ELECTROLYTIC PREPARATION OF FINE Pd–Ag
POWDERS OF ANY GIVEN CHEMICAL COMPOSITION

B. P. Yur'ev and S. P. Shkuryakova

In recent years, fine powders of alloys of the system palladium–silver have found their application in a number of branches of engineering. The work described below was undertaken with the aim of investigating an electrolytic process for the preparation of fine palladium–silver powders of any given composition. Our earlier articles [1, 2] dealt with the basic principles of the electrolytic preparation of multi-component powders of various compositions and combinations by the method of coreduction on the cathode of several metals under conditions of diffusional kinetics. In such a process, electrolysis generally involves the use of composite anodes, i.e., partly soluble and partly insoluble electrodes with separate current supplies.

In contrast to this, in the present work electrolysis was performed using a single, insoluble anode. A diagram of the apparatus employed for studying the electrolysis process in the manufacture of powders of the system palladium–silver is shown in Fig. 1. The principal part of the apparatus was the cylindrical electrolytic cell 1 with a conical bottom and the cylindrical insoluble platinum anode 3 rolled from gauze. The nickel wire cathode 2 was mounted in the middle part of the electrolytic cell, coaxially with the cylindrical anode. The electrolyte employed was an ammonia solution containing palladium and silver nitrates.

Solutions of this composition are used for the electrodeposition of dense silver–palladium alloy coatings [3, 4]. The electrolytic cell was supplied with current from a storage battery. During electrolysis in such a cell, a silver–palladium powder is formed on the cathode and hydrogen is evolved if the cathodic process of metallic ion reduction takes place under conditions of diffusional kinetics, i.e., at the limiting current for each of the metals [5]. To prevent the solution from becoming depleted of metallic ions, electrolysis was performed with continuous solution circulation. Spent electrolyte was removed from the electrolytic cell at a constant rate, and fresh solution was supplied at the same rate. To determine the quantity of electricity passing through the cell in the course of experiments a copper coulometer was incorporated into the electrical circuit of the apparatus.

Initially, a study was made, within a wide range of current densities, of the effects of metal concentrations, temperature, pH, and other parameters upon cathodic polarization curves for the separate and simultaneous reduction of silver and palladium in complex ammonia solutions. The polarization curves obtained invariably exhibited distinct limiting current steps corresponding to a transition to a metallic ion reduction process controlled by diffusional kinetics and to the formation of powdery deposits on the cathode. In the next phase of investigation, a study was made of the effect of various electrolysis parameters upon current efficiency and the chemical composition and particle size of the...
Fig. 2. Variation of current efficiency of deposition and chemical composition of silver-palladium powder with cathodic current density (1) and overall Pd+Ag concentration (2) in AgNO₃+Pd(NO₃)₂+NH₄OH solution at Pd/Ag = 1: 1) over-all Pd+Ag concentration 10 g/liter; 2) cathodic current density 10,000 A/m².

Fig. 3. Variation of current efficiency of deposition and chemical composition of palladium-silver powder with Pd/Ag ratio of solution. Electrolysis at Ag+Pd = 10 g/liter, Dc = 10,000 A/m², pH 9, and t = 20°C.

resultant palladium-silver powder. For this purpose, the powders obtained were subjected to chemical analysis and examined metallographically and by x-ray diffraction.

Figure 2 shows curves of current efficiency and the Pd/Ag concentration ratio of the powder plotted against cathodic current density and the total concentration of the metals in the solution. As the current density is increased from 500 to 5000 A/m² (at a constant total Pd+Ag concentration of 10 g/liter), the powder current efficiency falls, at first sharply and then only very slightly. The fall in powder current efficiency with rise in current density is due to a marked acceleration of hydrogen evolution on the cathode, because the rate of palladium and silver reduction under conditions of dual and diffusional kinetics cannot appreciably grow with increase in cathodic current density. At current densities ranging from 10,000 to 20,000 A/m², the ratios of the components in the powder and in the solution are equal. At current densities below 7000 A/m², the deposits forming on the cathode consist mainly of silver. The reason for this is that, with decreasing current density, the cathodic process of palladium and silver coreduction begins gradually to shift from the region of diffusional kinetics into that of dual kinetics. As a result, the rate of silver reduction begins to outstrip that of palladium reduction, and the powder becomes enriched in silver. The particle size of the powder steadily diminishes with increase in current density. The effects of overall metal concentration in the solution upon the current efficiency of deposition and the chemical composition and particle size of the powder were studied at constant current density.

The Pd/Ag ratio of the powder matches that of the solution when the over-all concentration of these components in the latter does not exceed 10 g/liter. At higher Pd+Ag contents of the solution, the powder becomes enriched in silver. This is due to the fact that, with rise in the total concentration of the metals in the solution, the process once again passes from the region of pure-diffusional kinetics into that of dual kinetics. The powder current efficiency rises with increase in overall concentration, because the rates of palladium and silver reduction on the cathode grow proportionally to the concentration of the metallic ions in the solution. The degree of powder dispersion falls with increase in the total concentration of the metals in the solution.

Figure 3 illustrates the effects of the ratio of palladium and silver concentrations in the solution upon the powder current efficiency and composition. The results obtained demonstrate that, as long as the cathodic process of metal reduction takes place under conditions of diffusional kinetics, the ratios of component