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54 **Amorphous transition metal alloy, thin gold coated, electrical contact.**

57 An electrical contact, and a method of forming an electrical contact, result in a structure that may utilize far less gold than conventional electrical contacts while having the same, or superior, desirable properties. The electrical contact includes an electrically conductive substrate with an amorphous transition metal alloy electrolytically deposited on the substrate. The amorphous transition metal alloy is a nickel phosphorus, or nickel cobalt phosphorus alloy, and has an uncovered coating of gold thereover. The gold coating is between about 1-30 microinches thick, preferably 5-15 microinches of hard gold.

AMORPHOUS TRANSITION METAL ALLOY,
THIN GOLD COATED, ELECTRICAL CONTACT

BACKGROUND AND SUMMARY OF THE INVENTION

The invention relates to an electrical
5 contact surface (such as an electrical switch
contact) having low contact resistance, relatively
low cost, acceptable solderability, and high
corrosion resistance. The electrical contact
surface, and method of formation thereof, according
10 to the present invention are particularly designed
to replace conventional electrical contact surfaces
wherein a gold layer of at least about 30
microinches thickness is applied over a crystalline
substrate.

15 In the electrical connector industry where
low voltage and/or current signals must be conducted
reliably, and in some situations where intermediate
voltage and/or current signals must be conducted,
gold is currently used to insure low contact
20 resistance, and thus effective conduction. Usually
the gold is applied over a crystalline base metal
such as copper, brass, or silver, with or without an
intermediate strike of nickel, and the thickness of
the gold layer is normally at least about 30 micro-
25 inches (e.g. 50-100 microinches). At a thickness of
50 microinches the cost of the gold layer is on the
order of 5 cents/cm². It is the characteristic of
gold -- with such a thickness -- that it is porous
and thus through time the underlying material, or
30 its corrosion products, may migrate to the surface
of the gold and unacceptably raise the contact
resistance. Additionally, certain organic materials
or sulfur compounds can polymerize on a gold surface

and cause high contact resistance. Additionally, gold has less than ideal solderability since it dissolves in and embrittles some solder alloys.

According to the present invention an electrical contact surface is provided which overcomes the drawbacks associated with the conventional electrical contact surfaces described above, so that in low and intermediate voltage and/or current signal situations effective conduction can be obtained at less cost and over longer periods of time. According to the present invention, an electrical contact surface is provided comprising an electrically conductive substrate (preferably a metal such as copper, bronze, brass, aluminum, or silver) with an amorphous (as opposed to crystalline) transition metal alloy electrolytically deposited thereon.

An "amorphous" alloy is one that has a geometric or topological configuration of the atoms forming the alloy that is different from crystalline (i.e. non-crystalline). Typically, metal alloys are crystalline. When X-ray diffraction tests are done on crystalline materials, it can be seen that the materials exhibit sharp peaks for the d-spacings between planes in the ordered crystal structure, the narrowness or width of these peaks relative to thick height gives an indication of the size of the crystals. For amorphous materials, there are no particularly sharp peaks, the amorphous material being characterized by lack of order in the atomic structure. The exact nature of the amorphous structures is not known, however there are a number of theories which attempt to describe the configurations of the atoms in amorphous materials. In this regard attention is directed to an article entitled

"Metallic Glasses" by Chaudhari et al, appearing in Scientific American, Volume 242, No. 4, 1980, pages 98-117.

- The amorphous transition metal alloy
- 5 according to the invention preferably is a nickel-phosphorus alloy, such as one having about 15-25 atomic percent phosphorus (preferably about 20 percent), with cobalt, or some other transition metals, utilizable in addition to, or in place of,
10 the nickel. Various materials may be added to the plating bath to enhance the corrosion protection of the electrical contact surface being formed, particularly advantageous materials being hexafluosilicate (SiF_6^{--}), hexafluotitanate (TiF_6^{--}), or hexafluozirconate (ZrF_6^{--}) ions.
15

After the amorphous nickel alloy has been electrolytically deposited on the substrate, the amorphous nickel alloy is preferably coated with a layer of gold. When the amorphous nickel alloy is
20 coated with a layer of gold of a given thickness, the contactor that results exhibits superior properties compared to conventional contactors wherein the same thickness of gold is coated on a crystalline metal alloy. For instance, a gold
25 thickness of less than 30 microinches over the amorphous nickel alloy produces an electrical contact structure according to the invention that is equal to, or superior to, conventional contactors wherein a coating of 50-100 microinches of gold is
30 provided. In fact, it is possible to obtain entirely acceptable contactors even when the gold coating is one microinch thick (at this thickness the cost of the gold is only about 0.1 cents/cm²), although a range of 5-15 microinches is preferred.
35 The electrical contact surface resulting has stable

contact resistance both initially and after exposure to a series of common atmospheric corrodants, and initially (soon after production) when tested pursuant to ASTM B667-80 has a contact resistance
- 5 less than 4 milliohms.

According to another aspect of the present invention, a method of producing an electrical contact surface is provided. The method comprises the steps of providing a plating bath for electrolytically depositing an amorphous transition metal
10 alloy on a conductive substrate, immersing the substrate in the bath, and then subsequently coating the amorphous electrolytically deposited alloy with a flash of gold. Nickel chloride, cobalt carbonate, and phosphorous acid are preferred bath constitu-
15 ents. A number of bath additives can be provided to influence contact resistance and corrosion protection in a positive way. Typical bath additives include boric acid, hydroxyacetic acid, acetic acid, β -alanine, succinic acid, surfactants of the
20 alkoxyated linear alcoholic class, SiF_6^{--} ions, TiF_6^{--} ions and ZrF_6^{--} ions. The bath temperature conditions, and the current density at the cathode, are maintained so that effective electrolytic
25 deposition takes place.

It is the primary object of the present invention to provide for the production of electrical contact surfaces that have low, stable contact resistance over extended periods of time
30 even when subjected to corrosive conditions, and at a relatively low cost. This and other objects of the invention will become clear from an inspection of the detailed description of the invention and from the appended claims.

DETAILED DESCRIPTION

A deposition of an amorphous transition metal alloy can be provided on a substrate by immersing the substrate (or a portion thereof) in a plating bath. Amorphous transition metal alloys have been found to have better corrosion resistance than crystalline materials, and a thinner coating of gold over an amorphous transition metal alloy produces a contactor having the same, or better, properties than a contactor formed by a thicker coating of gold over a crystalline material. Further, acceptable contacts can be obtained, according to the invention, with only a very thin coating of gold.

Typical transition metal alloys that are useful in forming electrical contact surfaces (such as electrical switch contacts) according to the invention are nickel and cobalt. Nickel is the preferred transition metal since it has the least cost for the most corrosion resistance, of suitable transition metals. However, generally comparable, and sometimes superior, results can be achieved substituting cobalt, for all or part of the nickel, in the plating bath.

An amorphous deposition of the nickel on the conductive substrate (which preferably comprises a metal such as copper, bronze, brass, aluminum, or silver, or alloys thereof) is formed when phosphorous acid is included in the plating bath, and a relatively high percentage of phosphorus is provided in the alloy that is formed. A phosphorus concentration of at least about 12%, and preferably of about 15-25 atomic percent is desired in order to achieve good corrosion resistance and low contact

resistance. Most preferably the amorphous deposited alloy has about 20 atomic percent phosphorus.

- 5 The bath temperature conditions, and the current density at the cathode, are controlled in order to maximize the corrosion resistance and minimize the contact resistance. Typically current density is about 50 amp./ft.² - 2500 amp./ft.², with a range of about 100-900 amp./ft.² preferred. Typical temperatures are 70-85°C with 75-80°C 10 preferred. Temperature is not critical, but lower temperature will have a tendency to increase the preference of cobalt for nickel in the plating where both are present in the bath.

Various additives may be provided in the 15 bath in order to positively affect the contact resistance and corrosion resistance. When the bath contains hexafluosilicate ions at a concentration of about 0.1 molar to the solubility limit (with the addition of small amounts of HF to maintain 20 solubility if necessary) the overall corrosion resistance of the amorphous nickel alloy may be enhanced. A generally comparable enhancement of corrosion resistance may also be obtained by substituting TiF_6^{--} or ZrF_6^{--} ions for part or all 25 of the SiF_6^{--} ions.

In a plating bath containing nickel or cobalt ions and phosphorous acid any suitable anode and cathode materials may be utilized. For instance the anode can either be inert (platinized titanium, 30 platinum, or graphite), or can be of nickel (or like transition metal to be deposited). If TiF_6^{--} , SiF_6^{--} or ZrF_6^{--} ions are included in the bath a nickel or cobalt anode must be used. With an inert anode additions of nickel or cobalt must be made 35 from time to time (preferably in the form of NiCO_3

or CoCO_3) to maintain the nickel content. With the nickel anode the content of nickel ion in the bath tends to rise since each two electrons at the anode cause the dissolution of about one nickel ion, while
- 5 at the cathode both nickel and phosphorus are being reduced. A nickel and an inert anode can be used together such that each carries only a portion of the current, and thus maintain a balanced bath with regard to nickel. Phosphorous, in the form of
10 phosphorous or hypophosphorous acid, and preferably in the form of phosphorous acid, must be added from time to time -- irrespective of the anode construction -- to maintain the proper bath balance, although the proportion of phosphorous acid is not
15 critical and the bath balance can be maintained rather easily.

After deposition of the nickel phosphorous alloy, or the like, on a substrate, a coating of gold is applied over the amorphous alloy.
20 Preferably this is accomplished by providing an electrodeposit that is applied for a controlled time at a controlled current density. The thickness of the gold coating is determined by the desired end properties of the contactor produced. Within wide
25 ranges, whatever the thickness of the gold coating on the amorphous alloy, the contactor that results can be expected to have enhanced properties compared to contactors formed by the same thickness of gold coating over a crystalline material. In fact,
30 acceptable electric contacts can be produced even when the thickness of the gold coating is about 1 microinch. Preferably the gold coating is in the range of 5-30 microinches, and more preferably 5-15 microinches.

The gold used for the coating preferably is hard gold, although soft gold is also practical although usually with somewhat less desirable results. The thickness of the amorphous transition metal alloy on the substrate is not particularly critical. It merely need be thick enough to achieve the desired results according to the invention. A preferred thickness is in the range of about 50 microinches - 150 microinches. Ranges of 25 microinches - 1000 microinches are practical.

In the typical manufacture of an electrical contact according to the invention (which may be of a wide variety of forms, such as edge card connectors, contact leaf springs, rigid electrical switch contact structures, etc.), desirably, the electrically conductive substrate is formed into the desired final contact shape. It is then immersed in a cleaner, and then deionized water, and then a dilute hydrochloric acid solution. Then it is placed in the Ni-Co-P plating bath and after plating it is rinsed in deionized water. Then the gold plating is provided thereon in any conventional way, such as in a gold plating bath maintained at about 30-35°C with a current density of about 10 amp./ft.². After the gold plating is applied it is again immersed in deionized water. :

Alternatively, for many electrical contact shapes (such as edge card connectors), it is possible to plate blanks or coupons first, and only after they have been plated and a gold strike applied are they formed into the desired shape.

The following are examples of the practice of the invention:

Example 1

A plating bath was formed with the following composition:

= .75 M/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
5 .25 M/l NiCO_3
1.25 M/l H_3PO_3

An electrically conductive substrate was immersed in the bath, which was maintained at a temperature of about 80°C , and with a current density at the cathode of about 150 ma/cm^2 . When removed from the bath, the substrate had an amorphous nickel-phosphorus alloy thereon. A one (1) microinch strike of gold was provided on the amorphous alloy. The electrical contact surface that resulted had a contact resistance that was substantially as low as a similar substrate with a 50 microinch or greater coating of gold, the contact resistance was stable over time, and as stable in corrosive environments (such as when subjected to the SO_2 test -- 100 percent relative humidity and 1 percent concentration of sulfur dioxide, room temperature, over forty hours --, and the mixed gas test -- the same conditions as the SO_2 test only adding 1 percent nitrogen dioxide and 1 percent chlorine). The electrical contact surface formed was much less expensive than the conventional one, and had better solderability characteristics.

Example 2

In this example, the bath composition, temperature, and current density characteristics were substantially the same as in example 1. After the substrate with an amorphous nickel-phosphorus

alloy was removed from the bath, an approximately 10 microinch strike of gold was provided on the amorphous alloy. The electrical contact surface that resulted had contact resistance, and other
5 properties, equal, or superior to, an electrical contact surface formed utilizing similar materials in crystalline form, and with a 50 microinch coating of gold.

Example 3

10 The bath composition in this example was as follows:

 .2 M/l NiCl_2 .6 (H_2O)
 .8 M/l NiSO_4 .6 (H_2O)
 .5 M/l H_3PO_3
15 .5 M/l H_3PO_4

 The bath temperature conditions, current density, and like parameters, were substantially the same as for example 1, and after deposition of the amorphous nickel-phosphorus alloy on the substrate a
20 1 microinch flash of gold was applied. By testing, the electrical contact surface formed was found to have acceptable contact resistance (i.e. less than 4 milliohms when tested according to ASTM B667-80) and corrosion resistance, although it was not as good as
25 the electrical contact surface produced in example 1.

Example 4

 The bath composition for this example was as follows:

.88 M/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
.25 M/l NiCO_3
1.25 M/l H_3PO_3
.4 M/l H_3BO_3
- 5 .2 M/l Acetic acid
.1 M/l CoCO_3

The bath temperature was maintained at about 75°C , with a current density at the cathode of about 200 ma/cm^2 . An analysis of the plating
10 resulting from immersion of the substrate in this bath showed bulk values (in atomic percent) of $6.8 \pm 4\%$ cobalt, 0.6 oxygen, 73.3 percent nickel, and 19.3 percent phosphorus. A 1 microinch strike of gold was provided on the amorphous alloy. The
15 electrical contact surface formed had low contact resistance and high corrosion resistance, and was an excellent substitute for conventional electrical contact surfaces of gold about 50 microinches thick (or thicker) applied over a crystalline base metal.

20 Example 5

A member of platings were produced on electrically conductive substrates to produce platings having about 20% phosphorous, X% cobalt, and 80-X% nickel, utilizing the constituents indicated in the
25 following table:

	Bath Constituent	X=5%	X=10%	X=15%
5	NiCl ₂	.75M	.75M	.75M
	NiCO ₃	.22M	.175M	.13M
	CoCO ₃	.03M	.075M	.12M
	H ₃ PO ₃	1.25M	1.25M	1.25M
	H ₃ PO ₄	.20M	.20M	.20M

Plating was accomplished at 75-78°C using a
 10 hard anode (e.g. platinum or platinized titanium)
 and a current density of about 100 amp./ft.².

The sum of the nickel plus cobalt is one
 mole/liter in each formulation, and CoCO₃ is the
 source of all the cobalt in each of the formula-
 15 tions. Therefore, the Co⁺²/Ni⁺² ratio in the bath
 is M/1 CoCO₃/(1-M/1 CoCO₃). The Co/Ni ratio in the
 plating is %Co/(80-%Co). The relationship between
 Co⁺²/Ni⁺² in the bath and Co/Ni in the plate is:

20	$\text{Co}^{+2}/\text{Ni}^{+2}$	Co/Ni	$\text{Co}^{+2}/\text{Ni}^{+2}$ in plate
	<u>in bath</u>	<u>in plate</u>	<u>Co/Ni in bath</u>
(1)	.031	.067	2.2
(2)	.081	.143	1.8
(3)	.136	.231	1.7

It is evident that the cobalt is being
 25 plated preferentially to the nickel and that at low
 cobalt levels this preference is slightly greater.
 Operating at lower temperature will make the
 preference (Co/Ni in plating) greater, as will

operating at higher current density. Further, these formulations produce lower than nominal amounts of cobalt when they are new, i.e. for the first 100 amp-minutes/liter the baths will produce only ca. 1/2 to 2/3 the desired cobalt content in the plating.

The plating, formed as actual electrical connectors, having 10% Co were coated with 5, 10, or 15 microinches of hard gold, or 5 microinches soft gold, and subjected to durability cycling utilizing conventional techniques, and exposure in a BCL Class III environment, and utilizing the same material on both the PC boards and the connector openings. The following results were achieved, wherein

R_C = the contact resistance and
 σ = a measure of the deviations of the individual contact values from their average

TABLE 1. 70% Ni - 10% Co - 20% P
 EDGE CARD CONNECTORS

	Plating (Microinches of Gold)	Wear Cycles	Before Cycling		After Cycling		4 days	
			R_C	σ	R_C	σ	R_C	σ
20	5 Hard	100	15.4	1.70	16.0	1.59	17.7	1.75
	10 Hard	100	11.0	0.92	10.2	0.63	14.0	9.46
	15 Hard	100	11.0	1.25	11.0	0.92	10.8	1.06
25	5 Soft	100	15.4	1.49	21.3	6.81	27.2	19.3
	5 Soft	250	13.8	2.31	18.9	3.58	35.1	20.2
	5 Soft	500	13.6	2.24	27.1	16.8	34.1	32.8
30	5 Hard	100	13.9	1.42	13.9	1.68	13.0	1.80
	5 Hard	250	15.3	1.34	14.2	2.05	15.0	1.63
	5 Hard	500	13.2	1.31	15.1	2.41	38.8	29.1

TABLE 1. (Cont.)

	Plating (Microinches of Gold)	<u>10 days</u>		<u>15 days</u>		<u>20 days</u>		<u>Disturbed</u>	
		<u>R_c</u>	<u>σ</u>	<u>R_c</u>	<u>σ</u>	<u>R_c</u>	<u>σ</u>	<u>R_c</u>	<u>σ</u>
5	5 Hard	17.0	2.01	20.2	6.30	69.1	104.	17.8	3.94
	10 Hard	18.8	6.03	11.3	1.48	13.0	8.3E	12.7	7.64
	15 Hard	11.3	1.01	14.0	7.26	16.4	1.54	11.7	0.64
	5 Soft	23.2	13.4	35.7	22.5	23.4	13.6	21.3	4.33
10	5 Soft	21.6	8.56	86.7	102.	61.2	87.2	15.3	0.94
	5 Soft	28.5	16.8	40.8	40.0	51.3	41.7	38.8	37.8
	5 Hard	13.0	1.94	30.6	35.1	16.8	7.64	13.3	1.70
	5 Hard	16.3	1.63	18.7	8.16	15.7	2.92	31.1	17.9
	5 Hard	25.0	25.5	23.8	21.8	15.5	1.77	15.4	2.18

15 These results indicate improved performance of the electrical connectors according to the invention compared to a 50 microinch plating of hard gold over conventional sulfamate nickel.

20 While the invention has been herein shown and described in what is presently conceived to be the most practical and preferred embodiment thereof, it will be apparent to those of ordinary skill in the art that many modifications may be made thereof within the scope of the invention, which scope is to
25 be accorded the broadest interpretation of the appended claims so as to encompass all equivalent structures and methods.

CLAIMS:

1. An electrical contact having a contact resistance soon after production of less than 4 milliohms, and comprising an electrically conductive substrate; and characterized by: an amorphous transition metal alloy deposited on said substrate; and an uncovered coating of gold over said amorphous transition metal alloy, said gold coating being between about 1-30 microinches thick.

2. An electrical contact as recited in claim 1 further characterized in that said transition metal alloy is a nickel-phosphorus alloy.

3. An electrical contact as recited in claim 2 further characterized in that said nickel-phosphorus alloy includes about 15-25 atomic percent phosphorus; and includes about 5-15 atomic percent cobalt.

4. An electrical contact as recited in claim 3 further characterized in that said uncovered coating of gold is hard gold between about 5-15 microinches thick.

5. A method of forming a structure comprising the steps of: (a) immersing a substrate in a plating bath including transition metal alloying elements; and (b) controlling the bath temperature conditions and current density at the cathode to effect electrolytic deposition of the transition metal alloying elements, in amorphous form, on the substrate; and characterized in that the substrate is an electrically conductive

substrate, and characterized by the further step of
(c) applying a coating of gold having a thickness
of between 1-30 microinches to the electrolytically
deposited amorphous transition metal alloy, to
5 produce an electrical contact structure having an
uncovered gold surface.

6. A method as recited in claim 5 further
characterized in that step (a) is practiced
utilizing a plating bath containing phosphorus acid
10 and nickel alone, or nickel and cobalt.

7. A method as recited in claim 5 further
characterized in that step (b) is practiced so that
the temperature of the bath is between about 70-
85°C, and so that the current density at the cathode
15 is between about 100-900 amp./ft.² and to effect an
electrolytic deposition of the amorphous material so
that it has a thickness of about 25-1000 micro-
inches; and further characterized in that step (a)
is practiced by including in the plating bath
20 between 0.1 molar to the solubility limit of ions
selected from the group consisting of TiF_6^{--} , SiF_6^{--}
and ZrF_6^{--} ions.

8. A method as recited in claim 7 further
characterized in that steps (a) and (b) are
25 practiced so that the amorphous alloy deposited on
the substrate is a nickel cobalt phosphorus alloy,
including about 15-25 atomic percent phosphorus, and
at least 5 atomic percent cobalt.

9. A method as recited in claim 5 further characterized in that step (c) is practiced so as to apply a coating of hard gold having a thickness of between 5-15 microinches.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	METAL FINISHING ABSTRACTS, volume 22, no. 3, May/June 1980, Teddington, Middlesex (GB) page 187H, & JP - A - 54 110470 (HITACHI)	1, 2, 5	C 25 D 3/50 C 25 D 5/10 C 25 D 7/00 H 01 H 1/02
A	GB-A-1 507 782 (LEA-RONAL)		
A	DE-B-1 059 738 (DÜRRWÄCHTER)		
A	US-A-4 101 389 (UEDAIRA) * the entire document *		
A	METAL FINISHING, volume 82, no. 1, January 1984, pages 59-65, C. RAJAGOPAL et al.: "Electrode-deposition of corrosion resistant amorphous nickel alloys on mild steel"		TECHNICAL FIELDS SEARCHED (Int. Cl. 3) C 25 D 3/56 C 25 D 5/10 C 25 D 7/00 H 01 H 1/02
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 31-08-1984	Examiner VAN LEEUWEN R.H.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			