(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 4 333 008 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
06.03.2024 Bulletin 2024/10

(21) Application number: 23192933.2

(22) Date of filing: 23.08.2023

(51) International Patent Classification (IPC):
H01H 1/023 (2006.01) *H01H 1/00* (2006.01)

(52) Cooperative Patent Classification (CPC):
H01H 1/023; H01H 1/0036

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: 31.08.2022 JP 2022137422
25.11.2022 CN 202211488752

(71) Applicant: Tanaka Kikinzoku Kogyo K.K.
Tokyo 100-6422 (JP)

(72) Inventor: SATO, Tsubasa
Hiratsuka-shi, Kanagawa, 254-0076 (JP)

(74) Representative: Hoffmann Eitle
Patent- und Rechtsanwälte PartmbB
Arabellastraße 30
81925 München (DE)

(54) CONTACT MEMBER FOR MICRO-LOAD SWITCHING CONTACT

(57) The present invention relates to a contact member for a micro-load switching contact including a surface contact layer of a Au alloy thin film formed on a substrate. The Au alloy thin film constituting the surface contact layer includes 15% by mass or more and 30% by mass or less of a first additive metal containing Ag, and 0.5% by mass or more and 3% by mass or less of a second additive metal containing any one or more of Cr, Mn, Fe, Co, Ni, Cu, and Zn, with the balance being Au and unavoidable impurities. The thin film of the Au alloy has a hardness in terms of Vickers hardness of 240 Hv or more and 400 Hv or less. The contact material applied to the contact member of the present invention is excellent in environmental resistance and low contact resistance, and is ensured to have wear resistance and adhesion resistance required when in the form of a thin film.

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Description

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0001] The present invention relates to a contact member used in a contact portion of a switching contact operating in a micro-load region such as a miniature relay. More particularly, it relates to a contact member that contains a surface contact layer of a Au-based alloy thin film formed on an appropriate substrate, is excellent in sulfidation resistance, has a low contact resistance, and is excellent in balance of adhesion resistance and wear resistance.

DESCRIPTION OF THE RELATED ART

[0002] In contact portions (fixed contacts and movable contacts) of switching contacts (a relay, a switch and the like) for micro load, such as a miniature relay and a micro relay, mounted on various electric/electronic circuits, a Au alloy containing Au as a principal component (of a content of about 90% by mass or more) is conventionally used. Au is a metal that is chemically stable and excellent in environmental resistance, and exhibits a low contact resistance stably even under a micro load. On the other hand, Au is a metal having low hardness and great plastic deformability, and hence is easily deformed by slight sliding and repeating on/off operation in a contact portion. Such deformation exposes a clean surface of the material, and causes viscosity of the contact. Therefore, as a contact material for a micro-load switching contact, a Au alloy obtained by adding Ag, Ni, or the like to Au is used for attaining both a low contact resistance and adhesion resistance. For example, Patent Document 1 describes a contact member for a micro load including a surface contact layer in which a contact material in a tape shape of a Au alloy obtained by adding, to Au or Au-10 mass% Ag alloy, Mo, W, Y, Zr, Hf, Ni, Fe, Co, or Ti as an additive element in a trace amount is cladded on a base material.

Prior Art Document

Patent Document

[0003] Patent Document 1:
Japanese Patent Application Laid-Open No. 8-287759

SUMMARY OF THE INVENTION

Technical Problem

[0004] In recent years, in order to meet a requirement of cost reduction of various relays and switches including a micro-load switching contact, examination is being made on change from a contact member in which a bulk material of a contact material is cladded on a substrate (base material) as described in Patent Document 1 to a contact member in which a thin film of a contact material is formed on a substrate as a surface contact layer. Thinning of a contact material contributes to cost reduction by reduction of the amount of the material used. Since a contact material used in a micro-load switching contact contains Au as a principal component as described above, the effect of cost reduction is particularly great. Even when the contact material is formed as a thin film, however, the lifetime is required to be equivalent to that of a conventional one, and therefore, it is necessary to cause a contact material formed as a thin film to have higher wear resistance than that of a conventional one.

[0005] For improving the hardness and wear resistance of a Au alloy, the content of an additive element may be increased. Regarding the contact material described in Patent Document 1 described above, the hardness of the contact material is increased by increasing the contents of Ag, and Mo, Ni or the like. The increase in concentration of the additive element may affect the environmental resistance although the hardness is increased. For example, since Ag is a metal easily sulfurized, simple increase of the Ag content lowers the sulfidation resistance of the contact material to degrade low contact resistance. The Ag content in the Au alloy of Patent Document 1 is specified to 10% by mass or less probably because balance between adhesion resistance and sulfidation resistance is regarded significant.

[0006] Besides, as a method for forming a thin film to be used as a surface contact layer, thin film forming processes such as vacuum deposition and sputtering are applied. In a thin film formed by such a thin film forming process, adhesion to a substrate is a significant property. In this respect, application of thin film materials to a micro-load switching contact has not been sufficiently examined yet, and it is deemed to be necessary to examine also adhesion of a surface contact layer of a thin film.

[0007] The present invention has been devised under this background, and an object is to provide a contact member that is applied to a micro-load switching contact, uses a thin film of a contact material as a surface contact layer, is excellent in environmental resistance and low contact resistance, and is ensured to have wear resistance/adhesion resistance required when in the form of a thin film.

Solution to Problem

[0008] In order to solve the above-described problems, the present inventors have decided to examine, on the basis of a Au alloy as a contact material to be used as a surface contact layer, an additive metal and the composition range thereof that can suitably work in the form of a thin film. Specifically, the present inventors have selected Ag as an essential additive metal for improving the hardness of the Au alloy, and have optimized the content thereof. Then, the inventors have decided to examine, in a AuAg alloy in which the Ag content is optimized, the type and the content of a second additive metal capable of complementing a property that is insufficient in the form of a thin film.

[0009] FIG. 1 illustrates measurement results of contact resistance in an initial state (after production) and contact resistance after a test of exposure to a sulfidation atmosphere (H_2S (90 mmHg) at 60°C) obtained in a AuAg alloy having a Ag content varied. Referring to the results of this preliminary test, in the AuAg alloy in the initial state, variation in the contact resistance is small even when the Ag content is increased. The contact resistance of the AuAg alloy is increased by increasing the Ag content only after the sulfidation test, and it is thus confirmed that the AuAg alloy has a problem of sulfidation resistance. Based on the results of this preliminary test, however, the present inventors considered that the sulfidation resistance of a AuAg alloy can be ensured even when the Ag content is not limited to 10% by mass or less as in the conventional technique (Patent Document 1). According to FIG. 1, even when the Ag content is over 10% by mass, a difference in the contact resistance is small between the initial state and the state after the sulfidation test of the alloy as long as the Ag content is in a range of 20% by mass or less. Besides, the present inventors considered that the difference in the contact resistance is within a permissible range in a region where the Ag content is comparatively low even in an alloy having a Ag content over 20% by mass. This determination is reached because the present inventors considered that the difference in the contact resistance between the initial state and the state after the sulfidation test can be eliminated if a second additive element capable of improving the sulfidation resistance of the AuAg alloy is used.

[0010] The addition of the second additive element to a AuAg alloy can not only ensure the sulfidation resistance but also contribute to hardness increase of the alloy in the form of a thin film. In the AuAg alloy in which the upper limit of the Ag content is over that of the conventional one as described above, although the hardness is increased to some extent, the hardness may be insufficient for use as a contact material in the form of a thin film. Therefore, it is a useful method to search an additive element that ensures the sulfidation resistance and has a function of increasing the hardness of a AuAg alloy. Accordingly, the present inventors examined an additive element that can ensure sulfidation resistance and further increase the hardness or ensure adhesion in consideration of optimization of the Ag content in a AuAg alloy, resulting in accomplishing the present invention.

[0011] Specifically, the present invention that solves the above-described problems is drawn to a contact member for a micro-load switching contact, containing a surface contact layer of a thin film of a Au alloy formed on a substrate, in which the Au alloy includes 15% by mass or more and 30% by mass or less of a first additive metal containing Ag, and 0.5% by mass or more and 3.0% by mass or less of a second additive metal containing any one of Cr, Mn, Fe, Co, Ni, Cu, and Zn, with the balance being Au and unavoidable impurities, and the thin film of the Au alloy has a hardness in terms of Vickers hardness of 240 Hv or more and 400 Hv or less. Now, the contact member for a micro-load switching contact of the present invention will be described in detail.

(A) Structure of Contact Member for Micro-load switching Contact of the Invention

[0012] As described above, the contact member of the present invention is composed of the substrate, and the surface contact layer containing the thin film of the Au alloy formed on the substrate.

(A-1) Surface Contact Layer

[0013] A contact material constituting the surface contact layer is a Au alloy obtained by adding, to Au, Ag as a first essential additive metal, and at least any one of Cr, Mn, Fe, Co, Ni, Cu, and Zn as a second essential additive metal. The technical sense and the content of these constituent elements of the Au alloy are as follows.

- Ag (First Additive Metal)

[0014] Ag is an essential additive metal added for ensuring hardness with suppressing increase of contact resistance of the resultant Au alloy to be used as the surface contact layer. If the purpose is simply the increase of the hardness, an additive metal different from Ag may be used. For ensuring low contact resistance of the contact material, however, although it is necessary to suppress change in contact resistance caused by sulfidation/oxidation and the like during use, the contact resistance value of the contact material itself in an initial state should be low first of all. In this regard, Ag is a metal having good conductivity, and even when added to Au, the increase of the contact resistance of the resultant alloy is comparatively suppressed. Addition to a Au alloy of another metal different from Ag having a function of increasing hardness largely increases, as compared with Ag, contact resistance of the resultant alloy itself. Therefore, as the additive metal for increasing hardness with low contact resistance of the resultant Au alloy obtained first of all, Ag is essential.

[0015] A content of Ag in the thin film of the Au alloy of the present invention is 15% by mass or more and 30% by mass or less. A content of Ag less than 15% by mass is insufficient from the viewpoint of ensuring the hardness. On the other hand, as the Ag content is increased, sulfidation resistance of the resultant alloy is reduced, and hence low contact resistance becomes difficult to ensure. The present inventors considered that a Ag content over 30% by mass largely reduces the sulfidation resistance even in consideration of improvement of the sulfidation resistance by the second additive element, and hence, 30% by mass is specified as the upper limit of the Ag content. The Ag content of the present invention is more preferably 18% by mass or more and 25% by mass or less. When the Ag content is 15% by mass or more, which is larger than that in the conventional technique (Patent Document 1), the proportion of Au is reduced, and hence the present invention contributes to cost reduction of the contact material.

- Cr, Mn, Fe, Co, Ni, Cu, and Zn (Second Additive Metals)

[0016] These additive metals are added for further increasing the hardness of the Au alloy. As described above, although the hardness of the Au alloy is increased by adding Ag, the amount thereof to be added is limited. Therefore, it is difficult to ensure wear resistance and adhesion resistance of the surface contact layer formed as a thin film only by adding Ag. By adding a trace amount of each metal of Cr, Mn, Fe, Co, Ni, Cu, and Zn, the hardness of the Au alloy is increased, and the wear resistance and the like of the resultant Au alloy thin film are ensured.

[0017] In addition, these additive metals contribute to improvement of sulfidation resistance and adhesion resistance of the Au alloy thin film. The sulfidation resistance is improved probably because a very thin oxide layer is formed on the alloy surface by the additive metal, and this oxide layer prevents sulfur from entering the alloy. Besides, the adhesion resistance is improved probably because plastic deformation of a surface layer is suppressed by the hardness increased as described above, and hence a clean surface of the contact surface is difficult to be exposed.

[0018] At least any one of Cr, Mn, Fe, Co, Ni, Cu, and Zn may be added, and only one of these may be added, or some of these metals may be added together. These additive metals are added in an amount of 0.5% by mass or more and 3% by mass or less in total. When the amount added is less than 0.5% by mass, the hardness of the resultant Au alloy cannot be expected to be increased, and is poor in the wear resistance and the adhesion resistance. On the other hand, when the amount added is over 3% by mass, the contact resistance of the Au alloy is increased from the initial state, and in addition, the sulfidation resistance tends to be poor.

[0019] The Au alloy constituting the surface contact layer of the contact member of the present invention contains the first additive metal (Ag), and the second additive metal(s) (at least any one of Cr, Mn, Fe, Co, Ni, Cu, and Zn), with the balance being Au. Au is a metal excellent in stability of contact resistance under a micro load as the contact material of a micro-load contact, and is an essential and principal metal component in use of the present invention.

[0020] The Au alloy of the present invention is, however, allowed to contain unavoidable impurities. As the unavoidable impurities, Zn, Ca, Al, Cu, and the like may be contained. These impurities are contained in an amount of preferably 0.2% by mass or less, and more preferably 0.1% by mass or less in total.

[0021] The composition of the Au alloy thin film of the present invention can be analyzed/measured by subjecting, to inductively coupled plasma emission spectral analysis (ICP), a solution in which the Au alloy thin film peeled off from the contact material is dissolved. Besides, the composition of the alloy can be analyzed/measured by subjecting a surface or a cross-section of the Au alloy thin film to electron microprobe analysis (EPMA), energy dispersive X-ray spectroscopy (EDX), X-ray fluorescence analysis (XRF), or the like.

[0022] It is to be noted that the surface contact layer of the Au alloy thin film can be formed by a thin film forming process such as sputtering, plating, vacuum evaporation, or chemical vapor deposition. The surface contact layer of the contact member of the present invention is, however, preferably a sputtered film. This is because sputtering is particularly suitable for adjusting the composition and the thickness of the Au alloy thin film corresponding to the surface contact layer. The Au alloy thin film of the present invention formed by sputtering tends to have a high crystal orientation on the (111) plane as compared with a bulk material having the same composition.

[0023] The crystal orientation on the (111) plane in the Au alloy thin film of the present invention can be calculated in accordance with the following Wilson's equation (Expression (1)). In the following Expression (1), "IF (hkl)" indicates a relative intensity of diffraction intensity on the (hkl) plane obtained by X-ray diffraction analysis of the Au alloy thin film of the present invention. Besides, "IFR (hkl)" is a relative intensity of diffraction intensity on the (hkl) plane of a standard sample. The Au alloy thin film of the present invention has an orientation index N on the (111) plane obtained in accordance with the Expression (1) of preferably 1.6 or more.

[Expression 1]

$$N = \frac{IF(hkl)}{IFR(hkl)} \qquad \text{Expression (1)}$$

[0024] The Au alloy thin film of the present invention is composed of the Au alloy containing a trace amount of the second additive metal(s) in the Au-Ag alloy. As database for identification of attribution (on the (hkl) plane) of a diffraction peak observed in a diffraction pattern obtained by X-ray diffraction analysis of the Au alloy thin film, and a relative intensity of the diffraction intensity of a standard sample used for calculating the orientation index N based on Expression (1) described above, PDF Card No: 604771 of ICDS (international crystal structure database) can be used.

[0025] The thickness of the surface contact layer of the contact member of the present invention is preferably 0.1 μm or more and 100 μm or less. When the thickness is less than 0.1 μm, no matter how high the hardness of the thin film is increased, the thin film is poor in durability against wear. On the other hand, when the thickness is over 100 μm, it is difficult to make contribution to downsizing of a switching contact, and increase in thickness also affects the cost of the contact member. In the present invention, a contact member reliable as a thin film of 100 μm or less is intended to be obtained by increasing the hardness of the Au alloy, and hence the upper limit of the thickness is 100 μm. The thickness of the surface contact layer is more preferably 0.1 μm or more and 10 μm or less.

[0026] The hardness of the Au alloy thin film used as the surface contact layer of the contact member of the present invention is, in terms of Vickers hardness, 240 Hv or more and 400 Hv or less. When the hardness is less than 240 Hv, the surface contact layer formed as a thin film cannot be provided with sufficient wear resistance and abrasion resistance. Besides, when the composition of the constituent metals described above is employed, it is difficult to produce a thin film having hardness beyond 400 Hv.

[0027] It should be noted that the description "240 Hv or more and 400 Hv or less in terms of Vickers hardness" does not mean only the hardness measured by the Vickers hardness test (i.e. Vickers hardness). This description also means that the Vickers hardness measured by other hardness tests is 240 Hv or more and 400 Hv or less. Hardness measured by other methods includes one measured by the nanoindentation method. In the present invention, the surface contact layer including a Au alloy thin film may be formed as a very thin film with a thickness of about 1 to 2 μm in some cases, and hence, the nano indentation method is suitable for measuring the hardness of such a thin film with the influence of the base (substrate) eliminated. The nano indentation method is a measurement method using a specific measuring device (nano-indenter), and is a method in which the hardness is measured based on a load and a push depth obtained in pushing a pressing head (indenter) provided in the measuring device into a measurement target. Since the load applied by the pressing head of the nano-indenter is precisely controlled by electromagnetic control, and the movement of the head is also precisely electrically measured, this method is applicable to the hardness measurement of a very thin film. The hardness measurement by the nano indentation method is standardized by International Organization for Standardization (ISO) as instrumented indentation test (ISO 14577). Through the measurement with a nano-indenter, a contact depth is obtained based on contact rigidity (stiffness) of a sample, and thus, nano indentation hardness can be calculated. In the present invention, the unit of the nano indentation hardness (H_{IT}) is N/mm^2. Then, the nano indentation hardness (H_{IT}) can be converted to Vickers hardness (Hv) in accordance with a conversion formula according to the types of the nano-indenter and the indenter used in the measurement.

(A-2) Substrate

[0028] The contact member of the present invention is composed of forming the Au alloy thin film used as the surface contact layer on the substrate. The substrate is a base material of the contact member to be incorporated into a switching contact, and is not especially limited in the size/shape. The substrate may function as a fixed electrode or a movable electrode of the switching contact in some cases. Such an electrode is set in accordance with specifications of the switching contact such as a relay or a switch to be mounted. Besides, the structure of the substrate does not affect properties of the surface contact layer characterizing the present invention.

[0029] As the constituent material of the substrate, the same material as that of a base material used in a conventional micro-load contact can be used. Examples of the constituent material of the substrate include Ag alloy, Cu or Cu alloy, and Ni or Ni alloy.

(B) Method for Producing Contact Member for Micro-load Switching Contact of the Present Invention

[0030] The contact member for a micro-load switching contact of the present invention can be produced by forming the Au alloy thin film having the above-described composition on the substrate preferably by sputtering method. In a spark plug method, a sputtering target, that is, a precursor material of a thin film, is sputtered in a reduced pressure/vacuum atmosphere, and sputtered particles (metal particles of Au, Ag, and the like) thus generated are deposited on a substrate surface to form a thin film.

[0031] In the present invention, the surface contact layer is formed by using an alloy sputtering target containing Au, Ag, and at least any one of Cr, Mn, Fe, Co, Ni, Cu, and Zn in the above-described composition range. It is noted that any one of Cr, Mn, Fe, Co, Ni, Cu, and Zn used as the second additive metal can form a solid solution alloy together with Au and Ag when used within the above-described composition range (0.5% by mass or more and 3% by mass or less in total). In other words, these second additive metals are useful additive metals because a homogeneous alloy sputtering target can be produced using these, and also from the viewpoint of forming a homogeneous Au alloy thin film in the end.

[0032] Conditions for forming the Au alloy thin film by sputtering method are not especially limited, and a general sputtering apparatus and general sputtering conditions can be employed for the film formation.

(C) Micro-load Switching Contact Including Contact Member of the Present Invention

[0033] The contact member of the present invention described so far is suitably used in a contact portion of a micro-load switching contact. A switching contact such as a relay or a switch is a device for electrically connecting/disconnecting a pair of signal lines, and it is a micro-load switching contact having rated and maximum switching current of 5 A or less that the present invention is applied to. Examples of such a switching contact include a miniature relay, and a micro relay.

[0034] A contact portion of the switching contact is composed of a contact pair consisting of a fixed contact that is in a fixed state and a movable contact that is in a movable state for turning signal/power supply on and off. The contact member of the present invention may be used in either one of, or both of the fixed contact and the movable contact. Besides, as the structure of the switching contact (such as a relay or a switch), the same structure as that of a known switching contact is applied.

Advantageous Effects of Invention

[0035] In a contact member of the present invention, a Au alloy thin film having optimized compositions of a first additive metal (Ag) and a second additive metal (Ni or the like) is applied as a surface contact layer. The surface contact layer of the present invention is excellent in hardness and wear resistance as well as favorable in characteristic balance between sulfidation resistance and adhesion resistance. In addition, application of the Au alloy thin film contributes to cost reduction and downsizing of the contact member.

BRIEF DESCRIPTION OF THE DRAWINGS

[0036]

FIG. 1 is a graph illustrating results of a preliminary test on relationship between a Ag content in a AuAg alloy and sulfidation resistance; and

FIG. 2 is a diagram illustrating an XRD diffraction pattern of a Au alloy thin film (surface contact layer) of Example 2.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0037] Preferred embodiments of the present invention will now be described with reference to Examples described below. In the present embodiment, Au alloy sputtering targets having adjusted contents of Ag corresponding to a first additive metal, and Mn, Fe, Co and Ni corresponding to a second additive metal were produced, and surface contact layers were formed by forming Au alloy thin films by sputtering to produce contact members.

[0038] As for each of the Au alloy sputtering targets, an alloy ingot was produced by melting and casting from an ingot raw material of each constituent metal, and a circular sputtering target having a diameter of 127 mm and a thickness of 2 mm was produced through cutting/rolling/shaping processing of the alloy ingot.

[0039] Then, the Au alloy sputtering target was used to form a Au alloy thin film on a substrate, and thus, each contact member was produced. In the present embodiment, the following substrates were prepared for producing samples for various evaluations:

- Substrate for measuring hardness: Ni plate (dimension: 30 mm x 30 mm x 2 mm in thickness)
- Substrate for measuring sulfidation resistance and contact resistance: clad tape material with a width of 0.5 mm on which a Ag-10 mass% Ni alloy tape (thickness: 0.08 mm) and a Cu-30 mass% Ni alloy tape (thickness: 0.12 mm)

are cladded (with the AgNi alloy surface used to be sputtered for forming a Au alloy thin film)

- Substrate for evaluating adhesion resistance: clad tape material with a width of 0.6 mm on which the same AgNi alloy tape and CuNi alloy tape as those described above are cladded

[0040] Then, the substrate and the sputtering target were set in a sputtering apparatus (model: CFS-8ES, manufactured by Shibaura Mechatronics Corporation), as sputtering conditions, ultimate vacuum was set to 5×10^{-3} Pa, Ar gas pressure thereafter was set to 0.5 Pa, RF power was set to 1000 W, and a target-substrate distance was set to 70 mm, and a Au alloy thin film was formed with the thickness monitored to obtain a contact member. In the present embodiment, the Au alloy thin film was formed on the whole surface of the substrate on the side of Ni or the AgNi alloy tape, and the thickness was set to 3 μm. After the set thickness was obtained, the contact member was taken out to measure the composition of the Au alloy thin film in each sample by ICP analysis, and thereafter, evaluation tests of various properties were performed.

[0041] As an example of the X-ray diffraction pattern obtained by performing X-ray diffraction analysis (X-ray source: Cu Kα ray) on the Au alloy thin film of each contact member produced as described above, a result obtained in a Au alloy thin film of Example 2 (Au-20 mass% Ag-1 mass% Fe) described below is illustrated in FIG. 2. It is understood from FIG. 2 that a Au alloy sputtered film of the present embodiment has a crystal orientation on the (111) plane. The orientation index N on the (111) plane of the Au alloy thin film of Example 2 measured based on this X-ray diffraction pattern was N = 2.10. On the other hand, the orientation index N on the (111) plane of a bulk material of Au alloy used as a reference example was N = 0.63. When similar XRD analysis was performed on other examples, the orientation index N on the (111) plane of the Au alloy thin films was 1.6 or more.

[Evaluation of Hardness, Initial Contact Resistance, Sulfidation Resistance, and Adhesion Resistance]

[0042] In contact members of Examples and Comparative Examples obtained by forming Au alloy thin films having various compositions, the hardness and the contact resistance in an initial state were measured. As the hardness measurement, a contact depth was measured with a nano-indenter (Nano-indenter HM 500, manufactured by Fischer Instruments K.K.) under conditions of a maximum indentation load applied by a Vickers indenter of 5 mN, time until application of the maximum indentation load of 20 seconds, a maximum load retention time of 5 seconds, and an unloading time of 20 seconds. Based on the thus obtained contact depth, the nano indentation hardness H_{IT} (N/mm^2) was calculated, and the hardness (Hv) in terms of Vickers hardness was obtained in accordance with the following equation:

[Expression 2]

$$Hv = H_{IT} \times 0.0945$$

[0043] The hardness of a surface contact layer is an evaluation item regarding the wear resistance, and the hardness in terms of Vickers hardness of 240 Hv or more was determined as acceptable (good). The contact resistance was measured by a four-terminal method. In consideration that the acceptable value of products currently available as contact members for micro-load contacts is 15 mΩ or less, the contact resistance smaller than this value was determined as acceptable (good).

[0044] Next, each contact member was evaluated for sulfidation resistance. In this evaluation test, the contact resistance was measured after exposing each sample to a sulfidation atmosphere (H_2S concentration: 3 ppm, temperature: 40°C, relative humidity: 80% RH) for 24 hours. As for the evaluation of sulfidation resistance, a contact resistance obtained after sulfidation of 15 mΩ or less was determined as acceptable (good), and a contact resistance over 15 mΩ was determined as unacceptable (poor).

[0045] Furthermore, an evaluation test of adhesion resistance of each Au alloy thin film was performed. In this evaluation test, a pair of (two) samples were prepared by forming 3 μm of a Au alloy thin film on a substrate. One of the samples was placed on the other sample to cross each other. At this point, the Au alloy thin films of these samples were in contact with each other. After thus setting the samples, one of the samples was reciprocated under application of a current of 5.5 mA. Here, a moving distance was set to 0.5 mm, and a moving speed was set to 0.5 mm/sec. With one reciprocation counted as one time of sliding, the sliding was performed up to a set number of times of sliding. In the present embodiment, the set number was 100, and adhesive force was measured every time of the sliding. For measuring the adhesive force, one of the samples was removed after stopping the sliding, and the adhesive force obtained at this point was measured with a load cell. Then, the maximum adhesive force was determined as the adhesive force of the sample. As the adhesive force is larger, the adhesion resistance is inferior. In the present embodiment, adhesive force of 4.5 gf or less was determined as acceptable (good), and adhesive force over 4.5 gf was determined as unacceptable (poor). It is noted that 4.5 gf, used as the reference value of the adhesive force, was set in consideration of average adhesive force measured by the above-described evaluation method in materials having caused problems due to adhesion in contact members having the same specification produced by the present applicant.

[0046] The alloy compositions and the results of the respective evaluation tests of the contact members (surface contact layers) produced in the present embodiment are shown in Table 1.

[Table 1]

	Alloy Composition (mass%)						Evaluation Results			
	First Additive Metal	Second Additive Metal				Au	Initial Contact Resistance (mΩ)	Hardness (in terms of Hv)	Sulfidation Resistance Contact Resistance (mΩ))	Adhesion Resistance (Adhesive Force (gf))
	Ag	Mn	Fe	Co	Ni					
Example 1	20	1	-	-	-	Balance	5.4(Good)	303(Good)	9.4(Good)	2.5(Good)
Example 2	20	-	1	-	-	Balance	4.68(Good)	287(Good)	7.01 (Good)	2.8(Good)
Example 3	20	-	-	1	-	Balance	5.76(Good)	299(Good)	11.3(Good)	3.3(Good)
Example 4	20	-	-	-	1	Balance	5.8(Good)	302(Good)	4.7(Good)	3.1 (Good)
Example 5	20.5	0.5	-	-	-	Balance	4.46(Good)	328(Good)	11.14(Good)	3.5(Good)
Example 6	20.5	-	-	0.5	-	Balance	4.14(Good)	320.9(Good)	13.95(Good)	3.7(Good)
Example 7	20.5	-	-	-	0.5	Balance	4.22(Good)	298(Good)	6.95(Good)	4.4(Good)
Example 8	19.6	-	-	-	3	Balance	6.81(Good)	373(Good)	6.5(Good)	1.1(Good)
Example 9	25	-	-	-	1	Balance	4.0(Good)	321 (Good)	5.7(Good)	2.8(Good)
Example 10	30	-	-	-	1	Balance	4.2(Good)	314(Good)	10.3(Good)	2.5(Good)
Comparative Example 1	21	-	-	-	-	Balance	3.35(Good)	205.9(Poor)	80(Poor)	10.5(Poor)
Comparative Example 2	20.9	0.1	-	-	-	Balance	3.39(Good)	207.6(Poor)	49(Poor)	5.99(Poor)
Comparative Example 3	20.9	- 0.1	0.1	-	-	Balance	3.59(Good)	227.4(Poor)	92(Poor)	11(Poor)
Comparative Example 4	20.9	-	-	0.1	-	Balance	3.71 (Good)	197.5(Poor)	25.3(Poor)	5.2(Poor)
Comparative Example 5	20.9	-	-	-	0.1	Balance	3.44(Good)	196.6(Poor)	17.3(Poor)	9(Poor)
Comparative Example 6	7	1	-	-	-	Balance	4.09(Good)	218.7(Poor)	4.7(Good)	1.6(Good)
Comparative Example 7	7	-	1	-	-	Balance	4.79(Good)	228.2(Poor)	4.6(Good)	1.9(Good)

(continued)

	Alloy Composition (mass%)						Evaluation Results			
	First Additive Metal	Second Additive Metal				Au	Initial Contact Resistance (mΩ)	Hardness (in terms of Hv)	Sulfidation Resistance Contact Resistance (mΩ))	Adhesion Resistance (Adhesive Force (gf))
	Ag	Mn	Fe	Co	Ni					
Comparative Example 8	7	-	-	1	-	Balance	4.19(Good)	213.5(Poor)	6.1 (Good)	3.9(Good)
Comparative Example 9	7	-	-	-	1	Balance	3.27(Good)	221.8(Poor)	6.9(Good)	3.2(Good)
Comparative Example 10	19.3	-	-	-	4.5	Balance	5.92(Good)	439(Good)	40(Poor)	0.8(Good)
Comparative Example 11	19	-	-	-	6	Balance	6.86(Good)	468(Good)	58.7(Poor)	0.6(Good)
Comparative Example 12	18.7	-	-	-	7.5	Balance	10.32(Good)	587(Good)	Unmeasurable (Poor)	0.63(Good)
Conventional Example	10	-	-	-	-	Balance	3.29(Good)	180(Poor)	3.22(Good)	6.33(Poor)

[0047] It was found, based on Table 1, that the contact resistance in an initial state is lower than the reference value in all of Examples, Comparative Examples, and Conventional Example, and thus, conductivity in an initial state was found to be favorable. Regarding the respective properties obtained in the form of a thin film, which correspond to the problems to be solved by the present invention, it is first understood that the Ag content needs to be increased for increasing the hardness related to wear resistance. A Au-10 mass% Ag alloy thin film of Conventional Example (Patent Document 1) had the hardness in terms of Vickers hardness of 180 Hv, which is obviously insufficient. When the Ag content is increased to 21% by mass as in Comparative Example 1, the hardness can be increased. When the hardness of the AuAg alloy thin film of Comparative Example 1 (205.9 Hv in terms of Vickers hardness) is considered, however, sufficient hardness cannot be obtained by simply increasing the Ag content. Only when the second additive metals of Ni and the like are added as in Examples 1 to 10, the hardness in terms of Vickers hardness of 240 Hv or more can be obtained. Since the second additive metal added in an amount of about 0.1% by mass is, however, less effective for increasing the hardness, the second additive metal needs to be added in a prescribed amount or more (Comparative Examples 2 to 5).

[0048] Regarding sulfidation resistance of the Au alloy thin film, it was confirmed also here, through comparison between Comparative Examples 2 to 5 (Ag content: 20.9% by mass) and Comparative Examples 6 to 9 (Ag content: 7% by mass), that the increase of the Ag content lowers the sulfidation resistance. In order to provide sulfidation resistance to a AuAg alloy having a Ag content of 15% by mass or more as those of Comparative Examples 2 to 5, the content of the second additive metal needs to be 0.5% by mass or more (Examples 1 to 10). Besides, in Comparative Example 1 (Ag content: 21% by mass) in which the Ag content was increased than in Conventional Example, the sulfidation resistance was lowered, but the sulfidation resistance was improved by adding Ni and the like as in the respective Examples. Accordingly, it was considered that the second additive metals of Ni and the like of the present invention are effective not only for the hardness increase but also for the sulfidation resistance.

[0049] Considering that one of the factors of adhesion is exposure of a clean surface due to plastic deformation, adhesion resistance is deemed to be a property related to the hardness. Therefore, Comparative Examples 1 to 5, in which the second additive metals are insufficiently added and hence the hardness was low, were poor in adhesion resistance. In Comparative Examples 6 to 9, in which the hardness was equivalent to or less than that of Comparative Examples 1 to 5, however, the adhesion resistance is acceptable, and hence, whether or not the adhesion resistance is favorable is not determined only by the hardness. Therefore, it is necessary to make favorable the Ag content and the contents of the second additive metals compositely.

[0050] Besides, since the Au alloy thin film in which the Ni content was over 3% by mass (Comparative Examples 10 to 12) was lowered in the sulfidation resistance, the upper limit of the amount of the second additive metal to be added is deemed to be limited. The second additive metal is deemed to be an essential additive metal affecting the hardness, the adhesion, and the sulfidation resistance of a Au alloy thin film, but it is probably necessary to precisely control the amount to be added to 3% by mass or less.

[Evaluation of Adhesion of Thin Film]

[0051] Next, the Au alloy thin films used as the surface contact layers of the contact members of Examples 1 to 10 were evaluated for adhesion to a substrate. In this evaluation test, a contact member in which the thin film had been formed was twisted clockwise 120 times, then twisted counterclockwise 120 times, and after the twisting, it was observed with a stereomicroscope whether or not the thin film had been peeled. In the evaluation of adhesion, when a part or the whole of the thin film was observed to be peeled, the adhesion was determined as unacceptable, and when the thin film was not peeled at all, the adhesion was determined as acceptable.

[0052] As a result of the adhesion evaluation test described above, the thin films were not observed to be peeled after the twisting in all the contact members of Examples 1 to 10. Accordingly, it was confirmed that these surface contact layers containing the Au alloy sputtered films are favorable also in the adhesion obtained in use as a contact member.

[0053] When the relationships between the structure of the Au alloy thin film and the respective properties of the hardness (wear resistance), the sulfidation resistance, the adhesion resistance, and the adhesion described above were summarized, it was confirmed that it is necessary to appropriately contain the first additive metal (Ag) and the second additive metals (Ni and the like) for ensuring the respective properties in a well-balanced manner after forming the thin film.

Industrial Applicability

[0054] The present invention is suitable as a contact member of a switching contact such as a relay or a switch driven under a micro load. The contact member of the present invention has suitable wear resistance, environmental resistance, and adhesion resistance even in the form of a thin film. Besides, adhesion of a Au alloy thin film is also considered, and hence a failure due to peeling of the thin film is also suppressed. The present invention is suitable as a switching contact for a micro load such as a miniature relay or a micro relay, and contributes to cost reduction of a device because an alloy thin film having a reduced amount of Au is used as a contact material.

Claims

1. A contact member for a micro-load switching contact, comprising a surface contact layer of a thin film of a Au alloy formed on a substrate,

   wherein the Au alloy comprises 15% by mass or more and 30% by mass or less of a first additive metal containing Ag, and 0.5% by mass or more and 3% by mass or less of a second additive metal containing any one or more of Cr, Mn, Fe, Co, Ni, Cu, and Zn, with the balance being Au and unavoidable impurities, and
   the thin film of the Au alloy has a hardness in terms of Vickers hardness of 240 Hv or more and 400 Hv or less.

2. The contact member for a micro-load switching contact according to claim 1, wherein the surface contact layer is a sputtered film of the Au alloy.

3. The contact member for a micro-load switching contact according to claim 1 or 2, wherein the surface contact layer has a thickness of 0.1 μm or more and 100 μm or less.

FIG. 1

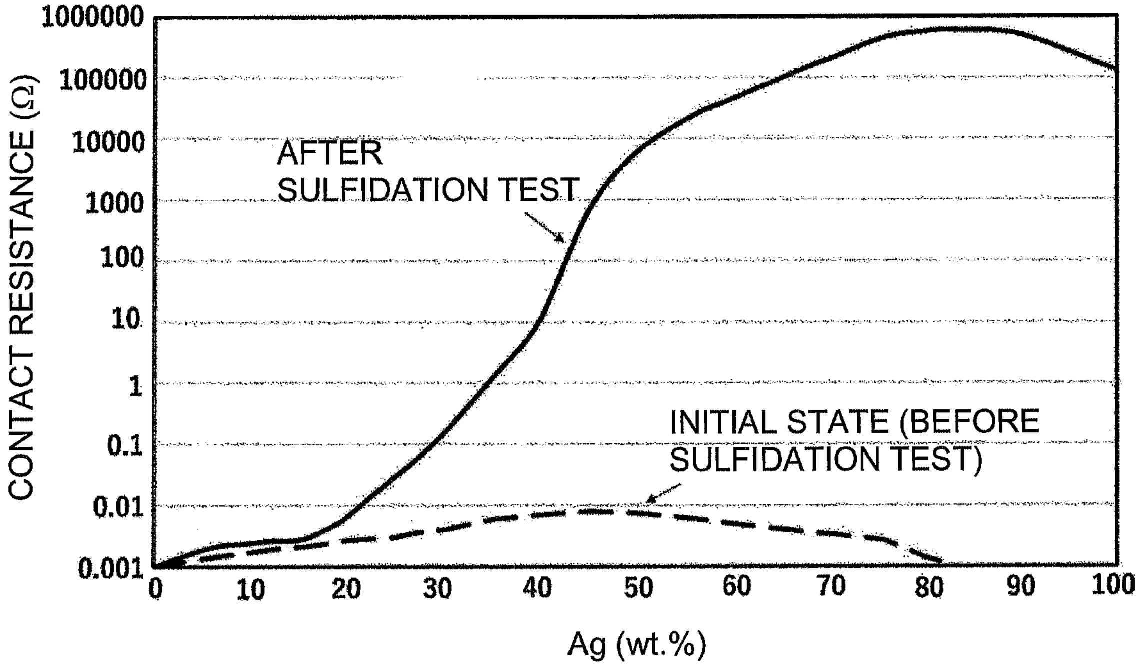
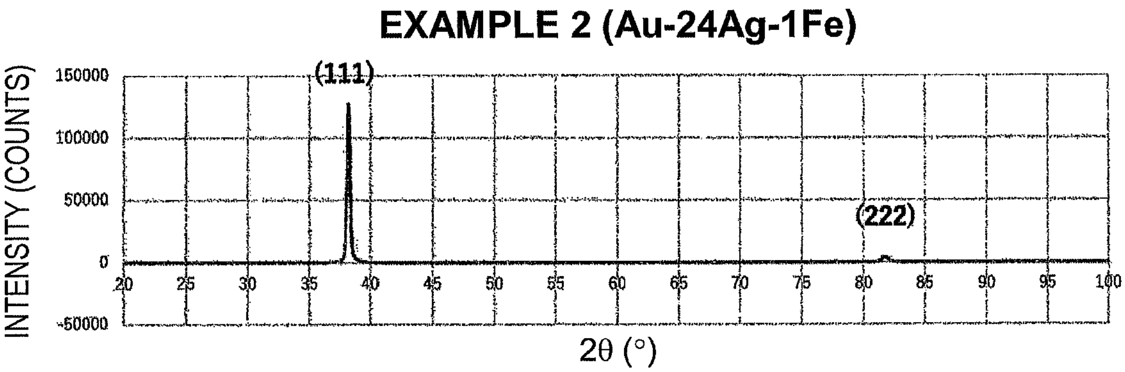

CONTACT RESISTANCE (Ω)
1000000
100000
10000
1000
100
10
1
0.1
0.01
0.001
AFTER SULFIDATION TEST
INITIAL STATE (BEFORE SULFIDATION TEST)
0
10
20
30
40
50
60
70
80
90
100
Ag (wt.%)

FIG. 2


EXAMPLE 2 (Au-24Ag-1Fe)
INTENSITY (COUNTS)
150000
100000
50000
0
-50000
(111)
(222)
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
2θ (°)

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EUROPEAN SEARCH REPORT

Application Number
EP 23 19 2933

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 3 067 908 A1 (OMRON TATEISI ELECTRONICS CO [JP]) 14 September 2016 (2016-09-14) * paragraph [0017] - paragraph [0018]; claim 1; figure 4 * -----	1-3	INV. H01H1/023 H01H1/00
A	US 4 337 133 A (AUGIS JACQUES A ET AL) 29 June 1982 (1982-06-29) * claim 1 * -----	1-3	
A	US 2016/172069 A1 (SUMIYA YOSHINORI [JP] ET AL) 16 June 2016 (2016-06-16) * claim 1 * -----	1-3	

TECHNICAL FIELDS SEARCHED (IPC)

H01H

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	22 January 2024	Socher, Günther

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22-01-2024

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 3067908 A1	14-09-2016	CN 105977063 A	28-09-2016
		EP 3067908 A1	14-09-2016
		JP 2016170967 A	23-09-2016
		US 2016268067 A1	15-09-2016
US 4337133 A	29-06-1982	NONE	
US 2016172069 A1	16-06-2016	CN 105283937 A	27-01-2016
		JP 5819547 B2	24-11-2015
		JP WO2014199837 A1	23-02-2017
		US 2016172069 A1	16-06-2016
		WO 2014199837 A1	18-12-2014

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Patent documents cited in the description

- JP 8287759 A **[0003]**