By Z. Ratajewicz & C. Saneluta

The presence of nickel in an ammoniacal electrolyte influences the position of a palladium polarization curve. Determination of the character of polarization of individual metals makes possible qualitative anticipation of the influence of such parameters as temperature, mixing, or electrolyte component concentrations, on the properties of deposits.

Palladium-nickel alloys with Pd content exceeding 75 percent are characterized by greater hardness and corrosion resistance than pure palladium. This accounts for their wide application to decorative finishes¹⁻³ and low-current contacts.⁴ For a considerable period, the Department of Electrochemistry of Lublin Technical University has conducted research in galvanic codeposition of palladium and nickel, palladium and silver, as well as into the properties of coatings of palladium alloys. This study includes the results of investigation into electrodeposition of Pd-Ni alloy in an ammonia bath. Voltammetric curves and the dependence of activation energy on the cathode potential in deposition of pure metals and their alloys were determined.

Experimental Procedure

Electroreduction reactions of Pd⁺², Ni⁺², and H⁺ions proceeded in parallel in a test system containing 16.5 g/dm³ of palladium, 12.0 g/dm³ of nickel, 50 g/dm³ of (NH₄)₂SO₄ and NH₃ in the quantity needed for pH 9.5. To distinguish partial polarization curves (describing separately the course of individual reduction processes) from complete curves, measurements were made by a galvanostatic method. A platinum electrode having one cm² surface with one side protected by a glass layer was used. The electrode potential was referenced to a saturated calomel electrode (SCE). The mass of deposited palladium and nickel was determined by polarographic method. Two temperatures were used: 25 and 55 °C. The conditions of deposition of pure Pd and Ni were identical to those of the alloys, but the solutions contained only one metal each.



Fig. 1—*Galvanostatic partial curves for palladium deposition: (1) Pd, 55* °C; (2) Pd alloy, 55 °C; (3) Pd, 25 °C; (4) Pd alloy, 25 °C.

Results & Discussion

Figures 1 and 2 show partial polarization curves of deposited palladium and nickel. They indicate that the presence of both Pd and Ni in the tested system cause a shift of the Pd polarization curve toward more negative potentials, while the curve for nickel is shifted more positive. In this specific case, the potential values get closer to each other, which indicates the possibility of obtaining alloy coatings of both high and low nickel content from the test solution. It is worth mentioning that dependences occurring in the bath are different from those in a P_2O_2 -Pd-Ni bath.⁵

The curves of Figs. 1 and 2 also indicate that in deposition of both single metals and alloys, increase of temperature always causes decrease of polarization in the Pd⁺² and Ni⁺² electroreduction reactions. To determine the character of polarization accompanying the reactions, activation energy for individual partial processes was calculated. As can be seen in Fig. 3, activation energy related to the Ni⁺² electroreduction reactions is much greater than for Pd⁺². The calculated values (ca. 40-100 kJ/mole) indicate that it is activation polarization that is dominant. The dependence of activation energy on the potential (which exhibits a considerable decrease with a drop in potential) suggests the conclusion that in the process, concentration polarization also occurs and, to a greater degree, the more negative the cathode potential is. Analysis of this dependence leads to the conclusion that the processes are accompanied mainly by concentration polarization, especially at potential values ranging from -700 to -850 mV, when lowest values are reached and dependence on potential is slight.

Because these dependences pertain to a static system, it can be assumed that when mixing is introduced into the alloy deposition, Pd⁺² electroreduction will become the dominant process and the deposits will contain the greater percentage of palladium. These experiments also made it possible to determine quantitatively the dependence of the palladium and nickel percentages in the deposits (Figs. 4 and 5), as well as the



Fig. 2—Galvanostatic curves for nickel deposition: (1) Ni, 55 °C; (2) Ni alloy, 55 °C; (3) Ni, 25 °C; (4) Ni alloy, 25 °C.



Fig. 3—Activation energy vs. electrode potential: (1) Ni; (2) Pd; (3) Ni alloy; (4) Pd alloy.

process current efficiency dependence on current density. The results obtained indicate that a current density increase brings about a simultaneous drop in palladium percentage and an increase in nickel. This occurs at both test temperatures, 25 and 55 °C, but at 55 °C, the change in coating composition proceeds more smoothly. The effect of temperature becomes conspicuous only at current densities greater than 1 A/dm². Under the given conditions, an increase in temperature results in increase in palladium content, with a corresponding decrease in nickel content. This is in contrast with the trend of temperature-dependent changes as reported by Wild and Blair.⁴ The functions depicted in Fig. 6 indicate that under static conditions, deposition of Pd-Ni coatings in an ammonia bath proceeded with an efficiency exceeding 80 percent.

Findings

The experiments performed have shown that the presence of nickel in an ammonia electrolyte influences the position of a palladium polarization curve toward more negative potential values. The presence of palladium influences nickel in just the opposite way.

Tests of the activation energy dependence on electrode potential has shown that in an electrolyte containing both metals, the polarization curves are drawn considerably closer to each other, compared to electrolytes containing only one of the metals. This occurs mainly because of the almost parallel shift of the nickel curve by more than 200 mV. Explanation



Fig. 5—Nickel content of deposit vs. current density: (1) 25 °C; (2) 55 °C.



Fig. 4—Palladium content of deposit vs. current density: (1) 25 °C; (2) 55 °C.

of the observed dependences requires further research into the electrocrystallization mechanisms of both metals and the changes in the double layer structure. It should be noted that activation energy changes related to codeposition of both metals in a pyrophosphate bath,⁵ where they occur in anion form, are of slightly different character from that of the ammonia bath. The values of activation energy in ammonia baths, with or without the presence of palladium, are much higher than in pyrophosphate baths.

Determination of the character of polarization of individual metals makes possible qualitative anticipation of the influence of such parameters as temperature, mixing, or electrolyte component concentrations on the properties of deposits.

Editor's note: Manuscript received, December 1995; approved, August 1997.

References

- 1. M. Konoe, Japan patent 86 52,389 (1984).
- 2. K. Shimada & S. Yahagi, Japan patent 86 79,785 (1984).
- 3. R. Le Penven, W. Levason & D. Pletcher, J. Appl. Electrochem., 20 (3), 399 (1990).
- 4. M.J. Wild & A. Blair, *Plat. and Surf. Fin.*, **70**, 32 (Nov. 1983).
- 5. Z. Ratajewicz, Cz. Saneluta & J. Sawa, *ibid.*, **81**, 89 (June 1994).



Fig. 6—Current efficiency vs. current density: (1) 25 °C; (2) 55 °C.





Ratajewicz

Saneluta

Dr. Zbigniew Ratajewicz is an associate professor at the Lublin Technical University, ul. Nadbystrzycka 38a, 20-618 Lublin, Poland, where he holds the chair of electrochemistry. He is a graduate of the Maria Sklodowska-Curie University in Lublin with MSc and PhD in chemistry.

Dr. Czeslaw Saneluta is a senior lecturer in electrochemistry at the Lublin Technical University. He holds an MSc from the Maria Sklodowska-Curie University, Lublin, and a PhD from the Silesian Technical University, Gliwice. He has been engaged in electrochemical plating of circuit boards and alloy plating of electrical contacts. Affordable Training Course Opportunity:

Pollution Prevention (P2) Concepts & Practices For Metal Plating & Finishing

Last chance to take it in 1997: November 17-19 • Albuquerque, NM

This new training course, just introduced in June, was developed through a partnership between the office of the U.S. Environmental Protection Agency and the AESF. Partially funded by the U.S. EPA, with "in kind" contributions from industry, the course is affordably priced so that as many people as possible in the industry will take advantage of it. The registration fee (hotel accommodations are not included) is \$200 to AESF members and \$250 to non-members. Each attendee will receive a notebook that contains copies of the course materials.

Is your shop looking for:

- Alternatives to solvent cleaning/degreasing?
- Better cyanide plating alternatives or controls?
- Improved methods for water reduction, closed-loop processing, source reduction and recycling?
- Better cadmium plating alternatives or controls?
- Alternatives to chromium finishing, including all uses, such as anodizing, plating and conversion coating?

If you're a shop owner/manager and your answer is "yes" to any of these questions, then the P2 course is for you. Call AESF Educational Services Department to register (407/281-6441).

*Hotel accommodations not included. Please call the hotel directly to make your reservations: Ramada Inn East, Albuquerque, NM (505/271-1000; \$65 single).

The support of the following is acknowledged in the successful completion of the P2 Training Program: The AESF CAMP, Inc., Concurrent Technologies, Inc., Environment Canada, The MFSA, The NAMF