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(54) METALLIC MATERIAL FOR ELECTRONIC COMPONENT, METHOD FOR MANUFACTURING SAID METALLIC MATERIAL, AND CONNECTOR TERMINAL, CONNECTOR, AND ELECTRONIC COMPONENT IN WHICH SAID METALLIC MATERIAL IS USED

(57) The present invention provides a metallic material for electronic components having a low adhesive wear. The metallic material for electronic components comprises a base material, on the base material, a lower layer constituted with one or two or more selected from a constituent element group A consisting of Ni, Cr, Mn, Fe, Co and Cu, on the lower layer, an intermediate layer, on the intermediate layer, an upper layer constituted with an alloy comprising one or two selected from a constituent element group B consisting of Sn and In and one or two or more selected from a constituent element group C consisting of Ag, Au, Pt, Pd, Ru, Rh, Os and Ir, and on the upper layer, a treated layer having C content being 60at% or more and O content being 30at% or less. The intermediate layer consists of one or two or more selected from the constituent element group A and one or two selected from the constituent element group B, and when the metallic material is heated at 250 °C for 30 seconds, an area ratio of oxide particles adhering to a surface of the treated layer is 0.1 % or less.

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Description

[Technical Field]

[0001] The present invention relates to a metallic material for electronic components, a method for producing the same, connector terminals, connectors and electronic components using the same.

[Background Art]

[0002] In connectors as connecting components for electronic devices for consumer use and for vehicle use, materials are used in which base plating of Ni or Cu is applied to the surface of brass or phosphor bronze materials and Sn or Sn alloy plating is further applied to the base plating. Sn or Sn alloy plating is generally required to have properties such as low contact resistance and high solder wettability, and further, recently the reduction of the insertion force has also been required at the time of joining together a male terminal and a female terminal molded by press processing of plating materials.

[0003] In this regard, Patent Literature 1 discloses a coating material comprising a conductive base material and a coating layer formed on the conductive base material. The coating layer comprises intermetallic compounds of Sn and precious metals on at least its surface. Patent Literature 1 discloses that, according to this, contact resistance is low and it has a low coefficient of friction and is effective for reducing insertion force.

[Citation List]

[Patent Literature]

[0004] [Patent Literature 1] Japanese Patent Laid-Open No. 2005-126763

[Summary of Invention]

[Technical Problem]

[0005] In the technique described in Patent Literature 1, the coating layer comprises intermetallic compounds of Sn and precious metals, and a thickness of Ag-Sn alloy layer comprising intermetallic compounds (Ag_3Sn) of Sn and precious metals is preferably 1 μm or more and 3 μm or less. However, in the present inventor's evaluation, the thickness could not reduce the insertion force sufficiently. Furthermore, since the alloy layer is in a state where intermetallic compound particles are dispersed in the Sn matrix, Sn is exposed. However, a surface of the alloy layer can corrode in corrosive environments. This leads to an increase in electrical resistance.

[0006] As described above, the conventional metallic material for electronic components having the Sn-Ag alloy / Ni base plating structure still has a problem that the insertion force cannot be lowered sufficiently.

[0007] The present invention has been achieved in order to solve the above-described problems, and an object of the present invention is the provision of a metallic material for electronic components, and connector terminals, connectors and electronic components using the same, having a low adhesive wear. The adhesive wear refers to a wear phenomenon that occurs due to the fact that an adhesive portion constituting the real contact area between solids is sheared by frictional motion. When the adhesive wear increases, the insertion force when the male terminal and the female terminal are fitted together increases.

[Solution to Problem]

[0008] The present inventors made a diligent study, and consequently have discovered that a metallic material for electronic components having a low adhesive wear can be produced by disposing a lower layer, an intermediate layer and an upper layer on a base material by using a prescribed metals, and controlling an amount of oxide particles on a surface of the treated layer after heating.

[0009] The present invention perfected on the basis of the above-described findings is, in an aspect thereof, a metallic material for electronic components comprising:

a base material;
on the base material, a lower layer constituted with one or two or more selected from a constituent element group A consisting of Ni, Cr, Mn, Fe, Co and Cu;
on the lower layer, an intermediate layer;

on the intermediate layer, an upper layer constituted with an alloy comprising one or two selected from a constituent element group B consisting of Sn and In and one or two or more selected from a constituent element group C consisting of Ag, Au, Pt, Pd, Ru, Rh, Os and Ir; and

on the upper layer, a treated layer having C (carbon) content being 60at% or more and O (oxygen) content being 30at% or less,

wherein the intermediate layer consists of one or two or more selected from the constituent element group A and one or two selected from the constituent element group B, and

when the metallic material is heated at 250 °C for 30 seconds, an area ratio of oxide particles adhering to a surface of the treated layer is 0.1 % or less.

[0010] In one embodiment of the metallic material for electronic components of the present invention, the treated layer further comprises one or more selected from the group consisting of S, P and N.

[0011] Another aspect of the present invention is a method for producing a metallic material for electronic components, comprising a step of placing a metallic material in a treatment solution containing 2.5 to 5.0 g/L of phosphate ester-based treatment solution and stirring ultrasonically to form a treated layer having C (carbon) content being 60at% or more and O (oxygen) content being 30at% or less on a surface of the metallic material,
wherein the metallic material comprises:

a base material;

on the base material, a lower layer constituted with one or two or more selected from a constituent element group A consisting of Ni, Cr, Mn, Fe, Co and Cu;

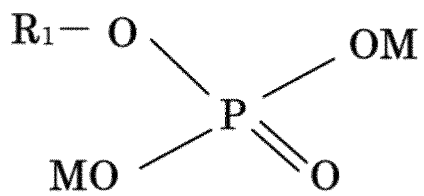
on the lower layer, an intermediate layer;

on the intermediate layer, an upper layer constituted with an alloy comprising one or two selected from a constituent element group B consisting of Sn and In and one or two or more selected from a constituent element group C consisting of Ag, Au, Pt, Pd, Ru, Rh, Os and Ir, and

wherein the intermediate layer consists of one or two or more selected from the constituent element group A and one or two selected from the constituent element group B.

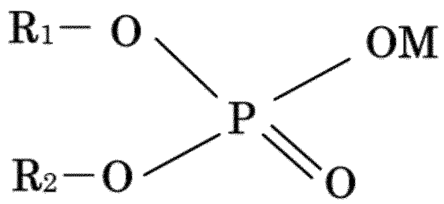
[0012] In one embodiment of the method for producing a metallic material for electronic components of the present invention, the phosphate ester-based treatment solution contains at least one of phosphoric acid esters represented by the following general formulas [1] and [2], and at least one selected from a group of cyclic organic compounds represented by the following general formulas [3] and [4]:

[Formula 1]



[1]

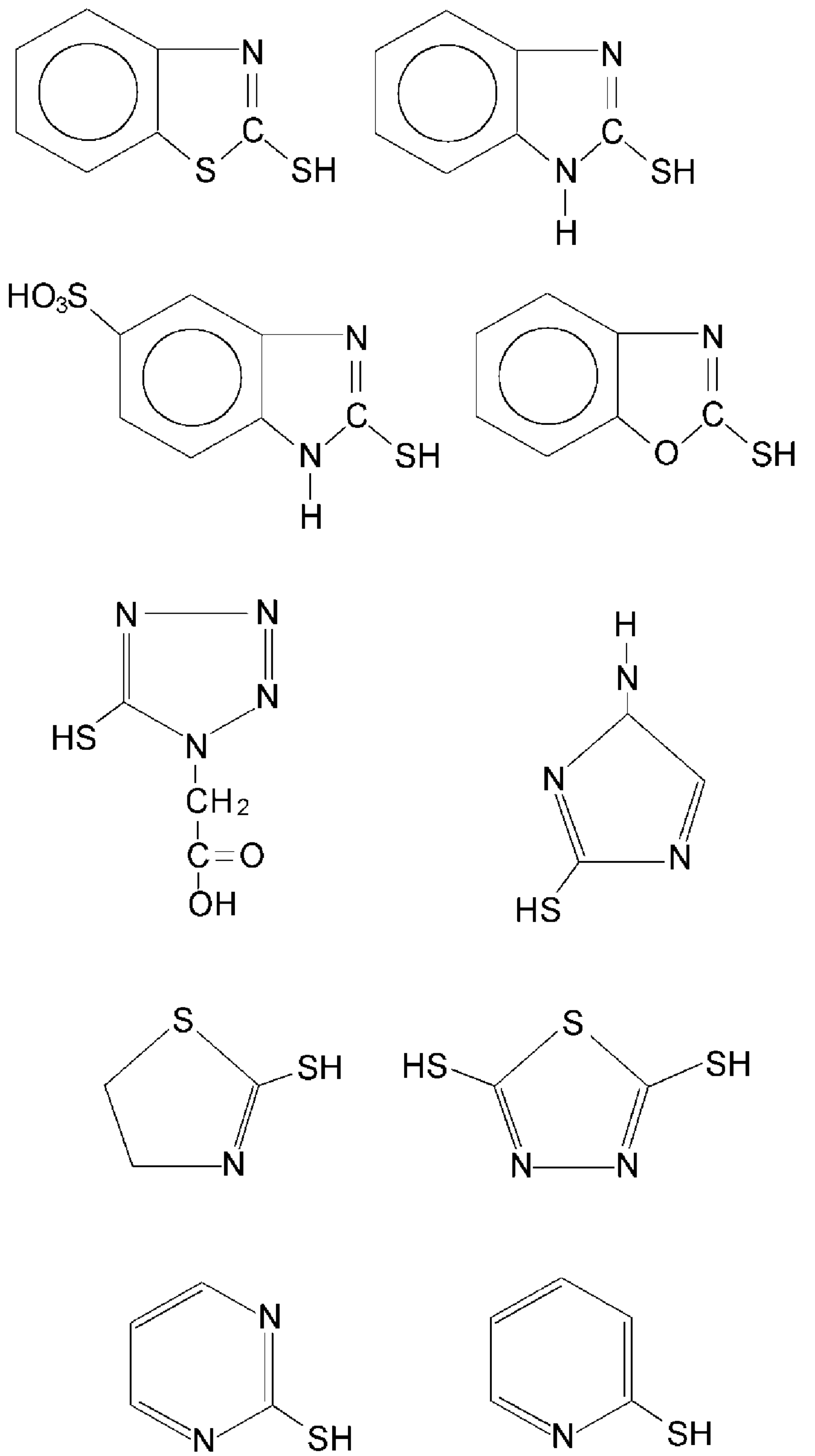
[Formula 2]



[2]

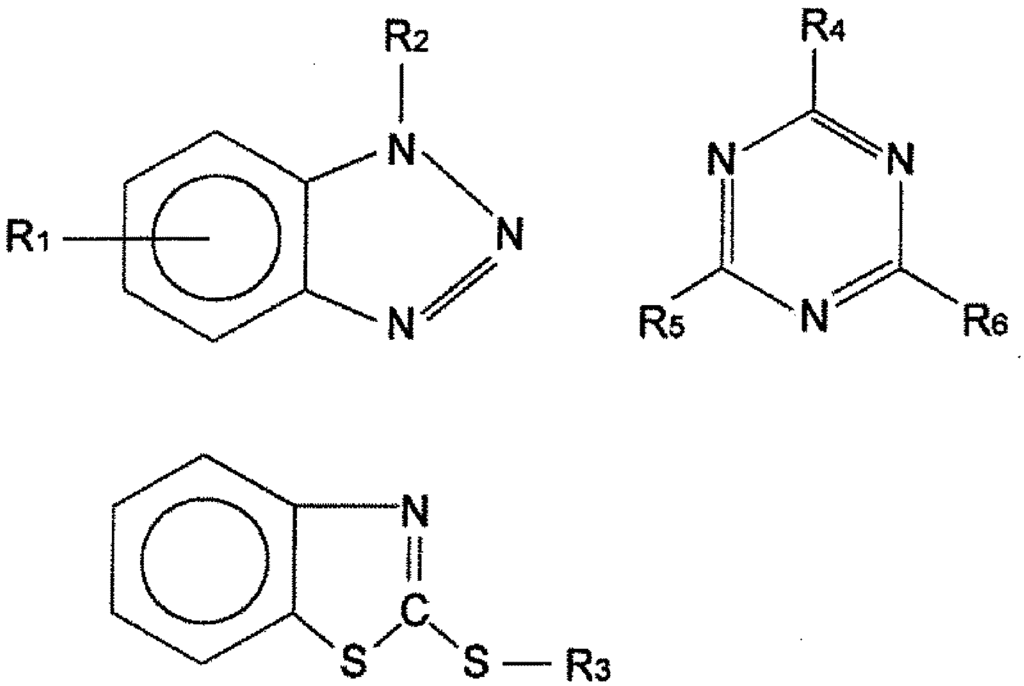
(wherein, in formulas [1] and [2], R1 and R2 each represent a substituted alkyl group and M represents a hydrogen atom or an alkali metal)

[Formula 3]



[3]

[Formula 4]



[4]

(wherein, in formulas [3] and [4], R1 represents a hydrogen atom, an alkyl group or a substituted alkyl group; R2 represents an alkali metal, a hydrogen atom, an alkyl group or a substituted alkyl group; R3 represents an alkali metal or a hydrogen atom; R4 represents -SH, an alkyl group-substituted or aryl group-substituted amino group, or represents an alkyl-substituted imidazolylalkyl group; and R5 and R6 each represent $-NH_2$, -SH or-SM (M represents an alkali metal).)

[0013] The present invention is, in yet another aspect thereof, a connector terminal comprising the metallic material for electronic components of the present invention in a contact portion thereof.

[0014] The present invention is, in yet another aspect thereof, a connector comprising the connector terminal of the present invention.

[0015] The present invention is, in yet another aspect thereof, an FFC terminal comprising the metallic material for electronic components of the present invention in a contact portion thereof.

[0016] The present invention is, in yet another aspect thereof, an FPC terminal comprising the metallic material for electronic components of the present invention in a contact portion thereof.

[0017] The present invention is, in yet another aspect thereof, an FFC comprising the FFC terminal of the present invention.

[0018] The present invention is, in yet another aspect thereof, an FPC comprising the FPC terminal of the present invention.

[0019] The present invention is, in yet another aspect thereof, an electronic component comprising the metallic material for electronic components of the present invention in an electrode thereof for external connection.

[0020] The present invention is, in yet another aspect thereof, an electronic component comprising the metallic material for electronic components of the present invention, in a push-in type terminal thereof for fixing a board connection portion to a board by pushing the board connection portion into a through hole formed in the board, wherein a female terminal connection portion and the board connection portion are provided respectively on one side and the other side of a mounting portion to be attached to a housing.

[Advantageous Effects of Invention]

[0021] According to the present invention, it is possible to provide a metallic material for electronic components having a low adhesive wear.

[Brief Description of Drawings]

[0022] [Figure 1] Figure 1 is a schematic diagram which shows the structure of the metallic material for electronic components according to the embodiments of the present invention.

[Description of Embodiments]

[0023] Hereinafter, the metallic material for electronic components according to the embodiments of the present invention are described. As shown in Figure 1, the lower layer 12 is formed on the base material 11, the intermediate layer 13 is formed on the lower layer 12 and the upper layer 14 is formed on the intermediate layer 13 in the metallic material 10 for electronic components according to the embodiments of the present invention.

<Composition of Metallic Material for Electronic Components>

(Base Material)

[0024] The base material 11 can be, not particularly limited, but for example, metal substrates such as copper and copper alloys, Fe-based materials, stainless steel, titanium and titanium alloys, aluminum and aluminum alloys. The base material 11 can be a composite of a metal base and a resin layer. The composite of a metal base and a resin layer is, for example, electrode parts on FPC or FFC substrate.

(Upper Layer)

[0025] The upper layer 14 is constituted with an alloy comprising one or two selected from a constituent element group B consisting of Sn and In and one or two or more selected from a constituent element group C consisting of Ag, Au, Pt, Pd, Ru, Rh, Os and Ir.

[0026] Sn and In are oxidizable metals, but are characterized by being relatively soft among metals. Accordingly, even when an oxide film is formed on the surface of Sn or In, for example at the time of joining together a male terminal and a female terminal by using a metallic material for electronic components as a contact material, the oxide film is easily scraped to result in contact between metals, and hence a low contact resistance is obtained.

[0027] Sn and In are excellent in the gas corrosion resistance against the gases such as chlorine gas, sulfurous acid gas and hydrogen sulfide gas; for example, when Ag poor in gas corrosion resistance is used for the upper layer 14, Ni poor in gas corrosion resistance is used for the lower layer 12, and copper or a copper alloy poor in gas corrosion resistance is used for the base material 11, Sn and In have an effect to improve the gas corrosion resistance of the metallic material for electronic components. As for Sn and In, Sn is preferable because In is severely regulated on the basis of the technical guidelines for the prevention of health impairment prescribed by the Ordinance of Ministry of Health, Labour and Welfare.

[0028] Ag, Au, Pt, Pd, Ru, Rh, Os and Ir are characterized by being relatively heat-resistant among metals. Accordingly, these metals suppress the diffusion of the composition of the base material 11 and the lower layer 12 toward the side of the upper layer 14 to improve the heat resistance. These metals also form compounds with Sn or In in the upper layer 14 to suppress the formation of the oxide film of Sn or In, so as to improve the solder wettability. Among Ag, Au, Pt, Pd, Ru, Rh, Os and Ir, Ag is more desirable from the viewpoint of electrical conductivity. Ag is high in electrical conductivity. For example, when Ag is used for high-frequency wave signals, impedance resistance is made low due to the skin effect.

[0029] In the upper layer 14, the ζ(zeta)-phase being a Sn-Ag alloy including Sn in a content of 11.8 to 22.9 at% is preferably present. By the presence of the ζ(zeta)-phase, the gas corrosion resistance is improved, and the exterior appearance is hardly discolored even when the gas corrosion test is performed.

[0030] In the upper layer 14, the ζ(zeta)-phase and the ε (epsilon)-phase being Ag_3Sn are preferably present. By the presence of the ε(epsilon)-phase, as compared with the case where only the ζ(zeta)-phase is present in the upper layer 14, the coating becomes harder and the adhesive wear is decreased. The increase of the proportion of Sn in the upper layer 14 improves the gas corrosion resistance.

[0031] In the upper layer 14, preferably only the ε(epsilon)-phase being Ag_3Sn is present. By the sole presence of the ε (epsilon)-phase in the upper layer 14, the coating becomes further harder and the adhesive wear is decreased as compared with the case where the ζ(zeta)-phase and the ε(epsilon)-phase being Ag_3Sn are present in the upper layer 14. The more increase of the proportion of Sn in the upper layer 14 also improves the gas corrosion resistance.

[0032] The presence of the ε(epsilon)-phase being Ag_3Sn and the β -Sn being a Sn single phase in the upper layer 14 is preferable. By the presence of the ε(epsilon)-phase being Ag_3Sn and β-Sn being a Sn single phase, the gas corrosion resistance is improved with a furthermore increase of the proportion of Sn in the upper layer 14 as compared with the case where only the ε(epsilon)-phase is present in the upper layer.

[0033] In the upper layer 14, preferably the ζ(zeta)-phase being a Sn-Ag alloy including Sn in a content of 11.8 to 22.9 at%, the ε(epsilon)-phase being Ag_3Sn and β-Sn being a Sn single phase are present. By the presence of the ζ(zeta)-phase, the ε(epsilon)-phase being Ag_3Sn and β-Sn being a Sn single phase, the gas corrosion resistance is improved, the exterior appearance is hardly discolored even when a gas corrosion test is performed, and the adhesive wear is decreased. The composition concerned is created by diffusion and involves no structure in an equilibrium state.

[0034] The upper layer 14 should not be present as solely composed of β-Sn. When the upper layer is present as solely composed of β-Sn, the adhesive wear is significant, whiskers occur and, for example, the heat resistance and the fine sliding wear resistance are degraded.

[0035] The upper layer 14 preferably includes the metal(s) of the constituent element group B in a content of 10 to 50 at%. When the content of the metal(s) of the constituent element group B is less than 10 at%, the gas corrosion resistance is poor, and sometimes the exterior appearance is discolored when a gas corrosion test is performed. On the other hand, when the content of the metal(s) of the constituent element group B exceeds 50 at%, the proportion of the metal(s) of the constituent element group B in the upper layer 14 is large, and hence the adhesive wear is increased and whiskers also tend to occur. Moreover, the fine sliding wear resistance is sometimes poor.

(Treated Layer)

[0036] The treated layer having C (carbon) content being 60at% or more and O (oxygen) content being 30at% or less is provided on the upper layer 14. The treated layer is formed by a surface treatment such as a sealing treatment performed after forming the upper layer 14. C (carbon) contained in the treated layer is a component resulting from surface treatment such as sealing treatment. The treated layer can further comprise one or more selected from the group consisting of S, P and N. When C (carbon) content is 60at% or more and O (oxygen) content is 30at% or less in the treated layer, lubricity is increased.

[0037] An area ratio of oxide particles adhering to a surface of the treated layer is controlled to be 0.1 % or less when the metallic material is heated at 250 °C for 30 seconds. The oxide particles adhering to the surface of the treated layer after the heating adversely affects the adhesive wear of metallic material for electronic components. Accordingly, the metallic material for electronic components having a low adhesive wear can be provided by controlling the area ratio of oxide particles to be 0.1% or less.

(Intermediate layer)

[0038] The intermediate layer 13 consists of one or two or more selected from the constituent element group A consisting of Ni, Cr, Mn, Fe, Co and Cu and one or two selected from the constituent element group B consisting of Sn and In. According to such a configuration, it has an effect of improving heat resistance and solder wettability. Furthermore, in this case, the thickness of the intermediate layer 13 is preferably 0.01 μm or more and less than 0.40 μm. Sn and In are excellent in the gas corrosion resistance against the gases such as chlorine gas, sulfurous acid gas and hydrogen sulfide gas; for example, when Ni poor in gas corrosion resistance is used for the lower layer 12, and copper or a copper alloy poor in gas corrosion resistance is used for the base material 11, Sn and In have an effect to improve the gas corrosion resistance of the metallic material for electronic components. Ni, Cr, Mn, Fe, Co and Cu provide a harder coating as compared with Sn and In, accordingly make the adhesive wear hardly occur, prevent the diffusion of the constituent metal(s) of the base material 11 into the upper layer 14, and thus improve the durability in such a way that the degradation of the heat resistance or the degradation of the solder wettability is suppressed.

[0039] When the thickness of the intermediate layer 13 is less than 0.01 μm, there is a possibility that a coating becomes hard and adhesive wear decreases. On the other hand, when the thickness of the intermediate layer 13 is 0.40 μm or more, there is a possibility that bending workability decreases, mechanical durability decreases, and plating scraping occurs.

[0040] As for Sn and In, Sn is preferable because In is severely regulated on the basis of the technical guidelines for the prevention of health impairment prescribed by the Ordinance of Ministry of Health, Labour and Welfare. As for Ni, Cr, Mn, Fe, Co and Cu, Ni is preferable because Ni is hard, adhesive wear hardly occurs, and sufficient bending workability is obtained.

[0041] The intermediate layer 13 preferably includes the metal(s) of the constituent element group B in a content of 35 at% or more. When the content of Sn is 35 at% or more, there is a possibility that a coating becomes hard and adhesive wear decreases.

[0042] The intermediate layer 13 can consist of Ni_3Sn and Ni_3Sn_2, and can consist of only Ni_3Sn_2 or only Ni_3Sn_4. The presence of Ni_3Sn, Ni_3Sn_2, and Ni_3Sn_4 may improve heat resistance and solder wettability.

[0043] The presence of Ni_3Sn_4 and β-Sn being a Sn single phase in the intermediate layer 13 is preferable. By the presence of these, a heat resistance and a solder wettability are improved compared to the case where Ni_3Sn_4 and Ni_3Sn_2 are present.

[0044] Furthermore, in this case, the thickness of the upper layer 14 is preferably 0.02 μm or more and less than 1.00 μm. When the thickness of the upper layer 14 is less than 0.02 μm, the gas corrosion resistance is poor, and the exterior appearance is discolored when the gas corrosion test is performed. On the other hand, when the thickness of the upper layer 14 is 1.00 μm or more, the thin film lubrication effect by the hard base material 11 or the lower layer 12 is lowered and adhesive wear may be increased. Furthermore, mechanical durability decreases, and plating scraping is likely to occur. The thickness of the upper layer 14 is preferably less than 0.50 μm.

(Lower Layer)

[0045] The lower layer 12 is constituted with one or two or more selected from a constituent element group A consisting of Ni, Cr, Mn, Fe, Co and Cu. Such a configuration prevents a diffusion of the constituent metal(s) of the base material 11 into the intermediate layer 13 or the upper layer 14.
[0046] The thickness of the lower layer 12 is preferably 0.05 μm or more. When the thickness of the lower layer 12 is less than 0.05 μm, the thin film lubrication effect by the hard lower layer is lowered and adhesive wear may be increased. Furthermore, the constituent metal(s) of the base material 11 is likely to diffuse into the upper layer 14, and a heat resistance and a solder wettability may deteriorate. On the other hand, the thickness of the lower layer 12 is preferably less than 5.00 μm. When the thickness of the lower layer 12 is 5.00 μm or more, a bending workability may be poor.

(Other Composition of Lower Layer)

[0047] The lower layer 12 can have a composition in which a total amount of metal(s) of the constituent element group A is 50 mass% or more, and a total amount of metal(s) of one or two or more selected from a group consisting of B, P, Sn and Zn is less than 50 mass%. Because the alloy composition of the lower layer 12 has such a configuration, the lower layer 12 is further hardened, the thin film lubricating effect is further improved, and the adhesive wear is further reduced. The alloying of the lower layer 12 further prevents the constituent metals of the base material 11 from diffusing into the upper layer, and may improve durability such as heat resistance and solder wettability.

(Other Composition of Upper Layer)

[0048] The upper layer 14 can have a composition in which a total amount of metal(s) of the constituent element group B and the constituent element group C is 50 mass% or more, and a total amount of metal(s) of one or two or more selected from a group consisting of As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, W and Zn is less than 50 mass%. Because the alloy composition of the upper layer 14 has such a configuration, adhesive wear may be reduced, whisker generation may be suppressed, and furthermore, durability such as heat resistance and solder wettability may be improved.

(Other Composition of Intermediate Layer)

[0049] The intermediate layer 13 can have a composition in which a total amount of metal(s) of the constituent element group C is 50 mass% or more, and a total amount of metal(s) of one or two or more selected from a group consisting of Bi, Cd, Co, Cu, Fe, In, Mn, Mo, Ni, Pb, Sb, Se, Sn, W, Tl and Zn is less than 50 mass%. Because the alloy composition of the intermediate layer 13 has such a configuration, adhesive wear may be reduced, whisker generation may be suppressed, and furthermore, durability such as heat resistance and solder wettability may be improved.

(Method for Producing the Metallic Material for Electronic Components)

[0050] In a method for producing the metallic material for electronic components according to the embodiments of the present invention, at first, a metallic material is prepared. The metallic material comprises the base material, on the base material, the lower layer constituted with one or two or more selected from the constituent element group A consisting of Ni, Cr, Mn, Fe, Co and Cu, on the lower layer, an intermediate layer, on the intermediate layer, an upper layer constituted with an alloy comprising one or two selected from the constituent element group B consisting of Sn and In and one or two or more selected from the constituent element group C consisting of Ag, Au, Pt, Pd, Ru, Rh, Os and Ir. The intermediate layer consists of one or two or more selected from the constituent element group A and one or two selected from the constituent element group B. The metallic material can be produced by Wet (electrical, electroless) plating, dry (sputtering, ion plating, etc.) plating, etc.
[0051] The upper layer 14, the intermediate layer 13 and the lower layer 12 may be formed, by forming a film of one or two or more selected from the constituent element group A on the base material 11, then forming a film of one or two selected from the constituent element group B, then forming a film of one or two or more selected from the constituent element group C, and by diffusion of the respective selected elements of the constituent element group B and the constituent element group C. For example, when the metal from the constituent element group B is Ag and the metal from the constituent element group C is Sn, the diffusion of Ag into Sn is fast, and thus a Sn-Ag alloy layer is formed by spontaneous diffusion. The formation of the alloy layer can further reduce the adhesion force of Sn, and the low degree of whisker formation and the durability can also be further improved.

[0052] After the formation of the upper layer 14, a heat treatment may be applied for the purpose of further suppressing the adhesive wear and further improving the low degree of whisker formation and the durability. The heat treatment allows the metal(s) of the constituent element group B and the metal(s) of the constituent element group C of the upper layer 14 to diffuse to form an alloy layer more easily, further reduces the adhesion force of Sn, and can further improve the low degree of whisker formation and the durability. The heat treatment may be performed in a reducing atmosphere or a non-oxidizing atmosphere.

[0053] For this heat treatment, treatment conditions (temperature × time) can be selected as appropriate. The heat treatment is not particularly required to be applied. When the heat treatment is applied, the heat treatment performed at a temperature equal to or higher than the melting point of the metal(s) selected from the constituent element group B allows the metal(s) of one or two selected from the constituent element group B and the metal(s) of one or two or more selected from the constituent element group A to form an alloy layer more easily, and also allows the metal(s) of one or two selected from the constituent element group B and the metal(s) of one or two or more selected from the constituent element group C to form an alloy layer more easily. When the heat treatment is applied, the heat treatment performed at a temperature equal to or higher than the melting point of the metal(s) selected from the constituent element group B allows the metal(s) of one or two or more selected from the constituent element group C and the metal(s) of one or two selected from the constituent element group B to form an alloy layer more easily.

[0054] Next, to the upper layer 14, or to the upper layer 14 after being subjected to heat treatment, a post-treatment may be applied for the purpose of further decreasing the adhesive wear and improving the low degree of whisker formation and the durability to produce the treated layer. The post-treatment is to place the metallic material in a treatment solution containing 2.5 to 5.0 g/L of phosphate ester-based treatment solution and stir ultrasonically to form the treated layer having C (carbon) content being 60at% or more and O (oxygen) content being 30at% or less on a surface of the metallic material.

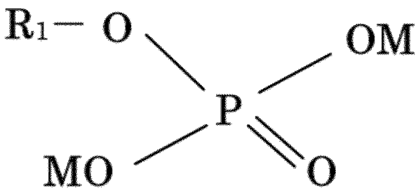
[0055] In the method for producing the metallic material for electronic components according to the embodiments of the present invention, as described above, for the formation of the treated layer provided on the surface of the metallic material (surface of the upper layer), a strong sealing membrane is produced by finely dispersing a sealing component in a treatment solution containing phosphate ester-based treatment solution at a high concentration of 2.5 to 5.0 g/L with stirring ultrasonically. By preventing oxidation due to heat treatment or the like, the area ratio of oxide particles adhering to the heated surface of the treated layer can be controlled to 0.1% or less. When the concentration of the phosphate ester-based treatment solution is less than 2.5 g/L, the concentration is low and there is a problem in corrosion resistance and heat resistance. When the concentration of the phosphate ester-based treatment solution exceeds 5.0 g/L, an adhesive wear becomes high. The concentration of the phosphate ester-based treatment solution is preferably 3.0 to 4.0 g/L. An electrolytic potential for forming the treated layer is preferably 2.0 to 3.5 V. When the electrolytic potential is less than 2.0 V, the strong sealing membrane cannot be produced and there may be a problem in corrosion resistance and heat resistance. When the electrolytic potential exceeds 3.5 V, there may be a problem of discoloration. The electrolytic potential is preferably 3.0 to 3.5 V.

[0056] The post-treatment reduces adhesive wear properties, improves lubricity, and improves durability such as heat resistance and solder wettability. A specific post-treatment includes phosphate treatment using an inhibitor, and further includes lubrication treatment and silane coupling treatment. For this heat treatment, the treatment conditions (temperature x time) can be selected as appropriate.

[0057] Prior to the post-treatment, it is desirable to remove the oxide on the surface oxidized by the heat treatment. The oxide may be removed by pickling or reverse electrolysis with the same solution as the post-treatment solution. This exposes a fresh, unoxidized alloy surface. Here, post-treatment components are adsorbed. More organic materials with a specific structure adhere to the surface where the alloy is exposed than the surface where the oxide is exposed. Accordingly, further improvement in lubricity and durability is expected. Of course, if the heat treatment is performed in a reducing atmosphere, the oxide removal treatment may not be performed.

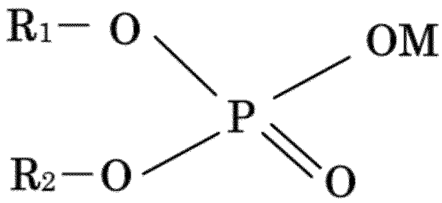
[0058] The post-treatment is preferably performed for the surface of the upper layer 14 by using an aqueous solution (referred to as the phosphoric acid ester-based solution) including one or two or more phosphoric acid esters and one or two or more cyclic organic compounds. The phosphoric acid ester(s) added to the phosphoric acid ester-based solution plays the functions as an antioxidant and a lubricant for plating. The phosphoric acid esters used in the present invention are represented by the general formula [1] and [2]. Examples of the preferable compounds among the compounds represented by the general formula [1] include lauryl acidic phosphoric acid monoester. Examples of the preferable compounds among the compounds represented by the general formula [2] include lauryl acidic phosphoric acid diester.

[Formula 5]



[1]

[Formula 6]

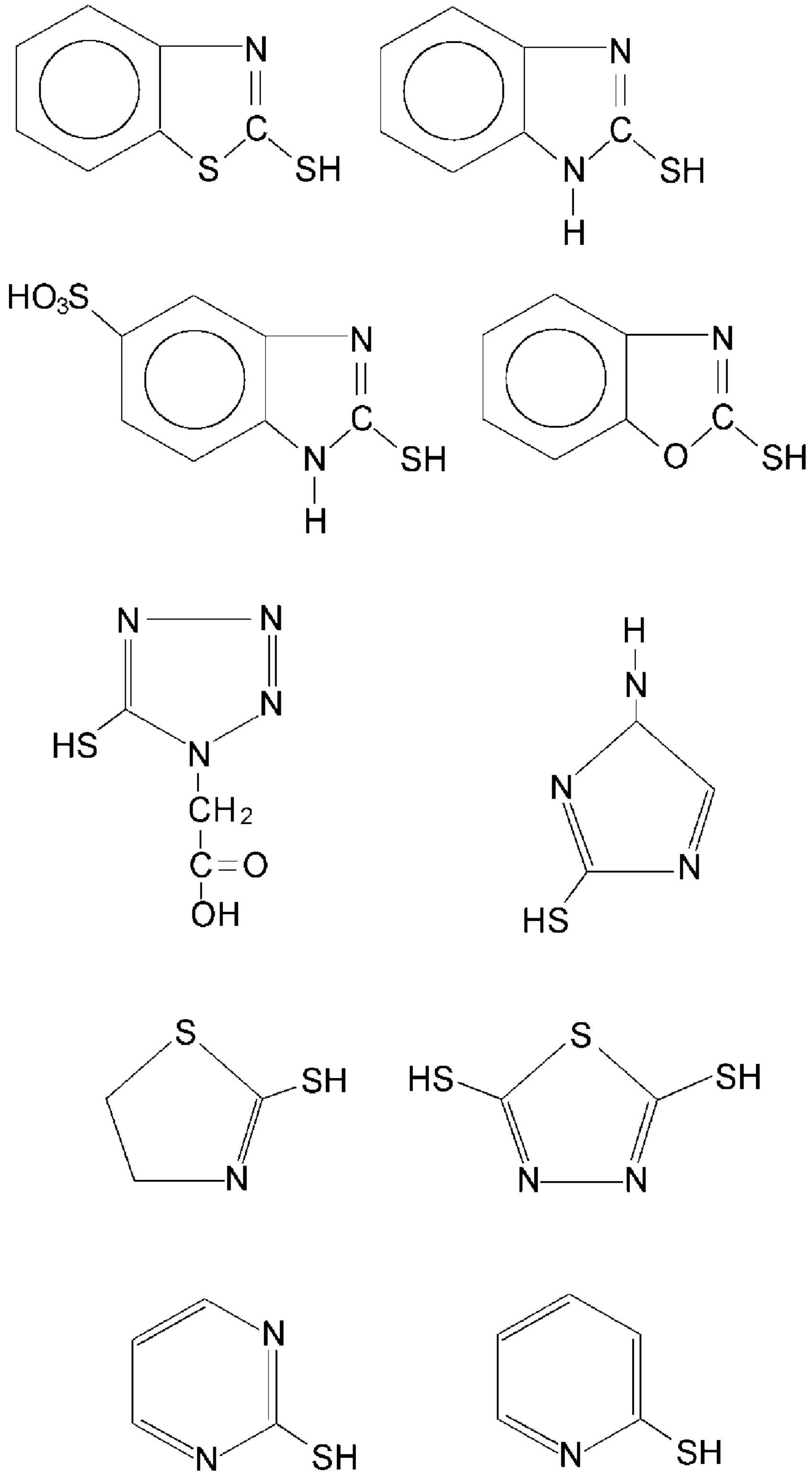


[2]

(wherein, in formulas [1] and [2], R1 and R2 each represent a substituted alkyl group and M represents a hydrogen atom or an alkali metal)

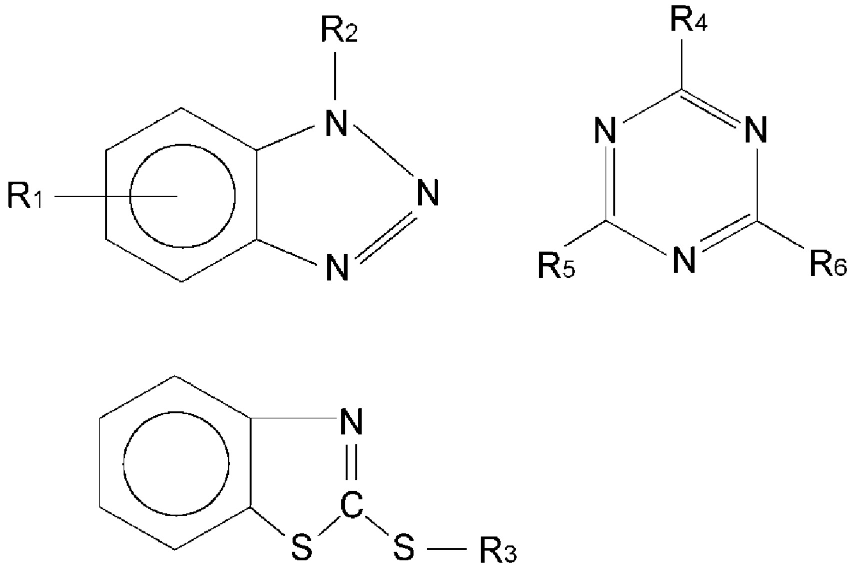
[0059] The cyclic organic compound added to the phosphoric acid ester-based solution plays the function as an antioxidant for plating. The group of the cyclic organic compounds used in the present invention are represented by the general formula [3] and [4]. Examples of the preferable compounds among the cyclic organic compounds represented by the general formulas [3] and [4] include: mercaptobenzothiazole, Na salt of mercaptobenzothiazole, K salt of mercaptobenzothiazole, benzotriazole, 1-methyltriazole, tolyltriazole and triazine-based compounds.

[Formula 7]



[3]

[Formula 8]



[4]

(wherein, in formulas [3] and [4], R1 represents a hydrogen atom, an alkyl group or a substituted alkyl group; R2 represents an alkali metal, a hydrogen atom, an alkyl group or a substituted alkyl group; R3 represents an alkali metal or a hydrogen atom; R4 represents -SH, an alkyl group-substituted or aryl group-substituted amino group, or represents an alkyl-substituted imidazolylalkyl group; and R5 and R6 each represent $-NH_2$, -SH or-SM (M represents an alkali metal).)

[0060] The post-treatment is furthermore preferably performed in such a way that both P and N are present on the surface of the upper layer 14. When P is absent on the plating surface, the solderability tends to be degraded, and the lubricity of the plating material is also degraded. On the other hand, when N is absent on the Sn or Sn alloy plating surface, sometimes the contact resistance of the plating material tends to be increased in a high temperature environment.

<Properties of Metallic Material for Electronic Components>

[0061] The maximum height (Rz) of the surface of the upper layer 14 is preferably 3 μm or less. The maximum height (Rz) of the surface of the upper layer 14 being 3 μm or less reduces the raised portions relatively tending to be corroded, thus smoothes the surface and improves the gas corrosion resistance.

<Applications of Metallic Material for Electronic Components>

[0062] Examples of the application of the metallic material for electronic components of the present invention include, without being particularly limited to: a connector terminal using, in the contact portion thereof, the metallic material for electronic components, an FFC terminal or an FPC terminal using, in the contact portion thereof, the metallic material for electronic components, and an electronic component using, in the electrode thereof for external connection, the metallic material for electronic components. The terminal does not depend on the connection mode on the wiring side as exemplified by a crimp-type terminal, a soldering terminal and a press-fit terminal. Examples of the electrode for external connection include a connection component prepared by applying a surface treatment to a tab, and material surface treated for use in under bump metal of a semiconductor.

[0063] Connectors may also be prepared by using such connector terminals formed as described above, and an FFC or an FPC may also be prepared by using an FFC terminal or an FPC terminal.

[0064] The metallic material for electronic components of the present invention may also be used in a push-in type terminal for fixing a board connection portion to a board by pushing the board connection portion into the through hole formed in the board, wherein a female terminal connection portion and the board connection portion are provided respectively on one side and the other side of a mounting portion to be attached to a housing.

[0065] In a connector, both of the male terminal and the female terminal may be made of the metallic material for electronic components of the present invention, or only one of the male terminal and the female terminal may be made of the metallic material for electronic components of the present invention. The use of the metallic material for electronic components of the present invention for both of the male terminal and the female terminal further improves the low degree of insertion/extraction force.

[Examples]

[0066] Hereinafter, both Examples of the present invention and Comparative Examples are presented; these Examples and Comparative Examples are provided for better understanding of the present invention, and are not intended to limit the present invention.

[0067] As Examples 1 to 7 and Comparative Examples 1 to 6, under the conditions shown in Table 1, electrolytic degreasing, acid cleaning, first plating, second plating, third plating and heat treatment were performed. Then, a metal oxide layer (tin oxide layer) was removed by pickling or cathode electrolysis, and anode electrolysis was performed. If heat treatment is performed in a reducing atmosphere, such a metal oxide layer is not formed, and in that case, the oxide removal step does not need to be performed.

(Materials)

[0068]

(1) Plate: thickness: 0.30 mm, width: 30 mm, component: Cu-30Zn
(2) Male terminal: thickness: 0.64 mm, width: 2.3 mm, component: Cu-30Zn
(3) Push-in type terminal: Press-fit terminal PCB connector, R800, manufactured by Tokiwa & Co., Inc.

(First Plating Conditions)

[0069]

(Condition 1) Semi-glossy Ni plating

Surface treatment method: Electroplating
Plating solution: Ni sulfamate plating solution + saccharin
Plating temperature: 55°C
Electric current density: 0.5 to 4 A/dm^2

(Condition 2) Glossy Ni plating

Surface treatment method: Electroplating
Plating solution: Ni sulfamate plating solution + saccharin + additives
Plating temperature: 55°C
Electric current density: 0.5 to 4 A/dm^2

(Condition 3) Ni-Co plating

Surface treatment method: Electroplating
Plating solution: sulfamic acid bath + cobalt sulfate
Plating temperature: 55°C
Electric current density: 0.5 to 4 A/dm^2

(Condition 4) Matte Ni plating

Surface treatment method: Electroplating
Plating solution: Ni sulfamate plating solution
Plating temperature: 55°C
Electric current density: 0.5 to 4 A/dm^2

(Condition 5) Ni-P plating

Surface treatment method: Electroplating
Plating solution: Ni sulfamate plating solution + phosphite
Plating temperature: 55°C
Electric current density: 0.5 to 4 A/dm^2

(Second Plating Conditions)

Ag plating

[0070]

Surface treatment method: Electroplating
Plating solution: Ag cyanide plating solution
Plating temperature: 40°C
Electric current density: 0.2 to 4 A/dm^2

(Third Plating Conditions)

Sn plating conditions

[0071]

Surface treatment method: Electroplating
Plating solution: Sn methanesulfonate plating solution
Plating temperature: 40°C
Electric current density: 0.5 to 4 A/dm^2

(Heat Treatment)

[0072] The heat treatment was performed by placing the sample on a hot plate, and verifying that the surface of the hot plate reached the predetermined temperature.

(Intermediate Treatment)

[0073] The sample after the heat treatment was immersed in dilute sulfuric acid (10 g/1 L) for 5 seconds. Thereafter, it was immersed in pure water for 5 seconds.

(Post-Treatment)

[0074] Furthermore, by using the A-12: phosphate-based treatment solution having the concentrations shown in Table 2 as the surface treatment solution, an anodic electrolysis (electrolytic potential and constant voltage electrolysis described in Table 2) was performed for 2 seconds, and a surface treatment was performed on the plating surface. For Examples 1 to 7 and Comparative Examples 2, 4 to 6, an ultrasonic stirring was performed at the time of initial make-up of electrolytic bath, and then the electrolysis was performed. The ultrasonic stirring conditions for the treatment solution were stirring by an ultrasonic disperser (ultrasonic frequency: 20 kHz, ultrasonic output: 500 W, 10 minutes). After these treatments, the sample was immersed for 2 seconds and then dried with warm air.

(Measurement of Thicknesses of Upper Layer, Intermediate Layer and Lower Layer, Determination of Compositions and Structures of Upper Layer)

[0075] The measurement of the thicknesses of the upper layer and the intermediate layer, and the determination of compositions and structures of the upper layer, of each of the obtained samples, were performed by the line analysis based on the STEM (scanning transmission electron microscope) analysis. The analyzed elements are the elements in the compositions of the upper layer, the intermediate layer and the lower layer, and C, S and O. These elements are defined as the specified elements. On the basis of the total concentration of the specified elements defined as 100%, the concentrations (at%) of the respective elements were analyzed. The thickness corresponds to the distance determined from the line analysis (or area analysis). As the STEM apparatus, the JEM-2100F manufactured by JEOL Ltd. was used. The acceleration voltage of this apparatus is 200 kV.
[0076] The determination of the structure of the upper layer is performed by checking the composition determined by STEM against the phase diagram.
[0077] The thickness of the lower layer was measured with a fluorescent X-ray film thickness meter (Seiko Instruments, SEA5100, collimator 0.1 mmΦ).
[0078] The measurement of the thickness of the upper layer, the intermediate layer and the lower layer and the

determination of the composition and the structure of the upper layer were performed by averaging 10 arbitrary points.

(Evaluations)

[0079] For each of the samples, the following evaluations were performed.

Concentration of C (carbon) in Treated Layer

[0080] The concentration of C (carbon) of the treated layer was measured by the following method.

[0081] By using XPS analyzer manufactured by ULVAC-PHI (Model: PHI5000 Versa Probe II), the measurement by XPS was performed under the following conditions to measure the concentration of C (carbon) on the outermost surface.

(Measurement Conditions)

[0082]

Ultimate vacuum: 2.2 x 10^{-7}Pa
Excitation source: Monochromatic AlK
Output: 25 W
Detection area: 100 μmφ
Angle of incidence: 90 degree
Extraction angle: 45 degree
Neutralizing gun: none
(Sputtering conditions)
Ionic species: Ar^+
Acceleration voltage: 2 kV
Sweep area: 3 mm x 3 mm
Rate: 0.4 nm/min (SiO_2 equivalent)

Area Ratio of Oxide Particles Adhering to Surface of Treated Layer after Heating

[0083] The area ratio of oxide particles adhering to the surface of the treated layer after heating at 250 °C for 30 seconds was measured by the following method.

[0084] By using scanning electron microscope (Model: SU-70) made by Hitachi High-Technologies, an EDS surface analysis was performed and it was confirmed that it was an oxide. Then, by using NSS (Noran System Six) particle analysis software, a secondary electron image having a luminance of 82% or more was recognized as oxide particles, and the area ratio was calculated.

[0085] For the heat treatment, the sample was placed on a hot plate and heated for 30 seconds after the surface of the hot plate reached 250 °C.

Adhesive Wear Property

[0086] Adhesive wear property was evaluated by performing insertion / extraction test with a plated male terminal using a commercially available Sn reflow plating female terminal (090 type Sumitomo TS / Yazaki 090II series female terminal non-waterproof / F090-SMTS).

[0087] The measuring device used for the test was 1311NR made by Aikoh Engineering, and the evaluation was performed with a male spin sliding distance of 5 mm. The number of samples was 5, and adhesive wear was evaluated using the insertion force. As the insertion force, a value obtained by averaging the maximum values of the respective samples was adopted. As a blank material for adhesive wear, the sample of Comparative Example 1 was adopted, and the adhesive wear property with respect to the sample of Comparative Example 1 was evaluated.

[0088] Tables 1 and 2 show the test conditions and the test results.

[Table 1]

		Fist plating			Second plating		Third plating		Heat treatment		
		Plating type	Plating condition	Thickness / μm	Plating type	Thickness / μm	Plating type	Thickness / μm	Tempe-rature /°C	Time / second	atmosphere
Example	1	Ni	4	1.0	Ag	0.2	Sn	0.1	650	10	N_2 gas
	2	Ni	4	0.5	Ag	0.3	Sn	0.2	650	10	N_2 gas
	3	Ni-Co	3	1.0	Ag	0.2	Sn	0.1	650	10	N_2 gas
	4	Ni-P	5	1.0	Ag	0.2	Sn	0.1	650	10	N_2 gas
	5	Ni	1	1.0	Ag	0.2	Sn	0.1	650	10	N_2 gas
	6	Ni	2	1.0	Ag	0.2	Sn	0.1	650	10	N_2 gas
	7	Ni	4	1.0	Ag	0.2	Sn	0.1	650	10	N_2 gas
Comparative Example	1	Ni	4	1.0	Ag	0.2	Sn	0.1	650	10	N_2 gas
	2	Ni	4	1.0	Ag	0.2	Sn	0.1	650	10	N_2 gas
	3	Ni	2	1.0	Ag	0.2	Sn	0.1	650	10	N_2 gas
	4	Ni	1	1.0	Ag	0.2	Sn	0.1	650	10	N_2 gas
	5	Ni	1	1.0	Ag	0.2	Sn	0.1	650	10	N_2 gas
	6	Ni	4	1.0	Ag	0.2	Sn	0.1	650	10	N_2 gas

[Table 2]

		A-12 Concentration (g/L)	Electrolytic potential (V)	Ultrasonic stirring	Lower layer		Intermediate layer		Upper layer		Concentration of C (at%)	Oxide (%)	Insertion force after heating at 250 °C for 30s (N)				
					Composition	Thickness (μm)	Composition	Thickness (μm)	Composition	Thickness (μm)			1st	2nd	3rd	4th	5th
Example	1	3.0	3.0	Done	Ni	1.0	Ni-Sn	0.12	Ag-Sn	0.26	64.0	<0.1	1.12	1.15	1.17	1.49	1.70
	2	3.0	2.0	Done	Ni	0.5	Ni-Sn	0.18	Ag-Sn	0.33	62.1	<0.1	1.18	1.22	1.34	1.61	1.80
	3	3.0	3.0	Done	Ni-Co	1.0	Ni-Sn	0.13	Ag-Sn	0.22	63.5	<0.1	1.15	1.16	1.23	1.51	1.73
	4	3.0	3.0	Done	Ni-P	1.0	Ni-Sn	0.15	Ag-Sn	0.25	64.3	<0.1	1.11	1.14	1.18	1.46	1.70
	5	2.5	3.0	Done	Ni	1.0	Ni-Sn	0.14	Ag-Sn	0.23	62.1	<0.1	1.15	1.19	1.25	1.57	1.81
	6	3.0	3.5	Done	Ni	1.0	Ni-Sn	0.13	Ag-Sn	0.22	66.3	<0.1	1.09	1.14	1.31	1.52	1.68
	7	5.0	3.0	Done	Ni	1.0	Ni-Sn	0.12	Ag-Sn	0.23	70.2	<0.1	1.19	1.22	1.29	1.55	1.72
Comparative Example	1	1.5	2.0	None	Ni	1.0	Ni-Sn	0.14	Ag-Sn	0.24	51.7	2.7	1.41	1.44	1.70	1.90	2.02
	2	1.5	2.0	Done	Ni	1.0	Ni-Sn	0.11	Ag-Sn	0.22	55.4	1.2	1.25	1.37	1.41	1.77	1.91
	3	3.0	3.0	None	Ni	1.0	Ni-Sn	0.11	Ag-Sn	0.22	59.8	2.4	1.28	1.41	1.65	1.86	2.07
	4	3.0	1.5	Done	Ni	1.0	Ni-Sn	0.13	Ag-Sn	0.23	53.1	1.5	1.32	1.39	1.50	1.81	2.01
	5	1.5	3.0	Done	Ni	1.0	Ni-Sn	0.13	Ag-Sn	0.24	56.2	1.6	1.23	1.38	1.45	1.72	1.98
	6	0.5	3.0	Done	Ni	1.0	Ni-Sn	0.12	Ag-Sn	0.23	27.8	5.1	1.52	1.65	1.71	1.94	2.23

(Evaluation Results)

[0089] Examples 1 to 7 were metallic materials for electronic components having excellently low adhesive wear.

[0090] In Comparative Examples 1 and 3, the electrolytic solution for forming the treated layer was not ultrasonically stirred, so the area ratio of the oxide particles was large and the adhesive wear property was high.

[0091] In Comparative Example 2, since the concentration of A-12 is low and the electrolytic potential when forming the treated layer is low, the concentration of C in the treated layer is low, that is, a sufficient sealing membrane could not be obtained and the number of oxide particles increases. For this reason, the adhesive wear property was high.

[0092] In Comparative Example 4, although the concentration of A-12 is high, the electrolytic potential at the time of forming the treated layer is low, so the concentration of C in the treated layer is low, that is, a sufficient sealing membrane could not be obtained and the number of oxide particles increases. For this reason, the adhesive wear property was high.

[0093] In Comparative Example 5, since the concentration of A-12 was low, the concentration of C in the treated layer was low, that is, a sufficient sealing membrane could not be obtained and the number of oxide particles increases. For this reason, the adhesive wear property was high.

[0094] In Comparative Example 6, the concentration of A-12 was low, and the concentration of C in the treated layer was low, that is, a sufficient sealing membrane could not be obtained and the number of oxide particles increases. For this reason, the adhesive wear property was high.

[Reference Signs List]

[0095]

10 Metallic material for electronic components
11 Base material
12 Lower layer
13 Intermediate layer
14 Upper layer

Claims

1. A metallic material for electronic components comprising:

a base material;
on the base material, a lower layer constituted with one or two or more selected from a constituent element group A consisting of Ni, Cr, Mn, Fe, Co and Cu;
on the lower layer, an intermediate layer;
on the intermediate layer, an upper layer constituted with an alloy comprising one or two selected from a constituent element group B consisting of Sn and In and one or two or more selected from a constituent element group C consisting of Ag, Au, Pt, Pd, Ru, Rh, Os and Ir; and
on the upper layer, a treated layer having C (carbon) content being 60at% or more and O (oxygen) content being 30at% or less,
wherein the intermediate layer consists of one or two or more selected from the constituent element group A and one or two selected from the constituent element group B, and
when the metallic material is heated at 250 °C for 30 seconds, an area ratio of oxide particles adhering to a surface of the treated layer is 0.1 % or less.

2. The metallic material for electronic components according to claim 1,
wherein the treated layer further comprises one or more selected from the group consisting of S, P and N.

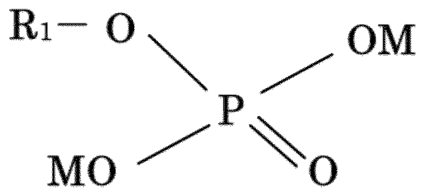
3. A method for producing a metallic material for electronic components, comprising a step of placing a metallic material in a treatment solution containing 2.5 to 5.0 g/L of phosphate ester-based treatment solution and stirring ultrasonically to form a treated layer having C (carbon) content being 60at% or more and O (oxygen) content being 30at% or less on a surface of the metallic material,
wherein the metallic material comprises:

a base material;
on the base material, a lower layer constituted with one or two or more selected from a constituent element

group A consisting of Ni, Cr, Mn, Fe, Co and Cu;
on the lower layer, an intermediate layer;
on the intermediate layer, an upper layer constituted with an alloy comprising one or two selected from a constituent element group B consisting of Sn and In and one or two or more selected from a constituent element group C consisting of Ag, Au, Pt, Pd, Ru, Rh, Os and Ir, and
wherein the intermediate layer consists of one or two or more selected from the constituent element group A and one or two selected from the constituent element group B.

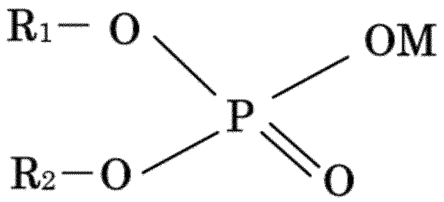
4. The method for producing a metallic material for electronic components according to claim 3, wherein the phosphate ester treatment solution contains at least one of phosphoric acid esters represented by the following general formulas [1] and [2], and at least one selected from a group of cyclic organic compounds represented by the following general formulas [3] and [4]:

[Formula 1]



[1]

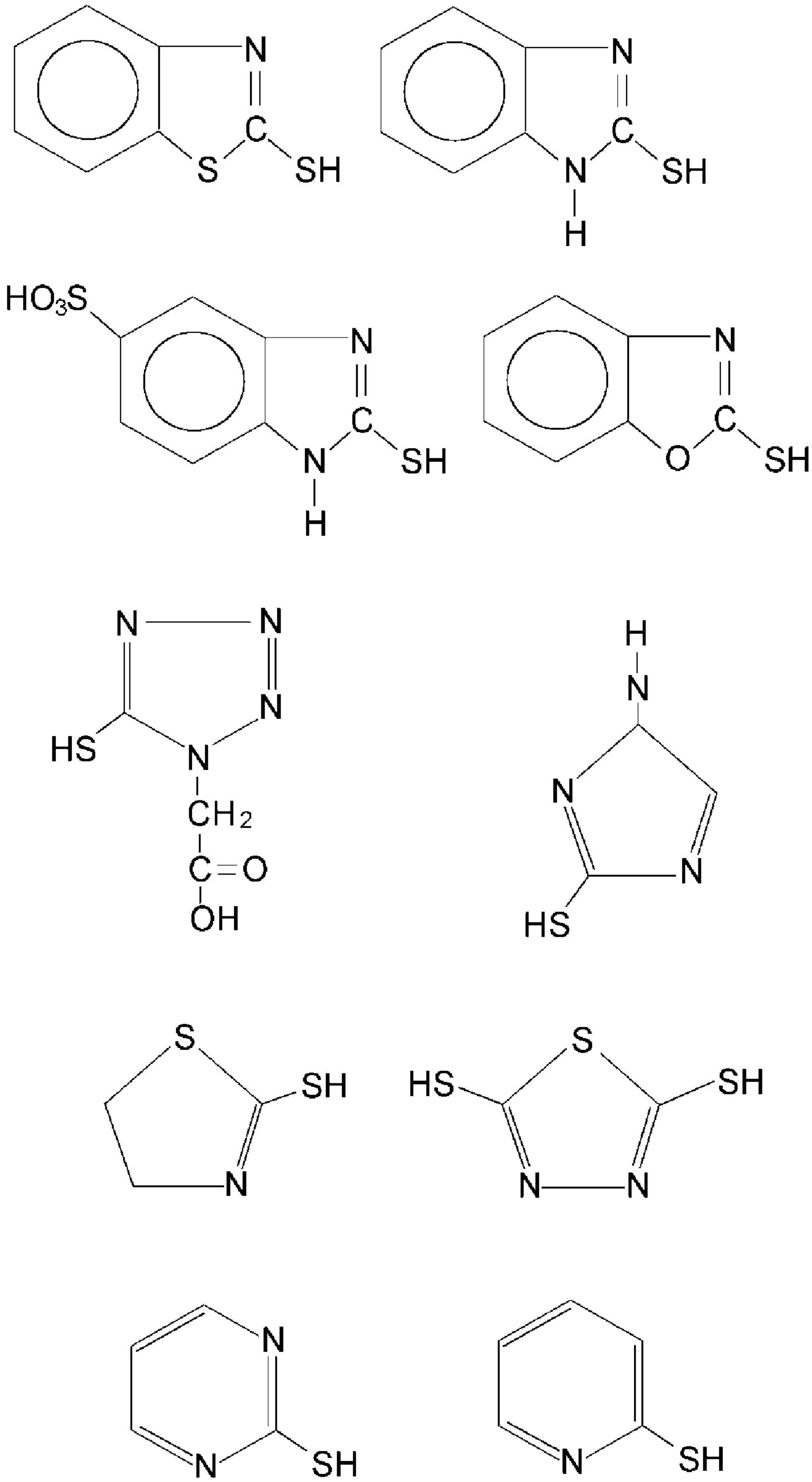
[Formula 2]



[2]

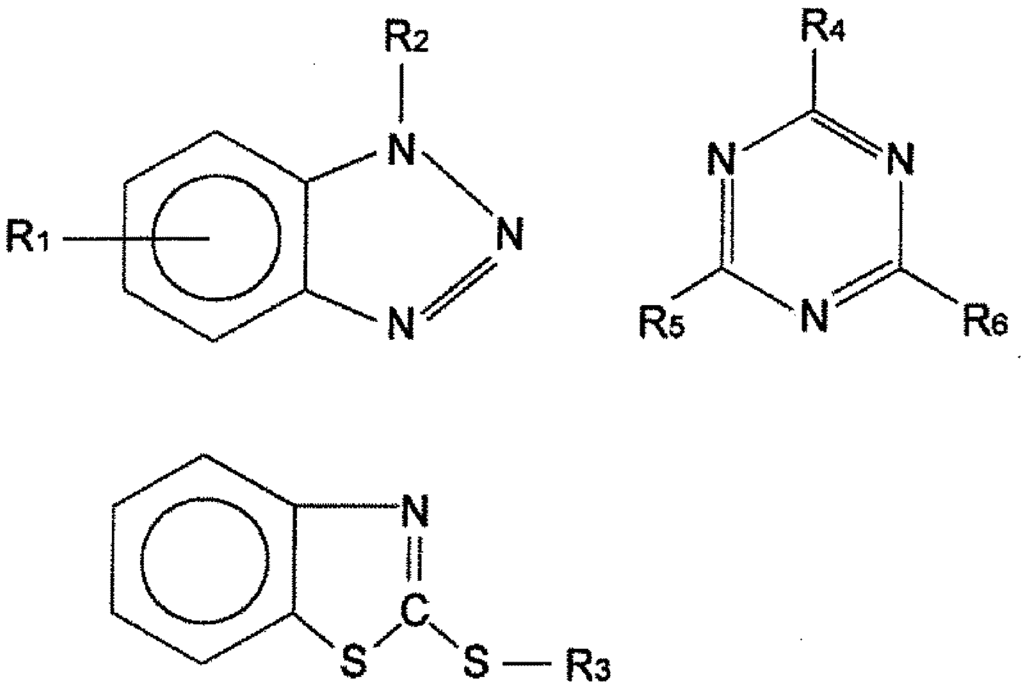
(wherein, in formulas [1] and [2], R1 and R2 each represent a substituted alkyl group and M represents a hydrogen atom or an alkali metal)

[Formula 3]



[3]

[Formula 4]



[4]

(wherein, in formulas [3] and [4], R1 represents a hydrogen atom, an alkyl group or a substituted alkyl group; R2 represents an alkali metal, a hydrogen atom, an alkyl group or a substituted alkyl group; R3 represents an alkali metal or a hydrogen atom; R4 represents -SH, an alkyl group-substituted or aryl group-substituted amino group, or represents an alkyl-substituted imidazolylalkyl group; and R5 and R6 each represent $-NH_2$, -SH or-SM (M represents an alkali metal).)

5. A connector terminal comprising the metallic material for electronic components according to claim 1 or 2 in a contact portion thereof.

6. A connector comprising the connector terminal according to claim 5.

7. An FFC terminal comprising the metallic material for electronic components according to claim 1 or 2 in a contact portion thereof.

8. An FPC terminal comprising the metallic material for electronic components according to claim 1 or 2 in a contact portion thereof.

9. An FFC comprising the FFC terminal according to claim 7.

10. An FPC comprising the FPC terminal according to claim 8.

11. An electronic component comprising the metallic material for electronic components according to claim 1 or 2 in an electrode thereof for external connection.

12. An electronic component comprising the metallic material for electronic components according to claim 1 or 2, in a push-in type terminal thereof for fixing a board connection portion to a board by pushing the board connection portion into a through hole formed in the board, wherein a female terminal connection portion and the board connection portion are provided respectively on one side and the other side of a mounting portion to be attached to a housing.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/038821

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C23C28/00(2006.01)i, C25D5/48(2006.01)i, C25D7/00(2006.01)i, H01R13/03(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. C23C28/00, C25D5/48, C25D7/00, H01R13/03

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2017
Registered utility model specifications of Japan	1996-2017
Published registered utility model applications of Japan	1994-2017

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2015-46268 A (JX NIPPON MINING & METALS CORP.) 12 March 2015 (Family: none)	1-12
A	JP 2014-41807 A (JX NIPPON MINING & METALS CORP.) 06 March 2014 & US 2015/0213918 A1 & WO 2014/017238 A1 & EP 2878704 A1 & TW 201412511 A & CN 104471113 A & KR 10-2015-0028344 A	1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 November 2017 (13.11.2017)	28 November 2017 (28.11.2017)

Name and mailing address of the ISA/	Authorized officer
Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Telephone No.

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Patent documents cited in the description

- JP 2005126763 A **[0004]**