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Intermetallic connector finishes.

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An intermetallic connector finish is obtained by combining a layer of base metal with a layer of semi-noble material to produce a mixture containing intermetallic or intermediate compounds with contact properties in excess of either of the pure materials taken alone.

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INTERMETALLIC CONNECTOR FINISHES

The present invention relates to connectors and more particularly to metallic finishes for the contacts of such connectors.

5 Electrodeposited gold has been traditionally used as a connector material because of its unique combination of properties including low wear rate and excellent corrosion resistance. However, the utilization of gold as a contact material has come
10 under close scrutiny since the marked increase in gold prices during recent years and it has become evident that the connector industry must consider alternative cheaper coatings.

 Several connector manufacturers are now using
15 cheaper tin contact finishes on commercial connectors but the poor wear rate as opposed to that achieved with gold finishes limits the use of the base metal to connectors which require only a 'short' operational lifetime.

20 Tin also suffers from the disadvantage that electrodeposited tin is prone to the formation of whiskers and is therefore not suitable for use on miniature connectors where the contact pitch is small and shorting could readily occur.

25 Silver is also used as an alternative contact

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finish on commercial connectors but is prone to silver migration and is susceptible to tarnishing in sulphurous atmospheres and has relatively poor wear resistance.

5 It is an object of the present invention to provide an intermetallic connector finish which is considerably cheaper than finishes containing large percentages of gold but which gives an acceptable wear rate and good corrosion resistance comparable to the
10 previous gold finishes.

 The present invention therefore provides a metallic finish for connectors including a mixture of silver and tin in which the silver and tin are combined in part or in whole to form an intermetallic or intermediate compound.
15 Intermediate and Intermetallic compounds are defined in Physical Metallurgy 2nd Edition edited by R. W. Cahn, North Holland, 1970 page 229.

 In a preferred embodiment the final finish contains from 25 to 100% by volume of the intermetallic or
20 intermediate compound.

 In a more specific embodiment a layer of silver is deposited on connector contacts, a layer of tin is deposited on the silver and the resultant layers are diffused to produce a combined silver-tin intermetallic connector
25 finish. Alternatively the layer of tin may be deposited

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first the layer of silver deposited onto the tin with subsequent diffusion to produce the intermetallic connector finish. Alternatively multiple layers of tin and silver may be deposited to the desired total thickness and composition. This would increase the rate of conversion to the intermetallic phase during diffusion.

In a preferred embodiment a layer of iron is deposited onto the connector contact prior to the deposition of the silver and tin to form a barrier between the contact material and the intermetallic or intermediate compound. The intermetallic or intermediate compound may be directly deposited from a carefully selected solution containing ions of silver and tin providing temperature and rate of deposition is carefully controlled.

Embodiments of the present invention will now be described by way of example.

According to the present invention a practical method for the preparation of the intermetallic containing contact finishes involves the successive electrodeposition of a layer of one pure metal over another followed by subsequent diffusion treatment.

In this work the diffusion may be achieved by heat treatment in a $90\text{N}_2/10\text{H}_2$ atmosphere, but glow discharge assisted diffusion is an alternative

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method which might be considered for production purposes. The resultant diffused structure consists of varying proportions of solid solution and hard intermetallic compounds depending upon the alloy composition, the heat treatment employed and the presence or absence of interaction with the substrate. Alternatively the finish may be directly deposited by electrodeposition with or without a subsequent diffusion process.

10 The choice of constituent elements is based upon the material cost, the ease of electrodeposition from commercially available solutions and the melting points of both the original metals the nature of the phase diagram and the melting point of the resultant intermetallic phases. Silver has been selected because it is a semi-noble metal. The combination with a low melting point material such as tin enables the use of relatively low diffusion temperatures if a diffusion process is to be used which should not cause any deterioration of the mechanical properties of the underlying substrate material. Diffusion may be conducted wholly in the solid state; or involving a transient liquid phase if the melting point of the lower melting point metal is exceeded. It is possible for the substrate

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material to diffuse into the above electroplated layers during the heat treatment; this may or may not have adverse effects upon the performance. A diffusion barrier may be employed to prevent this.

5 The intermetallics achieved by suitable diffusion treatments or electrodeposition have several properties which are required by contact finishes. The atomic ordering which is very common in intermetallic compounds gives them intrinsically greater hardness than a
10 pure metal or solid solution thereby imparting improved wear resistance. The strong chemical bonding of such phases indicated low reactivity and therefore good corrosion resistance. In addition the relatively high melting points of the intermetallic
15 compounds result in improved ambient temperature mechanical properties (in particular creep resistance) which is essential when contact finishes are mated under stress.

A preferred intermetallic contact finish is
20 obtained using diffused layers in the Ag-Sn system. Utilization of different relative plating thickness, diffusion temperatures and diffusion times enables the formation of varying proportions of Ag_3Sn intermetallic and silver or tin (Ag or Sn) solid solution as
25 determined from the phase diagram. A range of these

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materials have been tested on model connector contacts. In the simplest case these materials were prepared by the diffusion of tin and silver layers deposited directly onto a copper based alloy substrate without an intermediate barrier layer. The best of these finishes exhibit consistent low contact resistance ($<5m\Omega$) and low friction (60 grams per contact) during 500 operations with 100 and 150 gram contact loads. Furthermore, the wear rate of these diffused coatings was similar to that of a hard gold finish; in the above tests only 3 - 4 μm of the 10 μm coating has worn through after 500 operations. Tin-lead finishes of similar thickness were worn through to the substrate after 50 to 250 operations depending upon the deposit lead content.

A first example within this type of intermetallic connector finishes is as follows:-

A layer of 5 microns of tin is electrodeposited over a 5 micron layer of electrodeposited silver on a bronze substrate, and the layers interdiffused for 1 hour at 250°C in a mildly reducing atmosphere. The composition homogeneity and microstructure of the diffused layer were examined by standard metallographic sectioning and by X ray diffraction scanning electron microscopy and electron microprobe analysis.

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The resulting layer consisted of the Ag_3Sn intermetallic and a smaller proportion of pure tin. The intermetallic Ag_3Sn comprised the major proportion of the surface regions of the diffused layers. On testing in a model connector between a 1.5mm radius coated bronze cone and a flat coated bronze plate at 100 and 150 gram contact load the finishes exhibited consistent low contact resistance ($<5\text{m}\Omega$) and low friction (<60 grams) during 500 sliding operations. The wear rate of the coating was similar to that of a hard gold coating, only 3 - 4 microns has worn through after the 500 operations.

A second preferred example within this type of intermetallic connector finish is as follows:-

A layer of 2.5 microns of tin is electrodeposited over a 7.5 micron layer of electrodeposited silver on a bronze substrate and the layers interdiffused for one hour at 250°C in a mildly reducing atmosphere. The resulting layer consisted of the Ag_3Sn intermetallic and a proportion of pure silver. The intermetallic Ag_3Sn comprised the major proportion of the surface regions of the diffused layers. On testing in a similar fashion in a model connector, consistent low contact resistance and low friction were obtained. In addition low contact resistance ($<5\text{m}\Omega$) was maintained after

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exposure to the standard SO_2/CO_2 industrial atmosphere as specified for BS 9000 qualified components in both mated and unmated states for a 100 gram contact load for static conditions. Low contact resistance ($<5\text{m}\Omega$) was also maintained upon subsequent wiping.

In the above two examples the electrodepositions of the silver and tin layers may be in the reverse order with the silver being deposited on top of the layer of tin which is initially deposited on the bronze substrate.

The quantities of silver and tin will be the same.

Although the above samples possess favourable contact properties interaction with the substrate can give rise to variability in contact resistance behaviour. This variability is attributed to the non-planar diffusion of copper from the copper alloy substrate into the Sn/Ag regions during the diffusion treatments and the consumption of liquid tin by reaction with the copper alloy substrate. The use of an iron barrier layer between the Sn/Ag and copper alloy substrates has proved effective in preventing this interaction and diffusion of copper and has permitted the production of contacts with more reproducible properties.

Samples of $2\frac{1}{2}\mu\text{m}$ Sn electrodeposited over $7\frac{1}{2}\mu\text{m}$ Ag, electrodeposited over a $3\mu\text{m}$ iron barrier layer and deposited onto a copper alloy substrate had been

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diffused for 30 minutes at 250°C. The material largely comprises a layer of Ag₃Sn whilst a small amount of tin rich material remains at the surface and some silver rich material remains beneath the Ag₃Sn layer. The contact resistance of these samples is consistant over 1,000 wipes under 100 g contact load, the values being < 8mΩ. The corresponding friction is also consistent and below 100 g force/contact. The wear of 10μm coating is 4 - 6μm after 500 wipes and 7 - 8μm after 1,000 wipes.

When an iron barrier is employed optimum contact properties are achieved for a heat treatment of 30 minutes at 250°C. It has also been found that tin to silver thickness ratios should not be in excess of 1:3.

The corrosion resistance of samples of 2½μm tin electrplated over 7½μm silver electroplated over a 3μm iron barrier layer on a bronze substrate and diffused for 30 minutes at 250°C has been examined. The material shows no increase in contact resistance after 10 days exposure to the BS 2011 part 2.1 Db cyclic damp heat test in the mated and unmated states under loads of 100 and 200 grammes. No increase in resistance was observed after 56 days exposure to the BS 2011 part 2.1 Ca 1977 steady state damp heat test in the mated and unmated states and also after 20 days exposure to the SO₂/CO₂

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industrial atmosphere test in the mated state as specified for BS 9000 qualified components. Again no resistance increase was observed after 500 hrs storage at 85°C in air in the mated and unmated states.

5 The resistance of this material to silver migration is good. Silver migration was monitored using the so called "Water Drop" test. In this test a drop of deionised water is placed so as to bridge the gap between two conductor lines and the migration
10 of silver is observed upon applying a bias between the two conductors. The diffused tin silver layer shows no evidence of silver migration after 30 minutes at 5, 10 or 15 volts for a 1mm gap. Under the same test conditions silver shows clear evidence of migration
15 after only 2 minutes at 5 volts.

Silver Tin Alloys can also be directly electro-deposited from solutions containing silver and tin ions. Several formulations are possible. One example of such a solution has the following composition:

20	Silver Cyanide	AgCN	0.019M
	Potassium Stannate	K ₂ SnO ₃ 3H ₂ O	0.375M
	Potassium Hydroxide	KOH	1.25M
	Potassium Cyanide	KCN	1.40M

The deposit produced from this solution consists
25 mainly of the intermetallic compound Ag₃Sn.

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A second example of a solution of electrodepositing silver tin alloys has the following composition:

	Potassium Pyrophosphate	$K_4P_2O_7$	3.30M
	Potassium Silver Cyanide	$K Ag(CN)_2$	0.20M
5	Potassium Stannate	K_2SnO_3	3.80M

This solution produces a deposit containing 88% silver and 12% tin.

A third example has the composition:

	Potassium Pyrophosphate	$K_4P_2O_7$	0.39 - 0.67M
10	Potassium Ferrocyanide	$K_4Fe(CN)_6$	0.012M
	Silver Ferrocyanide	$Ag_4Fe(CN)_6$	0.020- 0.046M
	Tin Pyrophosphate	$Sn_2P_2O_7$	0.090- 0.13M

The relative concentrations of silver and tin ions in solution determine the composition and structure of the electrodeposit. Under certain conditions a deposit containing intermetallic or intermediate compounds and free tin can be produced.

Deposits have been prepared from the $Ag CN K_2 Sn O_3$ solution described above. The deposit plated at a temperature of $55^{\circ}C$ and at a current density of 6m Amps/cm² was shown by X ray diffraction to contain the Ag_3Sn intermetallic with traces of free tin and silver. The contact resistance values varied between 3 and 6.5 ohms during 500 wipe cycles under a 100gr contact load and the corresponding friction rose from

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50 to 100 grammes force during the test. The coating had worn through approximately 10 μ m during the 500 wipe operations.

5 To summarise the Ag-Sn intermetallic connector system offers a considerable improvement in contact properties over pure silver and pure tin. It also offers a considerable cost reduction if used as an alternative to gold..

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WHAT WE CLAIM IS:

1. A metallic finish for connectors including a mixture of silver and tin in which the silver and tin are combined in part or whole to form an intermetallic or intermediate compound.
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2. A metallic finish for connectors as claimed in claim 1 containing from 25 to 100% by volume of the intermetallic or intermediate compound.
3. A metallic finish for connectors as claimed in claim
10 1 in which a layer of iron is deposited on the connector substrate to provide a barrier layer between the substrate and the intermetallic or intermediate compound.
4. A method of producing a metallic finish for connectors in which a layer of silver is deposited on a connector
15 contact, a layer of tin is deposited on the silver and the resultant layers are diffused to produce a combined silver-tin intermetallic or intermediate connector finish.
5. A method of producing a metallic finish for connectors
20 as claimed in claim 4 in which a layer of iron is initially deposited on to the connector contact to form a barrier layer between the contact and the intermetallic or intermediate connector finish.
6. A method of producing a metallic finish for connectors
25 in which a layer of tin is deposited on a connector

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contact, a layer of silver is deposited on the tin and the result layers are diffused to produce a combined silver- tin intermetallic or intermediate connector finish.

5 7. A method of producing a metallic finish for connectors as claimed in claim 4 or claim 6 in which a plurality of silver and tin layers are deposited prior to the diffusion process.

8. A method of producing a metallic finish for connectors
10 by direct electrodeposition from a solution containing silver and tin ions to form a layer containing an intermetallic or intermediate compound.

9. A method of producing a metallic finish for connectors as claimed in claim 8 in which the
15 electrodeposition layer is subjected to a subsequent heat treatment.

10. A method of producing a metallic finish for connectors as claimed in claim 9 wherein an iron barrier layer is present on the connector substrate to separate the
20 deposition from the connector substrate.



European Patent
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EUROPEAN SEARCH REPORT

0033644

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<u>CH - A - 408 582</u> (WÜRTTEMBERGISCHE METALLWAREN-FABRIK) + Claims + -- <u>CH - A - 506 174</u> (W.C. HERAEUS GMBH) + Claims + -- <u>DE - B2 - 2 540 944</u> (W.C. HERAEUS GMBH) + Claims + -- <u>US - A - 4 141 727</u> (SHIDA et al.) + Claims + -- <u>US - A - 4 069 370</u> (HARMSSEN et al.) + Claims + -- <u>US - A - 3 562 467</u> (MOORADIAN) + Column 2 + -- <u>US - A - 3 598 550</u> (TAKAHASHI et al.) + Claims + ----	1,8 1 1 1 1 1 1,2	C 25 D 7/00 C 25 D 3/56 C 25 D 5/10 H 01 B 1/02 H 01 R 13/00 H 01 H 1/02
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 25 D H 01 B H 01 H 1/00 H 01 R B 32 B
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			& member of the same patent family corresponding document
X	The present search report has been drawn up for all claims		
Place of search	Date of completion of the search	Examiner	
VIENNA	22-04-1981	SLAMA	