Electrodeposition of Palladium-Silver Alloys from Ammoniacal Electrolytes

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A viable technique for the electrodeposition of palladium-silver alloys could find application during the manufacture of electrical contacts. Previously such a process has not been available but some alloys with useful physical properties can now be deposited from an ammoniacal system, while a better understanding of the mechanisms involved has been gained during the work reported here.

Applications of palladium and palladium alloys in the electrical contact field have recently been reviewed by Antler (1). Among these materials, palladium-silver alloys, particularly the 60 per cent palladium-40 per cent silver composition, are well established in the wrought form, as claddings, weldments or inlays, with advantages over the pure metal in terms of cost and durability. More recently, interest has extended in the direction of electrodeposited coatings of palladium and alloys as economic substitutes for gold plating, and in this context it is clearly attractive to consider the possibilities of producing palladium-silver alloys by electrodeposition, a technique which would permit, for example, the application of coatings to pre-formed contact fingers and other components in cases where the inlay technique is not practicable. While, however, a considerable amount of research work has been carried out to this end, notably from Russian sources, it would appear that no viable process has yet been developed.

Early attempts used a solution based on cyanide complexes of the two metals (2, 3), but the alloys produced, with a palladium content of 20 to 22 per cent, were of poor appearance and the cathode efficiency was very low. Improvements were later obtained in terms of increased cathode efficiency by optimising process parameters and bath formulation (4–6).

Deposits from thiocyanate-based electrolytes showed a broader compositional range, up to 70 per cent palladium (2, 7–12), the best coatings from this type of bath containing 2 to 10 per cent palladium. A bath formulation based on palladium and silver ammino-hydroxy salts gave semi-bright deposits with palladium contents from 15 to 85 per cent and good cathode efficiency of 85 to 95 per cent (13–16), while bright coatings have been reported from an electrolyte based on amino-acid complexes (17, 18). Solutions of palladate and argentate salts have been stated to give semi-bright coatings with palladium content between 10 and 60 per cent, with thicknesses up to 15 μm being obtainable (19).

Work has also been carried out using concentrated halide baths with lithium chloride to permit increased solubility of silver (20–22). This type of solution is very aggressive to base metals due to vigorous displacement reactions; however, good deposits were reported, with palladium contents ranging from 30 to 60 per cent. Attempts to deposit alloys from ammoniacal solutions of nitrito-complexes were unsuccessful (2), but when nitrate complexes are employed it has been reported that the full range of alloy compositions can be obtained simply by adjustment of the current density (23). Later reports claim the production of bright, pore-free deposits from this type of

Stirring motor

Shaft

PVC jacket

Cathode

Anode

Outlet

Teflon sleeve

Ø 75

Ø 50

15   15

Ø 10

6   6
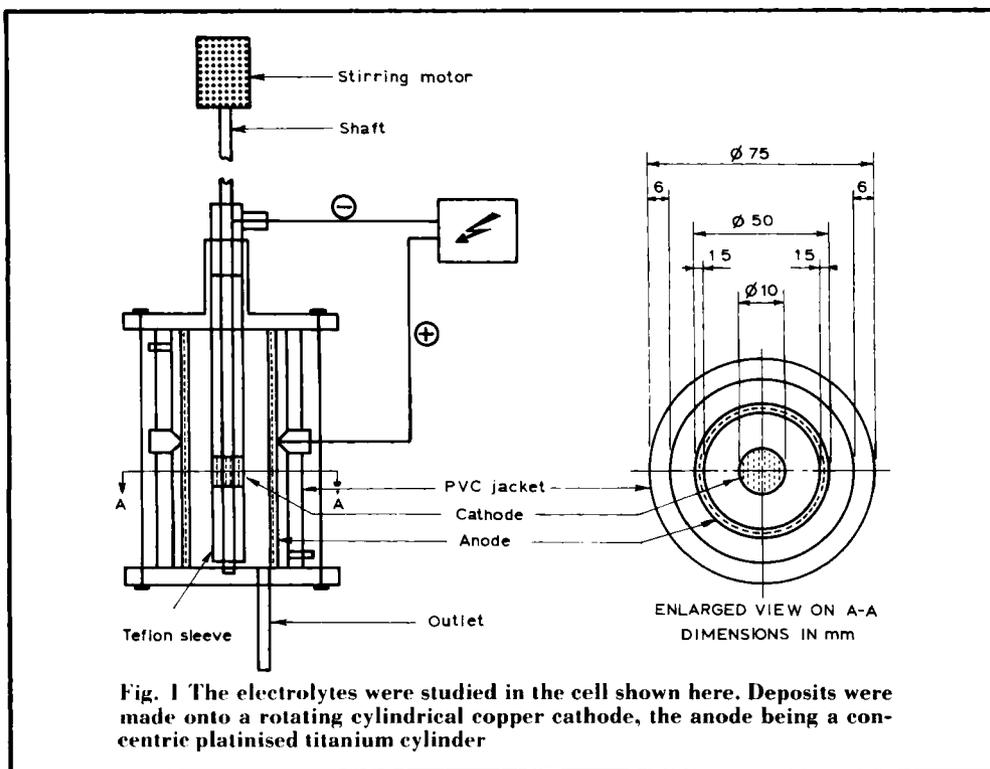
ENLARGED VIEW ON A-A
DIMENSIONS IN mm

Fig. 1 The electrolytes were studied in the cell shown here. Deposits were made onto a rotating cylindrical copper cathode, the anode being a concentric platinised titanium cylinder

solution, with thicknesses up to 20 μm (24).

The object of the present work was to study the mechanism in palladium-silver alloy deposition in order to gain a better understanding of the influence of process and compositional parameters on alloy composition and properties. For this purpose the ammoniacal solution with palladium and silver nitrates was selected in view of the possibility of obtaining a wide range of alloy compositions.

Experimental Conditions

The electrolyte compositions studied are given in the Table opposite.

Deposition was made on a copper cylinder (10 mm diameter, 10 mm high) attached to a Teflon shaft, the rotational speed (Ω) of which could be continuously adjusted from 0 to 10 revolutions per second. The anode was a concentric cylinder of platinised titanium, which was itself provided with a further jacket of PVC for temperature stabilisation. The electrolytic cell is shown as Figure 1. The cathode surface

was prepared for plating by an initial polish with 1 μm alumina paste, followed by cathodic degreasing at 10 mA/cm^2 in an alkaline cyanide solution, and a final activating dip in concentrated sulphuric acid, with intermediate water rinses. Immersion in the electrolyte was made under an applied voltage.

Deposition was carried out at room temperature (22°C) for times selected to produce coating thicknesses in the order of 2 μm. The applied current density (j_{tot}) was varied between 5 and 40 mA/cm^2, and the cathode rotational speed between 0 and 10 revolutions per second.

Deposition Mechanism Studies

Polarisation curves for (a) a solution containing 20 g/l of palladium only, and (b) a solution containing 20 g/l of palladium and 2 g/l of silver are shown in Figure 2. From these it is seen that silver begins to deposit at potentials less negative than for palladium, and that palladium deposition occurs when silver is

being deposited under limiting current conditions. The large plateau of curve (b) is associated with the limiting current of silver deposition, as will be quantitatively evidenced later. The fact that palladium, a more noble metal than silver, is deposited only at more negative potentials than the latter, is explained by the much greater stability of the palladium-ammino complex, the relevant stability constants being as follows (25):

$$K \quad Pd(NH_3)_4^{2+} = \frac{[Pd(NH_3)_4^{2+}]}{[Pd^{2+}][NH_3]^4} = 6.3 \times 10^{32}$$

$$K \quad Ag(NH_3)_2^{+} = \frac{[Ag(NH_3)_2^{+}]}{[Ag^+][NH_3]^2} = 1.6 \times 10^7$$

The influence of current density and rotational speed of the cathode on the composition of the alloys was studied for electrolytes containing 1 and 2 g/l of silver. The results, shown in Figures 3 and 4, are consistent with the hypothesis of a mass transport-controlled codeposition of silver, in that the silver content increases with agitation rate at constant current density, and decreases with increase in current density at constant agitation rate. As shown by comparison of Figure 3 with Figure 4, the increase in the silver content of the deposit is proportional to the increase in silver concentration in the electrolyte, which is again consistent with the mass transport model for silver incorporation.

Figures 3 and 4 also show the experimental conditions under which bright, semi-bright, and matt deposits are obtained. The thickness of the deposits was 2 μm. In general, deposits with a silver content below 25 atomic per cent are bright, while higher silver contents are associated with semi-bright or matt coatings. This may be explained on the basis that at low silver incorporation rates the deposit structure is essentially governed by the crystallisation
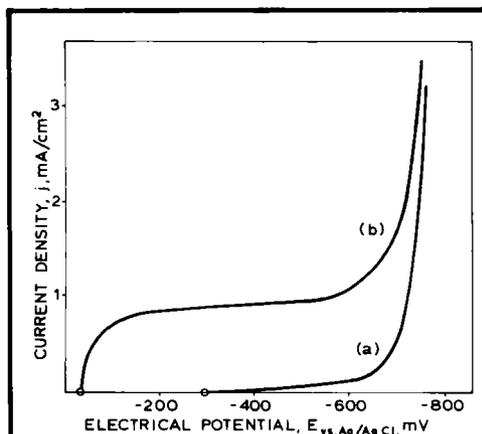

Fig. 2 Polarisation curves for palladium and palladium-silver electrolytes. Voltage scanning speed: 1 mV/s
(a) Palladium: 20 g/l
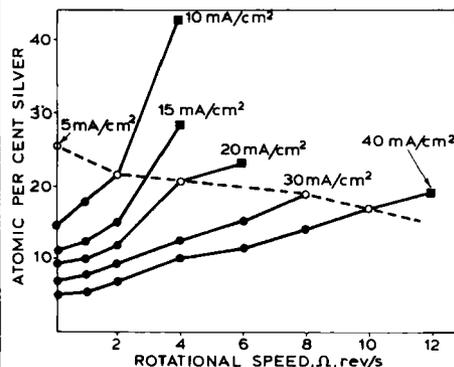(b) Palladium: 20 g/l; silver: 2 g/l

Fig. 3 Silver content of deposits as a function of rotational speed of cathode and current density for electrolyte 1.
● bright deposits; ○ semi-bright deposits; ■ matt deposits

mode for palladium, while at higher rates of silver incorporation the morphology of the deposit is progressively affected by the crystallisation of silver. Since silver deposition takes place under mass transport controlled

Electrolyte Compositions			
	1	2	3
Palladium, as $Pd(NH_3)_4(NO_3)_2$	20 g/l	20 g/l	20 g/l
Silver, as $Ag(NH_3)_4(NO_3)$	1 g/l	2 g/l	3 g/l
pH (adjusted by gaseous NH_3)	11.5	11.5	11.5

conditions, there is a tendency for the formation of dendrites and powder, leading to rougher deposits. The morphology of matt, semi-bright and bright deposits with various silver contents is illustrated in the scanning electron micrographs of Figure 5.

The variation of current efficiency with silver content is shown in Figure 6. The decrease in efficiency with increasing silver content can be explained by the increasing roughness of the deposits, leading to enhancement of hydrogen evolution at asperities and hence to a decrease in current efficiency for metal deposition. The current efficiency was calculated on the basis of Faraday's law from the metal contents of deposits, as determined by atomic adsorption on solutions prepared by dissolution in nitric acid, as follows:

$$CE\ (\%) = 100\ \frac{I_{Pd} + I_{Ag}}{I_{tot}} \qquad [i]$$

$$= 100\ \frac{\left(\dfrac{2m_{Pd}}{A_{Pd}} + \dfrac{m_{Ag}}{A_{Ag}}\right)\dfrac{F}{t}}{I_{tot}} \qquad [ii]$$

where I_{Ag} and I_{Pd} are partial currents for silver and palladium, I_{tot} is total current, m_{Ag} and m_{Pd} are weights of silver and palladium deposited, A_{Ag} and A_{Pd} are the atomic weights of the metals, F is the Faraday constant and t is the electrolysis time.

From the silver content of deposits, and on the assumption that silver is deposited under mass transport control, the limiting current density for silver deposition can be calculated from the results of Figures 3 and 4, and is plotted as a function of rotational speed of the cathode in Figure 7. The limiting current density values so obtained fit the following relationship:

$$j_{L_{Ag}} = 85.5\ \Omega^{0.559}\ .\ C_{Ag} \qquad [iii]$$

That is to say, the limiting current density is directly proportional to the silver concentration C_{Ag} in the electrolyte and is a function of $\Omega^{0.559}$. An exactly similar relationship between limiting current density and rotational speed was found in separate experiments with a ferri-ferrocyanide system, where it is well known

that the current is under full mass transport control, providing a quantitative demonstration of the fact that similar conditions apply to the incorporation of silver in the palladium-silver alloy. This being so, a model may be derived for the calculation of alloy composition as a function of deposition parameters, as given below.

During the electrodeposition of palladium-silver alloy, the total current density is due to contributions from the deposition of palladium, silver and hydrogen.

$$j_{tot} = j_{Pd} + j_{Ag} + j_H \qquad [iv]$$

The molar-ratio of silver in the deposit is:

$$x_{Ag} = j_{Ag}/(j_{Ag} + 1/2\ j_{Pd}) \qquad [v]$$

Assuming a 100 per cent current efficiency and combining Equations [iv] and [v],

$$x_{Ag} = 2\ j_{Ag}/(j_{Ag} + j_{tot}) \qquad [vi]$$

$$x_{Ag} = 2/(1 + J) \qquad [vii]$$

$$\text{where}\quad J = \frac{j_{tot}}{j_{L_{Ag}}} = \frac{j_{tot}}{85.5\ \Omega^{0.559}\ .\ C_{Ag}} \qquad [viii]$$

With Equation [vii] one can thus predict the silver content in the deposit for different total current densities, different silver concentrations in the electrolyte and different hydrodynamical conditions.

For not negligible drops in current efficiency, Equation [vii] has to be rewritten as follows:

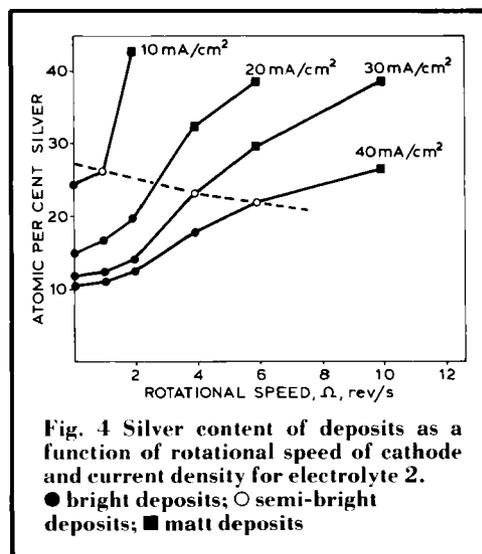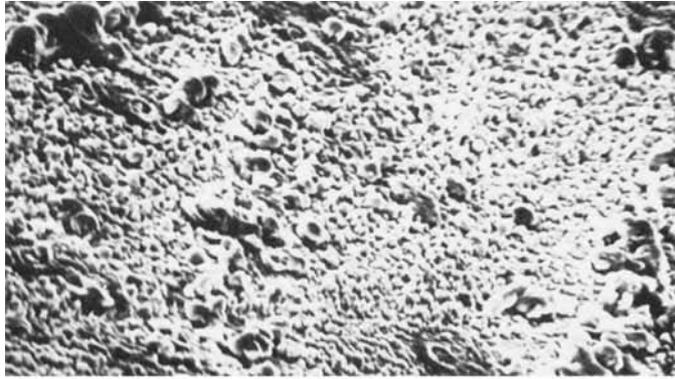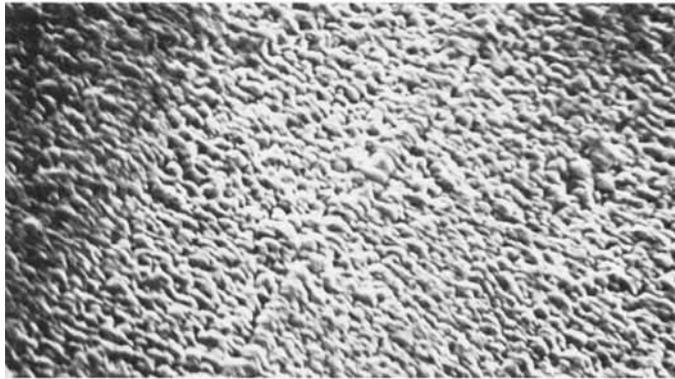$$x_{Ag} = 2/(1 + J \cdot CE) \qquad [vii^*]$$

Fig. 4 Silver content of deposits as a function of rotational speed of cathode and current density for electrolyte 2. ● bright deposits; ○ semi-bright deposits; ■ matt deposits

Fig. 5 Scanning electron micrographs of palladium-silver alloy deposits from electrolyte 3 (palladium 20 g/l; silver 3 g/l).

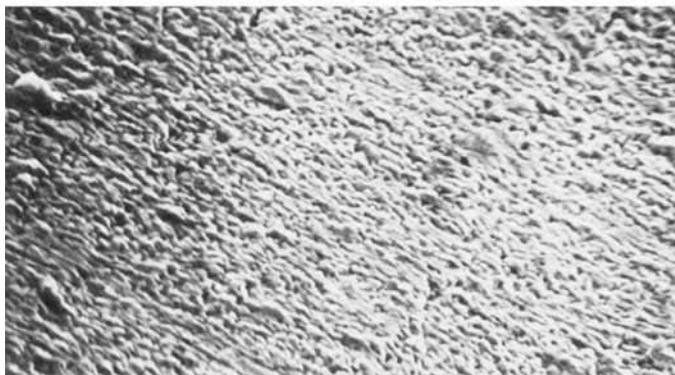(a)　$\Omega = 0$　rev/s;　j = 5 mA/cm²;　Ag = 52.5　at.% (matt)

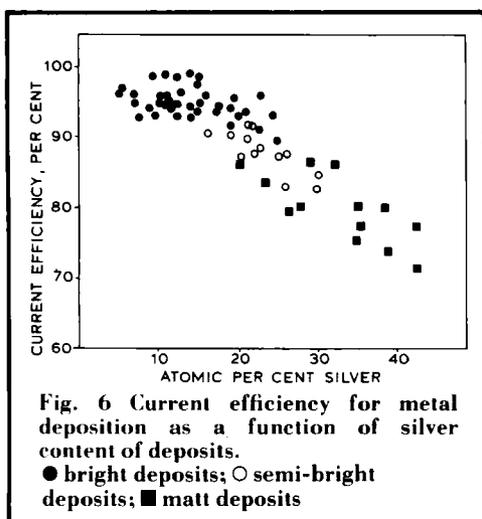(b)　$\Omega = 0$　rev/s;　j = 15 mA/cm²;　Ag = 29.3　at.% (semi-bright)

(c)　$\Omega = 0$　rev/s;　j = 30 mA/cm²;　Ag = 20.8　at.% (bright)

(d)　$\Omega = 3$　rev/s;　j = 30 mA/cm²;　Ag = 33.0　at.% (semi-bright)

Fig. 6 Current efficiency for metal deposition as a function of silver content of deposits.
● bright deposits; ○ semi-bright deposits; ■ matt deposits

Equation [vii] and the experimental results for $\Omega > 2/s$ are plotted in Figure 8. Agreement between calculated and measured values was very good. Only small deviations occur for experimental values corresponding to matt deposits.

Physical Property Measurements

For measurement of properties such as hardness and specific resistance it was necessary to produce alloy coatings of thickness at least 10 μm and of good surface finish, both on flat substrates (for hardness) and as isolated foils (for specific resistance). Since, at thicknesses in excess of about 2 μm, coatings tended to develop cracks due to internal stress associated with hydrogen occlusion, and also to deteriorate in surface finish, a multi-layer technique was adopted for this purpose, in which coatings were built up in successive increments of 2 μm, with intermediate polishing of the cathode with 1 μm alumina. Thus it was possible to produce bright, crack-free coatings up to 12 μm thick.

Deposition was made on both sides of brass plate cathodes (20 × 70 mm), which were masked to expose a total area of 16 cm² and suspended between platinised titanium anodes in an open vessel, with stirring by natural convection. To produce unsupported foils as required, the coating was removed from one side of the plate by grinding, and the supporting substrate was then dissolved by anodic

treatment at 280 mV in a solution of 200 g/l copper sulphate, 50 g/l sulphuric acid, to leave an isolated foil for measurements. A series of foils was produced in this way under the following conditions:

Electrolyte 1: $j_{tot} = 5, 10, 15, 20$ mA/cm²
Electrolyte 2: $j_{tot} = 10, 15, 20$ mA/cm²

Alloy Composition

Alloy composition as a function of current density under the above conditions is shown in Figure 9, together with analogous results pertaining to coatings produced on the copper electrodes used in the earlier work, with zero rotational speed. From the results it is clear that the change from the one type of cathode to the other has no significant influence on the composition-current density relationship.

Hardness

The Knoop hardness of coatings was determined as the mean of five measurements at various locations on the surface of 12 μm deposits at a load of 15 p, with indentation period of 30 seconds. It has been experimentally determined that the alloy thickness of 12 μm was sufficient to avoid any influence of the brass substrate on the Knoop-hardness values. Figure 10 shows the hardness of deposits from the two electrolytes as a function of composition. Since both curves are more or less parallel, it appears that the hardness is independent of deposition conditions and increases with increasing silver content.

Specific Resistance

Results of measurements of specific resistance by the four-point probe method (ASTM F390–78) are shown in Figure 11. As for hardness, this property increased with increasing silver content, being practically independent of electrolyte composition and bath conditions.

Contact Resistance

Contact resistance measurements were made on 2 μm coatings by the method according to the ASTM B667 specification, the test surface
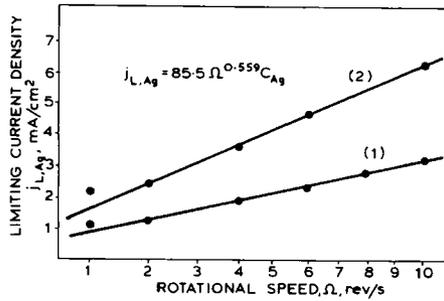
Fig. 7 Limiting current density for silver as a function of the rotational speed of the cathode.
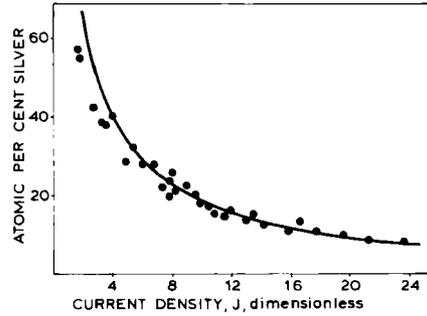(1) Electrolyte 1; (2) Electrolyte 2

Fig. 8 Silver content in the deposit as a function of the dimensionless current density J.
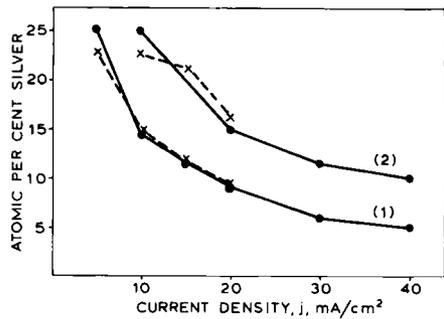——— according to equation [vii];
● experimental values

Fig. 9 Silver content of deposits as a function of current density for cylindrical (●) and vertical plate (×) electrodes by natural convection.
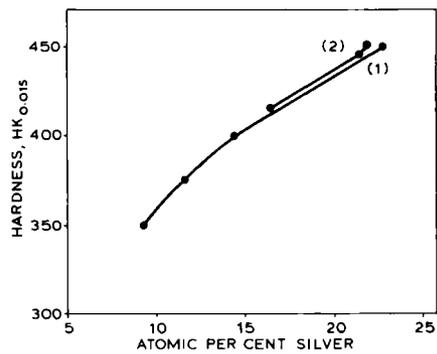(1) Electrolyte 1; (2) Electrolyte 2

Fig. 10 Knoop hardness of deposits as a function of silver content.
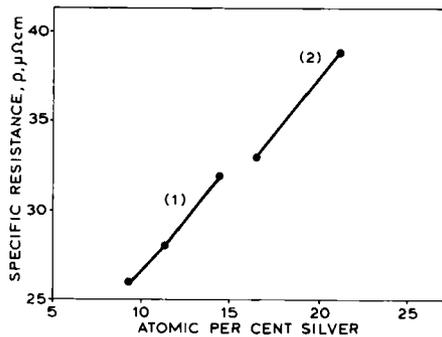(1) Electrolyte 1; (2) Electrolyte 2

Fig. 11 Electrical resistivity of electrodeposited palladium-silver foils as a function of the silver content.
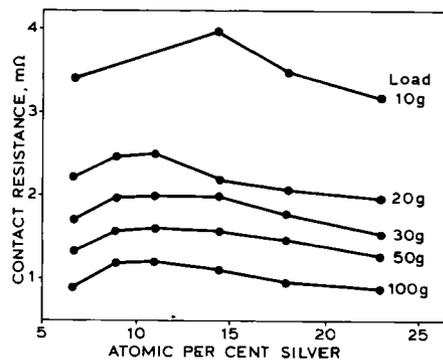(1) Electrolyte 1; (2) Electrolyte 2

Fig. 12 Contact resistance of palladium-silver alloy deposits as a function of silver content, for different loads

being flat, and the contact partner being a gold hemisphere of diameter 3.2 mm. The results, for loads between 10 and 100 g, are shown in Figure 12, indicating that, in contrast to hardness and resistivity, contact resistance is relatively little affected by alloy composition, but does depend strongly on the test load.

Concluding Remarks

The present investigation has resulted in a better understanding of the mechanism governing electrodeposition of palladium-silver alloys from an ammoniacal system, in particular in the clear demonstration that silver incorporation occurs under mass transport controlled conditions. On this basis it is possible to predict the silver content of deposits as a function of the experimental conditions. The palladium-silver system from ammoniacal baths provides, in fact, a very good example of the "regular" type of alloy deposition, according to the classification of Brenner (26).

Results of pulsed current plating studies, to be reported elsewhere, are also consistent with the mass transport model, but this technique permitted no increase in the silver content for bright coatings as compared to d.c. conditions.

From the applicational viewpoint, alloy deposits so far obtained show useful physical properties, despite the limitation of the silver content. From the process viewpoint, the very high ammonia content of the bath may constitute a potential disadvantage, certainly necessitating effective ventilation. However, it appears to have no adverse effect, as might have been expected, on the adhesion of deposits to copper and copper alloys, and, in total, provides a system of good stability, with very simple and easily monitored bath chemistry.

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