ELECTROLYTICALLY MIXED DEPOSITS OF PLATINUM AND PALLADIUM WITH RUTHENIUM

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The authors of [1-4] established that Pt–Ru and Pd–Ru alloys have higher activities in catalytic and electrochemical processes than the alloys' individual components. This is also true for electrolytically manufactured mixed oxides of these metals [5].

The present paper deals with the quantitative composition and some properties of electrolytically mixed deposits (e.m.d.) of platinum or palladium with ruthenium. Since the quantitative chemical analysis of Pt–Ru and Pd–Ru alloys is very difficult [6], we used the following method.

E.m.d. of Pt–Ru and Pd–Ru were deposited from solutions of variable composition:

$$1\,\%\,[x\mathrm{H_2PtCl_6} + y\mathrm{K_2RuNOCl_5}] \text{ or } 1\,\%\,[x\mathrm{PdCl_2} + y\mathrm{K_2RuNOCl_5}]\ *$$

on to a platinum substrate with apparent surface 2 cm^2.

The current density was 2 ma/cm^2 and 6 ma/cm^2 for Pt–Ru and Pd–Ru deposits respectively. The electrolysis times were 3 h and 40 min respectively. It was established in preliminary experiments that during electrodeposition the weight of the deposit is directly proportional to the electrolysis time and that the deposit's composition remains unchanged during this process. The anodes were two platinum plates 1 cm from either side of the cathode.

The total amount of deposited metals was determined gravimetrically, and the ruthenium content in the deposit by the radioactive tracer method. Labeled $K_2RuNOCl_5$ was synthesized by the method in [6] from commercial ruthenium chloride, to which was added radioactive ruthenium chloride containing Ru-106.

After electrodeposition the deposits were washed in bidistillate, the film of water was removed by drying, the specimens weighed and their radioactivities measured in an end-window counter. The amount of deposited ruthenium was calculated by comparing the radioactivity of the specimen with that of a deposit obtained by depositing pure ruthenium from a labeled solution of 7% $K_2RuNOCl_5$.

No correction was made for self-absorption of radiation in the layer of deposit because it was only a few per cent, owing to the low density of the deposits (< 5 mg/cm^2) and the high β-radiation energy (~3 MeV) of rhodium-106, which is the daughter product of ruthenium-106 decay. The results of two parallel experiments differed by less than 7%. Fig. 1 and 2 plot the quantitative compositions of the deposits versus solution composition; it will be seen that to a first approximation the ratio of the wt. per cent content of ruthenium in the solution (% Ru_s) and on the electrode (% Ru_e) is 1 : 1 for Pt–Ru deposits and 3 : 2 for Pd–Ru deposits. By changing the solution composition, we can therefore obtain mixed Pt–Ru and Pd–Ru deposits of any desired composition.

It should be noted that the weight of the deposits changes markedly with electrolyte composition. For example, when pure ruthenium is deposited from 1% $K_2RuNOCl_5$ the weight of the deposit is approximately 0.4-0.5 mg/cm^2 and increases steadily with H_2PtCl_6 concentration, reaching ~6 mg/cm^2 in pure chloroplatinic acid. This means that at high ruthenium contents in the solution the bulk of the current is consumed on secondary processes,

*To the solution was added enough HCl to make a 1 N solution.

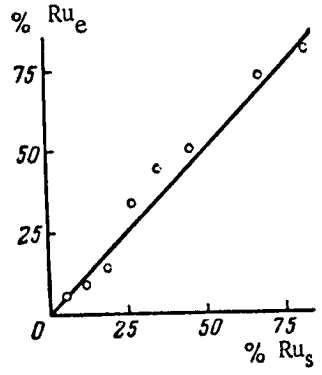

Fig. 1. Composition of e.m.d. of Pt–Ru, plotted versus solution composition.

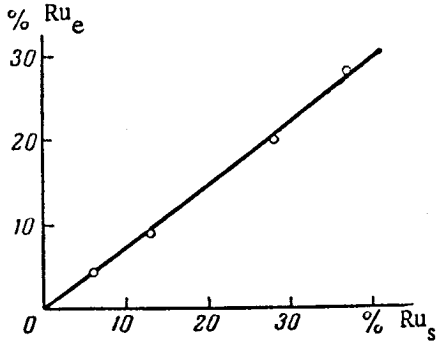

Fig. 2. Composition of e.m.d. of Pd–Ru, plotted versus electrolyte composition.

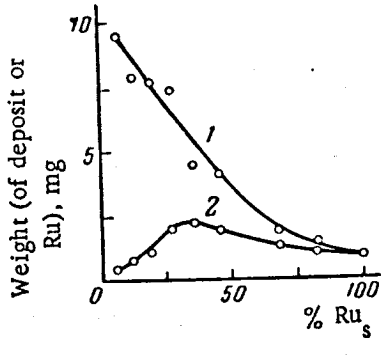

Fig. 3. Weight of Pt–Ru deposits (1) and total content of ruthenium in them (2), plotted versus solution composition.

i.e., the evolution of hydrogen and reduction of the NO group. Therefore, despite the fact that the percentage Ru content in the deposit is proportional to its content in the solution, the total Ru content in the deposit passes through a maximum (Fig. 3).

Deposition of ruthenium is therefore promoted when it is present together with platinum in solution.* This may be due to a decrease in the free energy of electrodeposition of ruthenium, with formation of alloy, or to a change in the velocities of secondary processes. Since this sytem is very complex, a final solution of this problem will require a further experimental study.

Electrolytically mixed deposits of Pt–Ru and Pd–Ru have various appearances and properties. The ligh-gray Pt–Ru deposits are firmly attached to the platinum substrate, while the dark-gray Pd–Ru deposits are less compact and less firmly attached to the substrate.

To determine the chemical and electrochemical resistances of e.m.d. of Pt–Ru, they were subjected to various treatments. It was found that electrodeposited ruthenium dissolves completely in 30 min during anode polarization in 1N KOH at current density 10 ma/cm^2.† During this process the solution becomes yellow. Ruthenium dissolves less readily in 1N H_2SO_4 in these conditions, and the solution becomes blue-green. The difference in color of the solutions is due to the different valence states of ruthenium [6].

E.m.d. of Pt–Ru (5-80% Ru) have unusually high chemical resistances. They are virtually undissolved during anode polarization in acids and in alkalis, and even when subjected to prolonged boiling in aqua regia. In the latter case, the platinum substrate is dissolved, while the amount of the electrodeposit remains practically unchanged. As regards their chemical resistances, e.m.d. of Pt–Ru therefore have the properties of alloys of these metals [6].

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*Similar phenomena are observed in the electrolytic manufacture of alloys of various metals (see, for example, [7]).
†The authors of [8] noted that anode dissolution of ruthenium occurs readily in alkali, and employed this for ruthenization of electrodes.