by this invention, resulting in a reduction in its electrical conductivity and thermal conductivity, and the formation of a surface layer which is easy to crack or peel.

The surface layer in which the boride is dispersed has a depth of 0.01 to 0.25 mm. This limitation is important to ensure the wear, adhesion and arc resistance required of the surface of any electrical contact that may be formed from the material according to this invention, while satisfying the requirements for the high electrical and thermal

conductivity in the inner portion of the alloy matrix. The distribution of a boride throughout the alloy matrix is not always beneficial for imparting high electrical and thermal conductivity. This purpose can be better attained if gold or silver of higher purity is employed in the matrix, or a reinforcing element is added thereto, depending on the characteristics required, while the boride is dispersed only in the surface layer.

The diffusion of boron may, on some occasions, fail to form a uniform layer of fine boride particles, depending on the composition of the material in the surface layer. On such occasions, it is advisable to achieve uniform boride distribution by reducing the quantity of a boride-forming metal element in the matrix alloy, or adding another element that may form a boride more easily.

The metallic material may, as a whole, comprise an alloy of a boride-forming element with gold or silver. This alloy may be prepared by melting the metals in question.

It has hitherto been usual to use a Ag-Ni alloy, Ag-CdO or Ag-InO as a silver-containing material for electrical contacts. Any of these materials per se can be used as the matrix alloy for this invention, or it is possible to add a boride-forming element thereto. Nickel and copper reduce the consumption of silver by an arc, or the like, and InO and CdO provide a clean surface.

Alternatively, an alloy is formed only in the surface layer of the metallic material. Most typically, a metal, such as vanadium or nickel, is coated on the surface of gold or silver as the matrix, and heated for diffusion into the matrix so that an alloy may be formed only in its surface layer. The metal, such as vanadium, can be coated on the matrix surface by a known method, for example, electroplating, chemical plating, vacuum deposition,

sputtering or spray coating. The diffusion of vanadium, etc. into the matrix may be effected by its thermal diffusion at a high temperature.

5 The metallic material can be of any shape, including that of a plate, bar or wire, depending on the purpose for which the alloy will be used.

10 The metallic material thus prepared is subjected to boronizing by a known method, for example, immersing the metallic material in a molten salt bath containing dissolved boron, burying the metallic material in a mixture of the powder of boron carbide, etc. and the powder of boron fluoride, ammonium chloride, etc. and heating it, or vacuum deposition of boron. The boron diffused in the metallic material combines with vanadium, etc. in the matrix alloy to form a boride or borides. At least one of the following borides is formed: AlB_2 , AlB_{10} , AsB , AsB_6 , CdB_6 , Co_2B , CoB , CrB , CrB_2 , FeB , Fe_2B , MgB_2 , MgB_4 , MoB , Mo_2B , NbB , NbB_2 , Ni_2B , PtB , Pt_2B_3 , TaB , TaB_2 , TiB_2 , VB , VB_2 , W_2B_5 , ZrB_2 , etc.

15 A layer in which boride particles are dispersed is, thus, formed in gold, silver or a gold or silver alloy. The smaller the boride particles, the better. According to the process of this invention, there is formed a boride having an average particle diameter of, say, 0.1 to 10 microns. The surface layer preferably contains 0.6 to 50 % by volume of boride particles, and has a thickness of 0.01 to 0.25 mm, and preferably 0.01 to 0.1 mm. A thicker layer can, if desired, be formed by a longer boronizing time, or a higher boronizing temperature.

20 The process of this invention facilitates the uniform distribution of fine boride particles exclusively in the surface layer of the metallic material. Moreover, it is less expensive than the conventional sintering method, and

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TABLE 1

<u>Boride</u>	<u>Specific resist- ance ($10^{-6} \Omega\text{cm}$)</u>	<u>Melting point ($^{\circ}\text{C}$)</u>	<u>Hardness (Hv)</u>
CrB ₂	21	1,850	2,100
MoB ₂	45	2,000	2,300
NbB	64	2,900	2,700
TaB ₂	68	3,100	2,000
W ₂ B ₅	21	2,800	3,000
TiB ₂	28	2,800	3,300
ZrB ₂	94	3,040	2,050
AlB ₂	-	1,350	2,000
Co ₂ B	-	1,265	1,500
CoB	-	1,400	2,000
FeB	-	1,390	1,800
Fe ₂ B	-	1,550	1,500
Ni ₂ B	14	1,220	1,800
VB	35	2,100	2,500
VB ₂	16	-	2,000
<u>Comparative</u>			
Au	2.30	1,063	40
Ag	1.63	960	50
Cu	.1.69	1,083	70
Phosphor bronze	14 to 19	1,050 to 1,070	180

produces a boride-dispersed alloy which is superior in properties to the product of the conventional method.

As is obvious from TABLE 1, the borides are higher than the conventional materials for electrical contacts in
5 hardness, melting point, decomposition temperature and chemical stability. Therefore, the metallic material produced by the dispersion of a boride only in its surface layer in accordance with the process of this invention has a surface layer which is excellent in wear, adhesion and arc
10 resistance, and thus provides a material for electrical contacts or sliding parts in which the surface layer forms a contact area. The product of this invention is sufficiently high in electrical and thermal conductivity as a material for electrical contacts, since the boride is a relatively good
15 electrical conductor and finely distributed only in the surface layer, while the matrix comprises gold, silver or a gold or silver alloy which is a still better conductor. The material as a whole is low in resistance, since the boride
20 exists only in its surface layer.

The process of this invention can produce a boride-dispersed alloy material having substantially any matrix composition so selected as to facilitate its working, such as bending, punching or coining, or improve its thermal
25 conductivity.

The invention will now be described in further detail with reference to several examples thereof.

EXAMPLE 1

A cobalt-gold alloy composed of 85.0 atom % of Au and
30 15.0 atom % of Co and in a shape having a diameter of 10 mm was prepared by melting 95 parts by weight of gold and 5 parts by weight of cobalt. The alloy was swaged into a diameter of 4 mm, and then, rolled into a plate having a

thickness of 1 mm. A sample measuring 4 mm by 20 mm was prepared from the plate. The sample was immersed for four hours in a molten salt bath containing 60 parts by weight of borax ($\text{Na}_2\text{B}_4\text{O}_7$) and 40 parts by weight of boron carbide (B_4C) powder having a particle diameter of 79 to 149 μm , and having a temperature of 900°C , whereby boron was diffused into the sample. The sample was removed from the bath, and air cooled.

The sample was cut to present a cross section, and it was examined by a microscope. The resulting microphotograph is shown in FIGURE 1, in which a layer in which a boride is distributed is shown at 1, and a cobalt-gold matrix alloy at 2. The results indicate the distribution of boride particles having a diameter of 2 to 10 μm up to a depth of about 0.08 mm below the surface of the alloy. The boride in the surface layer showed a ratio of about 18 % by volume. The boride was identified by X-ray diffraction and EPMA as CoB . The metal surrounding the boride was gold.

EXAMPLE 2

A nickel-gold alloy composed of 73 atom % of Au and 27 atom % of Ni was prepared by melting 90 parts by weight of gold and 10 parts by weight of nickel. Boron was diffused in the alloy by the method set forth in EXAMPLE 1. As a result, there was obtained a boride-dispersed alloy having a surface layer which was about 0.1 mm in depth, and in which a boride having a particle diameter of 5 to 20 μm had been distributed. The boride was identified as Ni_2B , and found to occupy about 32 % by volume in the surface portion.

EXAMPLE 3

Gold and vanadium were melted to form an alloy composed of 70 atom % of gold and 30 atom % of vanadium, and a columnar sample having a diameter of 6.4 mm and a length

of 24 mm was prepared therefrom. The sample was buried in a mixture consisting of 75 % by weight of boron carbide powder, 5 % by weight of ammonium chloride powder and 20 % by weight of alumina powder. The whole was placed in an alumina crucible, heated at 900°C for four hours, and air cooled in the crucible, whereby an alloy having a boride-dispersed surface layer 1 was produced. FIGURE 2 is a microphotograph showing a cross section thereof. The layer 1 had a thickness of about 0.06 mm. The boride had a particle diameter of about 5 to 15 μm , and was identified as VB_2 . The boride was found to occupy about 36 % by volume in the layer 1.

EXAMPLE 4

An alloy composed of 95 atom % of Ag and 5 atom % of Co was prepared by melting 97 parts by weight of silver and 3 parts by weight of cobalt. The alloy was boronized by the method employed in EXAMPLE 1 to yield a boride-dispersed alloy. The alloy was found to have a boride-dispersed layer containing very fine CoB particles having a diameter of about 0.5 μm . The layer had a thickness of 0.09 mm. The boride occupied about 6 % by volume in the layer.

EXAMPLE 5

An alloy composed of 93 atom % of Ag and 7 atom % of Ti was prepared by melting 97 parts by weight of silver and 3 parts by weight of titanium. The alloy was boronized by the method employed in EXAMPLE 1, whereby a boride-dispersed layer having a boride-dispersed layer 1 was produced. FIGURE 3 is a microphotograph showing a cross section thereof. The layer 1 had a thickness of about 0.25 mm. The boride had a particle diameter of about 2 to 15 μm , and occupied about 8 % by volume in the layer 1. The boride was identified by X-ray diffraction as TiB_2 .

WHAT IS CLAIMED IS:

1. A process for manufacturing a boride-dispersed alloy material comprising:

5 preparing a metallic matrix containing 0.5 to 40 atom % of at least one boride-forming metal element, the balance being gold, silver, a gold alloy or a silver alloy; and

diffusing boron into said matrix to form therein a surface layer in which fine particles of a boride of said boride-forming metal element are uniformly dispersed.

10 2. A process according to Claim 1, wherein said boride-forming metal element is selected from the group consisting of beryllium, magnesium, aluminum, silicon, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, gallium, arsenic, zirconium, niobium, molybdenum,
15 palladium, cadmium, tantalum, tungsten, and platinum.

3. A process according to Claim 1, wherein said boride-forming element exists only in said surface layer.

20 4. A process according to Claim 1, wherein said matrix is prepared by coating said boride-forming element on the surface of a matrix material selected from gold, silver, a gold alloy and a silver alloy, and heating said matrix material to cause diffusion of said element into said matrix material to form said surface layer.

25 5. A process according Claim 1, wherein said matrix is, as a whole, composed of an alloy of said boride-forming element and gold or silver.

30 6. Boride-dispersed alloy material comprising:
a substrate mainly composed of gold, silver, a gold alloy or a silver alloy, and
a surface layer formed in a surface portion of said

substrate, said surface layer having a diffusion structure in which fine particles of a boride are uniformly dispersed.

5 7. Boride-dispersed alloy material according to Claim 6, wherein said substrate is composed of gold and/or silver and least one element selected from the group consisting of beryllium, magnesium, aluminum, silicon, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, gallium, arsenic, zirconium, niobium, molybdenum, palladium, cadmium, tantalum, tungsten and platinum.

10 8. Boride-dispersed alloy material according to Claim 6, wherein said boride is composed of at least one mixture of a compound of boron and at least one element selected from the group consisting of beryllium, magnesium, aluminum, silicon, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, gallium, arsenic, zirconium, niobium, molybdenum, palladium, cadmium, tantalum, tungsten, and platinum.

20 9. Boride-dispersed alloy material according to Claim 6, wherein said boride is a mixture composed of at least one boride selected from the group consisting of AlB_2 , AlB_{10} , AsB , AsB_6 , CdB_6 , Co_2B , CoB , CrB , CrB_2 , FeB , Fe_2B , MgB_2 , MgB_4 , MoB_2 , Mo_2B , NbB , NbB_2 , Ni_2B , PtB , Pt_2B_3 , TaB , TaB_2 , TiB_2 , VB , VB_2 , W_2B_5 and ZrB_2 .

25 10. Boride-dispersed alloy material comprising a substrate mainly composed of gold or silver, and a surface layer formed in a surface portion of said substrate and having a diffusion structure in which fine particles of a boride are uniformly dispersed by diffusion, wherein said surface layer has a depth of from 0.01 to 0.25 mm and said fine boride particles included in said surface layer have an average diameter of 0.1 to 10 microns.

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FIG. 1

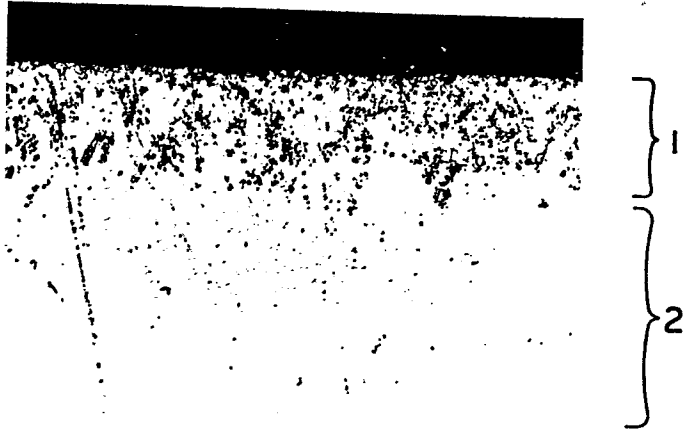


FIG. 2

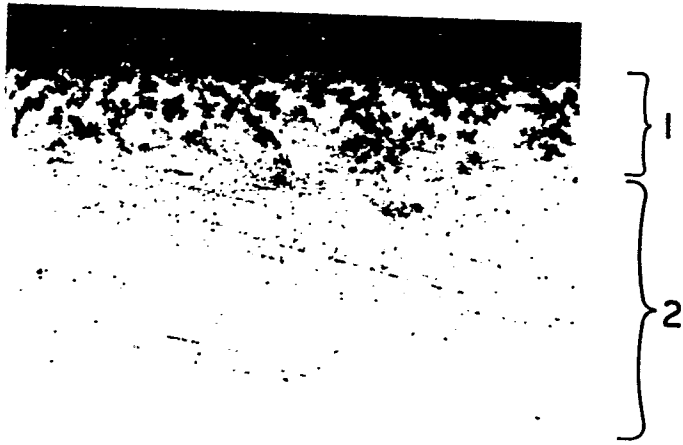


FIG. 3

