The Electrodeposition of Palladium from Chelated Complexes

PREFERRED CRYSTALLOGRAPHIC ORIENTATION GIVES IMPROVED PROPERTIES

By Ronald J. Morrissey

Technic Inc., Providence, Rhode Island

Recent advances in brightener chemistry have made it possible to electrodeposit microcrack-free, (111) oriented palladium of very high brightness and lustre. This preferred crystallographic orientation results in a major improvement in resistance to wear, still further increasing the attractiveness of palladium as a replacement for electrodeposited gold.

Palladium has long been used in electronic applications, most notably as wrought metal in relay contacts. As an electrodeposit, palladium is suitable for many of the same functional applications ordinarily filled by the hard acid golds. Considerations of price and availability have until recently favoured gold in these applications; and, except for a considerable effort in Britain during the late 1950s (1), the technological state of development of palladium electrodeposition has consistently lagged behind that of gold.

Rapid escalation of the gold price in the late 1970s caused an intensive re-evaluation of palladium versus gold, which is still continuing. At the same time, a number of improved electrolyte and brightener systems for depositing palladium began to appear. It seems to be virtually certain that the long-term price trend for gold must be upwards, and for this reason the development of economical alternatives, primarily palladium, has continued unabated.

This paper describes one of the most recent palladium electroplating systems, the use of chelated palladium complexes, and its development to date.

A New Commercial Electrolyte

While there is a very wide variety of electroplating systems for palladium, those ordinarily encountered employ an ammine complex in an ammoniacal electrolyte operating at pH values from 7.5 to about 9. Ammoniacal electrolytes in this pH range are corrosive to nickel and copper-based alloys, so that in order to protect the basis metal a strike coating of gold or silver is normally applied prior to palladium plating. It is obviously advantageous to eliminate this requirement if possible, and this has led to numerous attempts to reduce the corrosivity of ammoniacal systems, or alternatively, to develop completely non-ammoniacal electrolytes. One such non-ammoniacal system is based on the use of chelated palladium complexes, which, depending on the choice of chelating agent, operate at pH values in the range of about 3 to 7. A commercial bath operating on this principle was introduced in 1979, named Pallaspeed, and subsequently patented (2).

In its original configuration, the chelated palladium bath utilised essentially a single brightening agent in the form of a cyclic organic imide. Properties of deposits from this bath were given in a paper published in 1980 (3). Although bright and lustrous visually, the deposits were found to be microcracked, but

this condition could be minimised by operating the bath at elevated temperature, at the expense of a concurrent increase in grain size and loss of visual brightness. Photomicrographs of deposits plated from a citrate-phosphate electrolyte utilising this brightener system are shown in Figure 1, and X-ray diffraction data from these deposits are given in Table I. In most plating conditions deposits from the chelated bath utilising its original single-component brightener system were found to be strongly (110) oriented.

As will be shown subsequently, it is arguable that the occurrence of microcracking exerts little or no effect on the chemical inertness and corrosion resistance of palladium electrodeposits. The crystal orientation, however, is another matter. Palladium, like gold, is a face-centred cubic material, and in
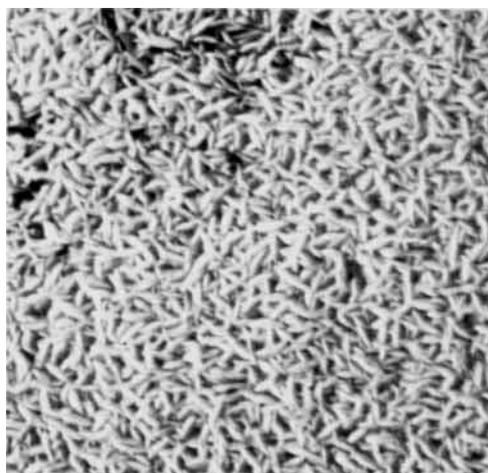

Fig. 1 This deposit from a chelated complex with original brightener system, at 10 mA/cm² and plating temperature 60°C, is crack-free, but large grains result from plating at this elevated temperature ×5000

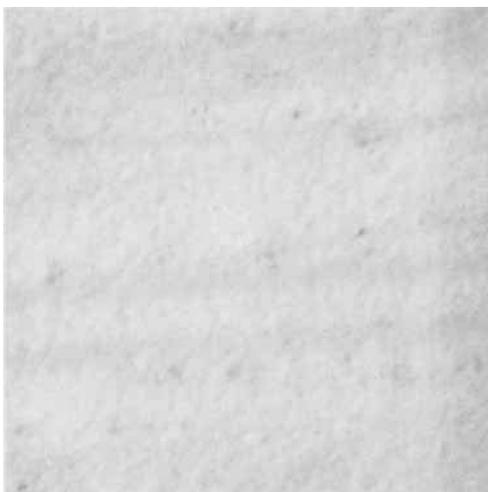| Table I			
X-Ray Diffraction Data for Palladium Electrodeposits, Citrate-Phosphate Electrolyte, Original Brightener System			
(Direct current, 60°C)			
Current density A/ft²	Reflection	Relative intensity, per cent	Orientation
2	(111)	100	(110)
	(200)	33	
	(220)	138	
	(311)	56	
4	(111)	100	(110)
	(200)	24	
	(220)	140	
	(311)	61	
6	(111)	100	(110)
	(200)	16	
	(220)	108	
	(311)	53	
10	(111)	100	(110)
	(200)	12	
	(220)	122	
	(311)	56	
15	(111)	100	(110)
	(200)	14	
	(220)	161	
	(311)	76	

Fig. 2 The deposit from chelated complex with revised brightener system, at 10 mA/cm² and plating temperature 60°C, is extremely fine-grained and essentially featureless ×5000

face-centred cubic crystals the slip plane, that is, the crystallographic plane in which adjacent atomic layers can slide over each other with minimum friction, is the (111). Virtually all palladium electrodeposits are (110) rather than (111) oriented, and on this basis one would expect that palladium electrodeposits should show rather large amounts of wear when tested against each other in sliding friction. Such effects were indeed noted by Sato and his colleagues (4), who recommended that a thin layer of gold be plated over palladium electrodeposits in order to improve the wear resistance.

In 1981 the brightener system of the chelated palladium bath was modified in a manner that completely altered the characteristics of the resulting electrodeposits. A major improvement in brightness was obtained, the deposit grain structure becoming essentially featureless when viewed at high magnification. Microcracking was eliminated. Photomicrographs of deposits from the citrate-phosphate electrolyte containing the revised brightener system are shown in Figure 2. With minor modifications to the electrolyte, the plating range can be extended. Figure 3 shows a deposit plated at 200 mA/cm² from a phosphate-borate system.
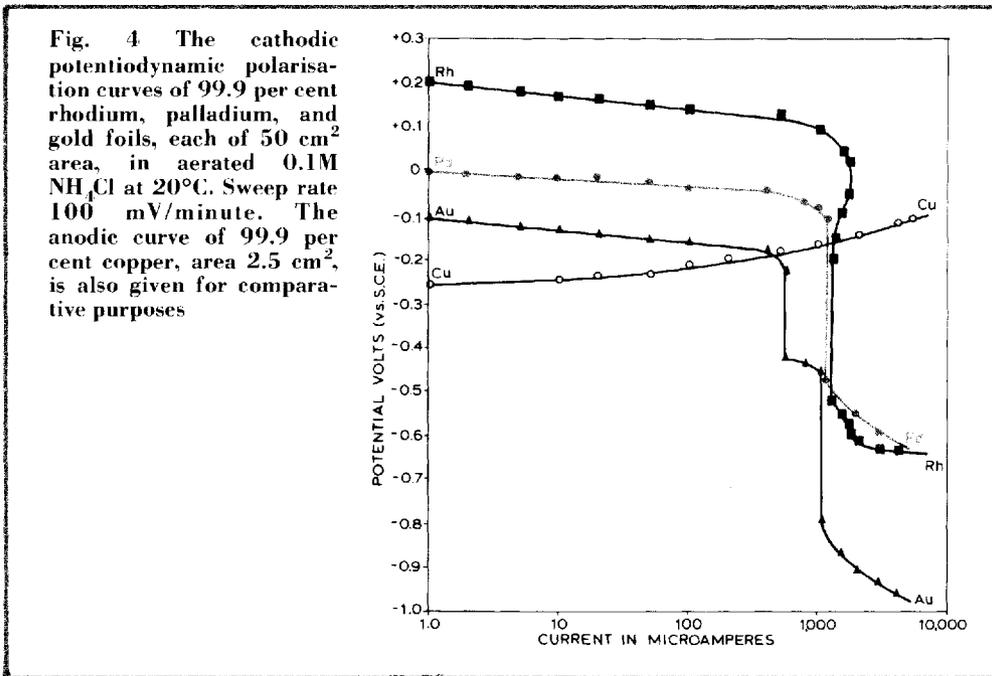
X-ray diffraction patterns from deposits pictured in Figure 2 are shown in Table II. Deposits from baths containing the revised brightener system are (111) oriented, which is the configuration favouring optimum wear performance. Entwistle (5) recently presented wear test data comparing (110) and (111) oriented palladium electrodeposits indicating, as expected, superior performance by the (111) deposits. His results also indicate that (111) palladium deposits overplated with a thin gold flash are markedly superior to the gold versus gold system in comparable conditions.

Porosity and Corrosion Resistance of Palladium Electrodeposits

Cathodic polarisation curves of gold, palladium, and rhodium specimens, each of area 50 cm², in 0.1 M NH_4Cl, together with a superimposed anodic curve of a 2.5 cm² copper specimen, are shown in Figure 4. It has been shown (3) that these curves, and their intercepts, correctly predict both the position

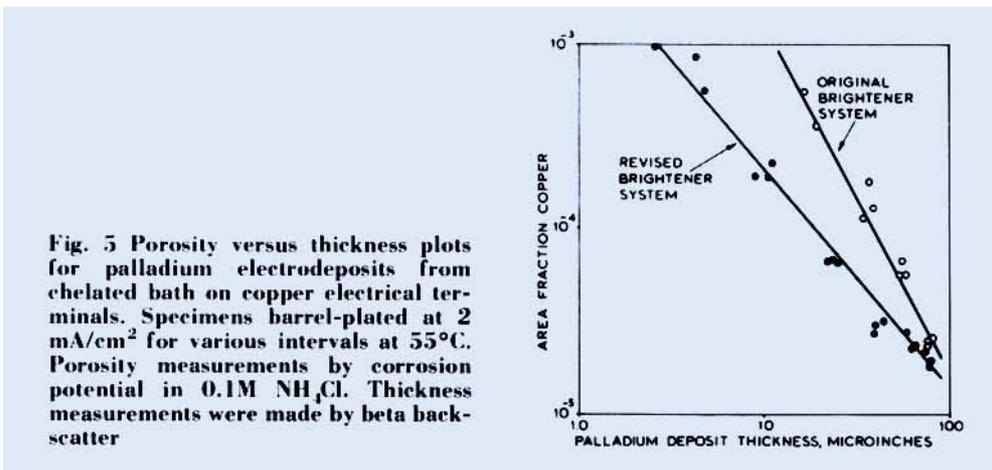Fig. 3 This plating was electrodeposited at 200 mA/cm² from chelated complex with revised brightener system at a plating temperature of 70°C. With sufficient agitation, crack-free deposits are obtainable at current densities exceeding 500 mA/cm². It should be noted that this photomicrograph is reproduced here at a magnification which is significantly larger than that used for the two previous figures ×7000

Fig. 4 The cathodic potentiodynamic polarisation curves of 99.9 per cent rhodium, palladium, and gold foils, each of 50 cm² area, in aerated 0.1M NH₄Cl at 20°C. Sweep rate 100 mV/minute. The anodic curve of 99.9 per cent copper, area 2.5 cm², is also given for comparative purposes

and the slope of porosity calibration curves (corrosion potential versus log area fraction copper) for gold-copper and palladium-copper couples in this electrolyte. The polarisation curves would indicate that in neutral electrolytes palladium is noble with respect to gold, and that the corrosion current (corrosion rate) of palladium-copper couples at a given ratio should be higher than that of corresponding gold-copper couples. There is a considerable body of evidence (6) to indicate that in point of fact the corrosion resistance of palladium electrodeposits, particularly over nickel, is somewhat better in most conditions than that of comparable gold deposits. This is widely thought to indicate the development of a thin passive oxide on palladium surfaces. The presence of microcracking does not appear to have

Fig. 5 Porosity versus thickness plots for palladium electrodeposits from chelated bath on copper electrical terminals. Specimens barrel-plated at 2 mA/cm² for various intervals at 55°C. Porosity measurements by corrosion potential in 0.1M NH₄Cl. Thickness measurements were made by beta backscatter

a great effect on the corrosion resistance of palladium electrodeposits.

Porosity versus thickness curves for palladium electrodeposits on copper are shown in Figure 5. These curves were determined by methods previously described (7) using the chelated palladium bath with the original and revised brightener systems. As expected, the curve for the revised brightener system is displaced downwards, indicating reduced porosity, and of shallower slope, which is characteristic of a higher degree of (111) preferred orientation.

Decorative Palladium Plating

The very substantial improvements in brightness and levelling of palladium deposits from the revised brightener system, together with the elimination of requirements for a prior gold strike, render the chelated palladium system an extremely attractive alternative to rhodium in decorative plating. The corrosion resistance of thin (0.1 to 0.25 μm) palladium electrodeposits on nickel is in general superior to that of corresponding rhodium deposits, and the difference in colour, while noticeable in a side-by-side comparison, is subtle. A 2250 litre chelated palladium bath installation at the Speidel Division of Textron, Incorporated, Lincoln, Rhode Island, is shown in Figure 6. This installation, operational since 1979, is believed to be the largest palladium plating facility in the world. Electrodeposited palladium is also used in optical frames both as a final finish and as an underplate for gold.

A Prognosis for Palladium

The economics of substitution of palladium for rhodium are highly favourable, the quality of palladium electrodeposits from the chelated

Fig. 6 Chelated palladium bath with a capacity of 2,250 litres, in automatic plating facility at Speidel Division of Textron, Inc., Lincoln, Rhode Island. This installation is believed to be the largest palladium plating facility in the world

Photograph by courtesy of the Speidel Division of Textron Inc.

Table II

X-Ray Diffraction Data for Palladium Electrodeposits, Citrate-Phosphate Electrolyte, Revised Brightener System

(Direct current, 60°C)

Current density A/ft²	Reflection	Relative intensity, per cent	Orientation
2	(111)	100	
	(200)	53	Random
	(220)	11	
	(311)	24	
4	(111)	100	
	(200)	13	
	(220)	2	(111)
	(311)	15	
6	(111)	100	
	(200)	9	
	(220)	0.5	(111)
	(311)	11	
10	(111)	100	
	(200)	11	
	(220)		(111)
	(311)	9	
15	(111)	100	
	(200)	16	
	(220)	1	(111)
	(311)	9	

bath with revised brightener system is excellent and it is considered highly probable that palladium will ultimately replace rhodium for most decorative applications. As a functional electrodeposit, the acceptance of palladium as a substitute for gold is at least partially linked to extrinsic factors such as monetary policy, the state of activity of the world automotive market, and the control of most primary palladium production by the Soviet Union. These factors and their long-term effects are of course extremely difficult to predict, but it is clear in any event that the past five years have seen really major advances in the technology of palladium electrodeposition and in the quality of the electrodeposits themselves. The availability of microcrack-free (111) oriented palladium electrodeposits must be considered a major breakthrough, combining the superior corrosion resistance of pure palladium with outstanding wear performance hitherto available only with gold or palladium alloy electrodeposits.

Acknowledgement

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