

Palladium-Nickel Electroplating

EFFECTS OF SOLUTION PARAMETERS ON ALLOY PROPERTIES

During a conference organised by the East Midland Branch of the Institute of Metal Finishing a paper on the electrodeposition of palladium-nickel alloys was presented by Dr. Christoph J. Raub and Dieter Walz of the Forschungsinstitut für Edelmetalle und Metallchemie, West Germany. A review of this paper is presented here.

In view of the current interest in electrodeposited palladium-nickel alloys as potential substitutes for gold plating in electronic and related applications, this experimental survey of electrolyte characteristics and deposit properties for a number of solutions of present and potential interest in this context is timely, covering, as it does, not only the more or less conventional ammino-chloride electrolyte, but reporting results for sulphate and sulphamate-based ammoniacal solutions, and for chloride baths in which ammonia is replaced by ethylene diamine.

For the ammino-chloride bath data are presented on the effect of deposition variables, for example pH, temperature and current density, on the physical properties (hardness, ductility) and composition of the deposits, including the hydrogen content, which, it is noted, has no influence on stress or crack formation in the case of the alloy deposit, in contrast to that observed for pure palladium coatings.

A point of particular interest arises from experimental studies with a rotating cylinder electrode, when it was found that within a range of relative electrode surface/electrolyte velocities corresponding to rotational speeds of 0 to 2000 r.p.m., the deposit composition remained practically constant at 35°C, pH 8.5, 3A/dm², this applying also in the current density range from 3 to 20 A/dm² at a constant rotational speed of 2200 r.p.m., results which imply that this type of solution should be readily adaptable to high speed deposition. In this context results are reported of actual tests made on a commercial electrolyte using a "Jet-Lab" high-speed plating cell, with electrolyte

velocities up to 2.4 m/second.

Additional points of interest relating to the ammino-chloride bath include a study of the effects of impurities, for example, copper, zinc, silver, iron, and cyanide, which have been somewhat neglected hitherto, and of build-up of ammonium chloride as a result of replenishment. The latter has little effect, and it is suggested that an electrolyte could be operated for about twenty "turn-overs" before any salting-up effect might be expected.

Other Electrolytes

A similar range of studies is reported for an ammoniacal sulphate electrolyte, which has the advantage that there is no precipitation of palladium salts at lower pH values, as in the case of the ammino-chloride bath. In this case there is very little influence of temperature on deposit composition or properties, but in high speed plating tests a very critical influence of current density was observed on the nickel content of coatings, for example, from 12 to 25 per cent nickel in the range from 5 to 20 A/dm². Over the same range, however, the hydrogen content of deposits was less than 1 ml/g, and could be still further reduced by a temperature increase.

In the case of an ammoniacal sulphamate electrolyte (0.1M palladium sulphamate; 0.1M nickel sulphamate; 50 g/l sulphamic acid), tests were possible over a pH range from 6 to 10. Main results were a marked effect of pH on nickel content (20 per cent at pH 6; 5 per cent at pH 10), and the generally very low hydrogen content which, at a pH of 8.5 remained at a level of only 0.2 to 0.3 ml/g over a current

density range from 1 to 5 A/dm². A similar critical effect of pH on electrolyte characteristics was found in tests of a commercial electrolyte of this type.

Finally, the authors also report preliminary results for an ammonia-free electrolyte based on ethylene diamine, the bath composition being 17.7 g/l palladium chloride, 5.9 g/l nickel chloride, and 80 g/l of the amine. In this case studies cover a wider pH range, a marked feature of the results being sharp peaks for both nickel and hydrogen contents at approximately the same pH value of about 5. Some results are also recorded for internal stress. The authors conclude that this type of solution has certain

advantages over the ammoniacal baths in terms of a stable pH value, absence of organic additives, and a milder chemical nature towards base metals and alloys such as copper and brass, against which must be set comparatively high values of compressive stress. This can, however, be minimised by selection of correct deposition parameters and/or by the use of stress reducers. It is to be hoped that further details concerning this type of solution, together with the results of studies, briefly mentioned, on the influence of various anions, such as chloride, sulphate, sulphamate and bromide, will be covered in a forthcoming publication which is in course of preparation.

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Platinum in Aluminide Diffusion Coatings

The oxidation and hot corrosion resistance of high temperature nickel-base superalloy components can be improved by aluminide coating. Further improvements can be achieved by the use of platinum in these coatings (1), although the mechanisms by which platinum achieves this is still uncertain (2). Now a paper by W. T. Wu of the Institute of Metal Research, in the People's Republic of China and A. Rahmel and M. Schorr of the Dechema Institute, West Germany attempts to clarify the role of platinum in hot corrosion environments dominated by either acidic or basic oxide fluxing action (3).

Potentiostatic tests and free corrosion potential measurements were carried out with specimens immersed in melts of 90Na₂SO₄ + 10K₂SO₄ at 900°C in air. Under potentiostatic conditions reflecting acidic fluxing of protective oxide scales, it was observed that both coating systems and the uncoated alloy showed similar degrees of hot corrosion attack.

However, under conditions of severe basic fluxing of oxide scales, where high chromium and conventional aluminide coated alloys show extensive surface degradation, platinum aluminide coatings offer a distinctive performance advantage.

The free corrosion potentials of platinum aluminide coatings reached a steady state value of approximately $E_{Ag} - 300mV$, as measured over a period of 540 hours. In comparison, the simple aluminide coatings and the base alloy achieved a free corrosion potential approximately 200mV less noble than that of

any platinum aluminide system here evaluated.

Under acidic fluxing conditions degradation of the platinum aluminide coatings began by the formation of (Al,Cr)₃S₄ sulphides adjacent to a platinum enriched alloy layer beneath an alumina protective scale.

Surface analysis of both coating types also revealed that the protective scales formed on platinum aluminides contained a high proportion of alumina. The presence of platinum in the outer scale also seemed to have a stabilising influence on alumina during acidic fluxing.

Similar effects of protective oxide modification and relative changes in coating element diffusion characteristics have also been observed at the Johnson Matthey Group Research Centre in nickel-base alloys containing platinum as an alloying element (4).

Clearly, the industrial need for new alloys and coating compositions with improved resistance to sulphur accelerated oxidation should spur further investigation into the mechanistic effects of platinum on oxide growth and stability. Wu and his two co-authors have provided some useful guidance in this direction.

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References

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