

ELECTRODEPOSITION OF PLATINUM METALS AND ALLOYS FROM CHLORIDE MELTS

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Abstract

The structure of platinum metals and their alloys deposited by the electrolysis of chloride melts have been investigated. The cathodic deposits were both in the form of compact layers and dendrites. All the alloys of platinum metals obtained are solid solutions in the whole range of composition. Depending on the experimental conditions the layers had columnar, stratum and spiral (dissipative) structures. The stratum and dissipative structures were observed in the case of alloys only.

Keywords: electrodeposition, melt, platinum metals, dendrites, alloys, chlorides

1. Introduction

Platinum metals are electrodeposited from aqueous solutions with insignificant cathodic current efficiency in the form of very thin, stressed and cracked coatings containing hydrogen. Plastic and hydrogen-free coatings of platinum metals were produced by the electrolysis of a toxic and unstable fused electrolyte - *NaCN-KCN* - at 500-600 °C [1-3]. Atkinson [4] carried out the investigation of the electrodeposition of Pt-metals from fused chloride electrolyte *LiCl-NaCl-KCl* at 400-500 °C under the air in an open bath. However, this electrolytic bath was found to be unstable because of the decomposition of platinum metal chlorides in the melt. In previous works [5-7], the use

of low-melting unhygroscopic ternary eutectic $NaCl-KCl-CsCl$ placed in a closed electrolyzer with an inert atmosphere allowed to obtain stable electrolyte which contains platinum metals chlorides. The study of the equilibrium potentials of platinum metals in melt $NaCl-KCl-CsCl$ [8,9] showed that iridium has the most positive potential in the line $Ir-Pt-Ru-Rh-Pd$, while palladium potential is most negative. The average valences of platinum metals ions were determined from the prelogarithmic coefficients of the equations of equilibrium potential isotherms and from the values of anodic efficiencies. The valence of platinum and palladium is 2.0 ± 0.08 , for iridium, ruthenium, rhodium it is 3.0 ± 0.07 . The partial pressures of chlorine in equilibrium with the melt were calculated too (its value is in the range 10^{-4} –100 Pa). These relatively low partial pressures of chlorine demonstrate sufficient stability of the chloride electrolytes containing platinum metals up to $700^{\circ}C$.

This paper deals with the investigation of the morphology and structure of Ir , Pt , Ru , Rh and Pd deposits, and of binary alloys $Ir-Pt$, $Ir-Ru$, $Pt-Rh$ produced under different conditions of electrolysis from chloride melts.

2. Experimental

The experiments were carried out in a hermetic quartz cell under pure helium or argon atmosphere. The ternary eutectic of $NaCl-KCl-CsCl$ (30-24.5-45.5 mol. %, melting point – $480^{\circ}C$) was used as the solvent. Chlorides of platinum metals were produced directly in the melt by the chlorination of the corresponding metal or its anodic dissolution. Binary alloys were produced by electrodeposition from two metal chlorides containing melt. Dense graphite, glassy carbon, or platinum metals were applied as the cathode materials. The counter electrodes (anodes) were usually made of the platinum metals. The morphology and structure of the metal deposits were investigated using optical and scanning electron microscopy, and X-ray diffraction method. The distribution of components in the alloys was determined by Electron Probe method. The cross- and longitudinal metallographic sections of the deposits of the Pt-metals and their alloys were electrochemically etched by alternating current in the solutions of HCl or $NaOH$.

3. Results and discussion

The dependencies of the structure of cathodic deposits of platinum metals upon temperature, current density, cathode material, concentration of the electroactive species, composition of the cell atmosphere (inert gas or chlorine), concentration of oxygen-containing impurities in the melt were studied.

The initial process on the cathode of the same metal is the discharge of the metal ions with the formation of a metallic phase both under the inert and chlorine atmosphere. When using cathodes made of graphite and glassy carbon, the recharge of higher valence

ions to lower valence ions and the ionization of chlorine precedes the process of the metal deposition. In this case, at low current densities the recharge process of Pt-metals ions makes the main contribution to the total process.

At 500-600 °C a drastic shift of the potential towards more positive values takes place when polarizing Pt-metals anodically at high current densities. At the same time, the anodic current efficiency decreases. These phenomena are caused by the fact that the platinum metal anode is covered with a film of poorly soluble (insoluble) complex chlorides of platinum metals (so-called "salt passivation"). This effect becomes more pronounced in the row $Pd < Pt < Rh < Ru < Ir$. For example, the thickness of the solid insoluble salt layer on the iridium anode is 1-10 mm and it consists of Cs_2IrCl_6 . In this case, the evolution of chlorine on the *Ir* anode is observed. It is necessary to keep moderate (rather low) anodic current densities to provide stable continuous work of the electrolytic bath.

The conditions of the growth of Pt-metal deposits of different structures were determined. The deposits can be classified as compact coherent layers (coatings), dendrites and powders. It was found that the temperature and concentration of oxygen-containing impurities in the melt influence significantly the structure of cathodic platinum metal deposits. At 500-650°C iridium and ruthenium deposits were obtained in the form of compact coherent layers, whereas at higher temperatures – in the form of dendrites. Platinum, rhodium, palladium were deposited as dendrites in the whole range of temperatures. The compact coherent layers of platinum on *Mo*, *W* and glassy carbon substrates were obtained only from the low-melting electrolyte $AlCl_3-NaCl$ at 200-360 °C [10]. It can be explained by the general physical rule that compact coherent layers (coatings) are formed at the temperatures that do not exceed the metal re-crystallization temperature, which is proportional to the melting temperature of the given metal [11]. For platinum metals the optimum ratio of the deposition temperature to the melting temperature is equal to 0.22-0.35 (Kelvin temperature). These values are less than average values for the compact layers of non-noble metals (0.35-0.4).

The structure of all compact coherent deposits of iridium and ruthenium obtained is mainly columnar (Fig. 1a-b). The surfaces of different compact deposits for each metal have the same crystallographic faces (Figs. 2a,c). For example, all iridium layers (fcc lattice) obtained by electrolysis under inert atmosphere are faceted by the close-packed faces (111), (110), (100) in different proportions. The change of the electrolyzer atmosphere from the inert gas to chlorine results in the smoothing of the surface and decreasing of the grain size for iridium and ruthenium (Figs. 2a,b). The average grain size in the compact layers on graphite substrates varies in the range 3-20 μm (at a height of 200 μm from the substrate). When the level of oxygen-containing impurities in the melt is above a certain value, ruthenium coatings are cracked. The cracking effect is intensified as the temperature decreases and the cathodic current density increases.

Epitaxial growth of the layers up to a certain thickness was observed during the elec-

trodeposition of platinum metals on their own and other platinum metals substrates (Fig.2d). After that the growth of the layer with coarse crystalline columnar structure took place. Grain size in this layer was always bigger than in the layers on graphite substrates.

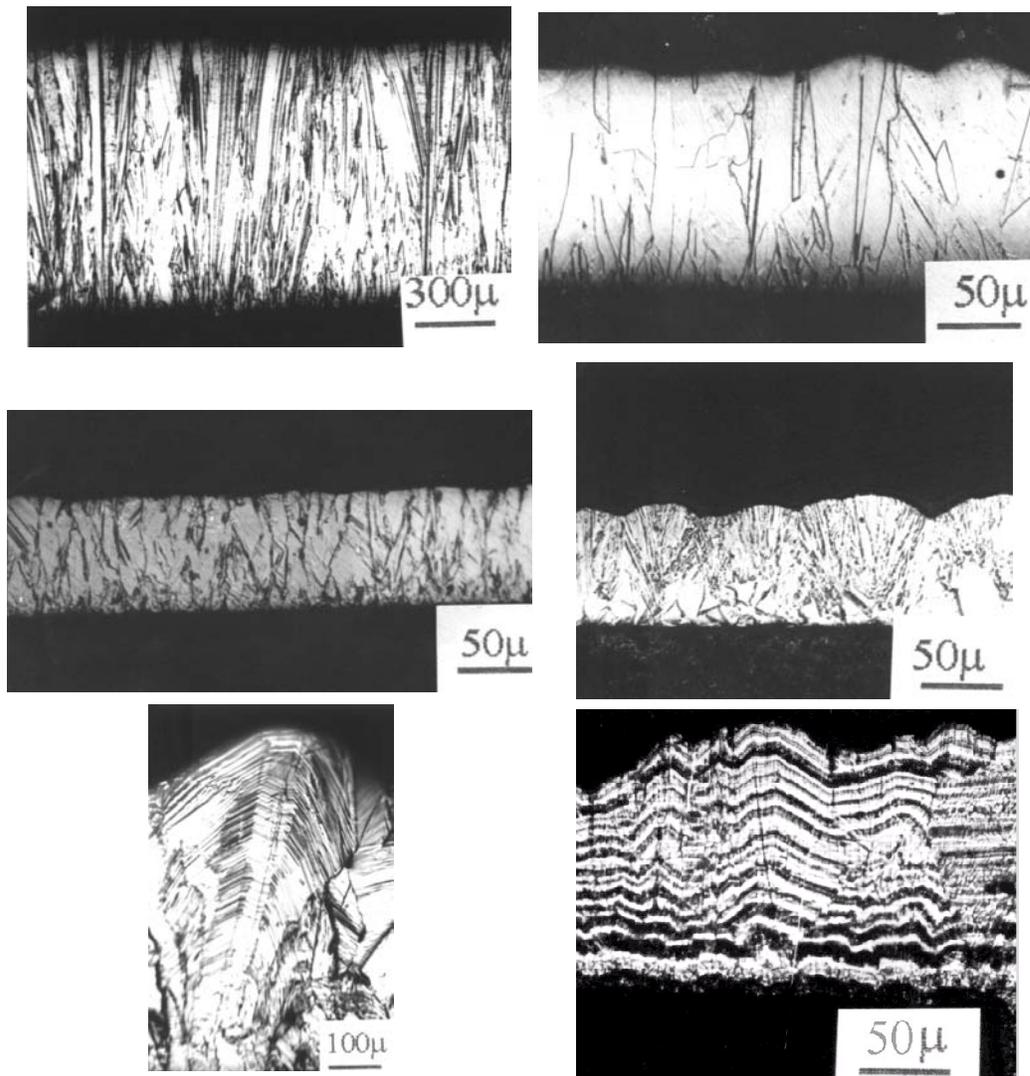


Figure 1. Cross-sections of the compact coherent layers of metals and alloys with the columnar (a-c), "bush" (d), stratum (e, f) structure: a - Ir, b - Ru, c - alloy Ir-Pt (9 at. % Pt), d - alloy Ir-Pt (40 at. % Pt), e - alloy Ru-Ir (2 at. % Ir), f - alloy Ru-Ir (12 at. % Ir).

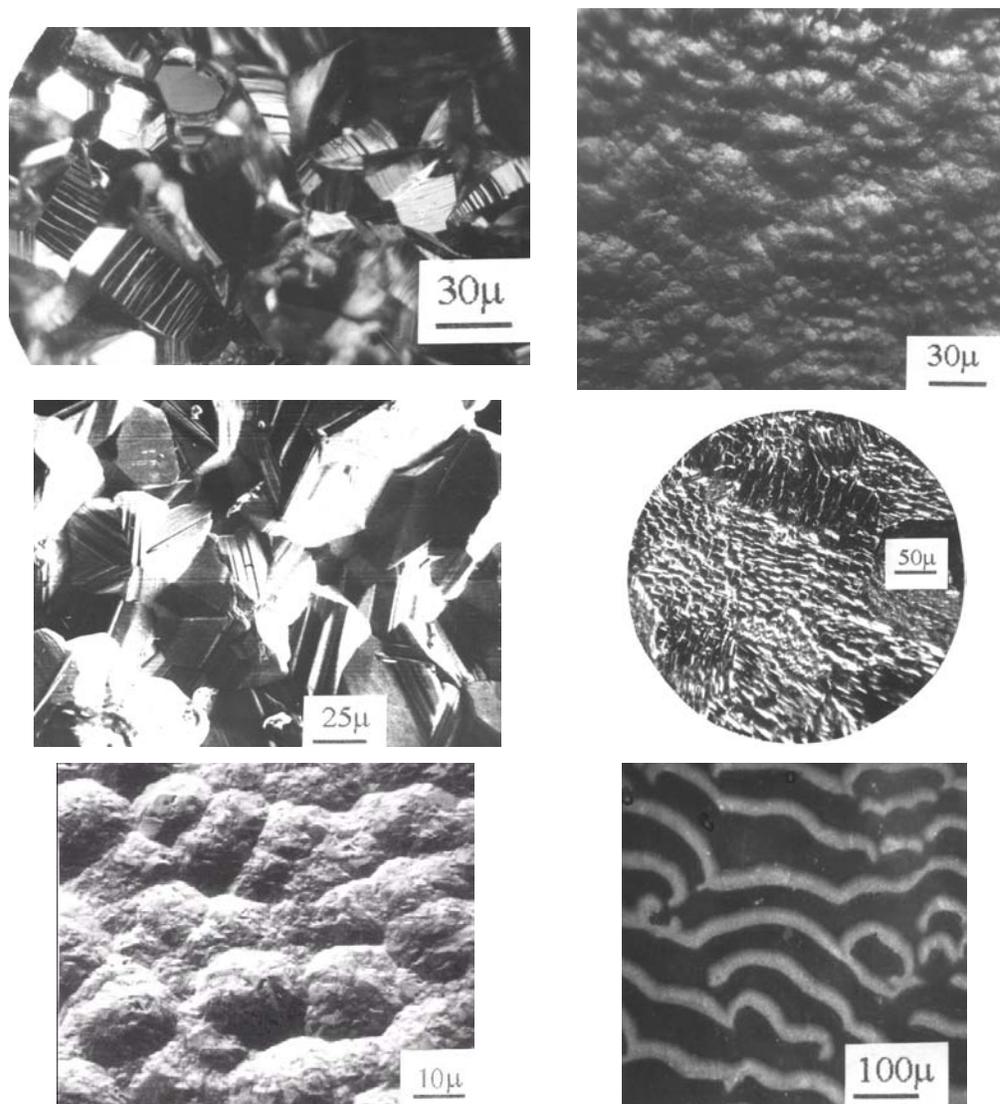


Figure 2. Microstructure of the metal and alloy surfaces: a - Ir (under the inert atmosphere), b - Ir (under chlorine atmosphere), c - Ru (texture $(11\bar{2}0)$), d - Rh (epitaxial layer on a Pt plate), e - alloy Ir-Pt (18 at. % Pt), f - spiral structure of Ir-Ru alloy.

All the *Ir* and *Ru* deposits had axial texture. The texture (111) is typical for iridium layers obtained under the inert atmosphere, whereas the texture (110) – for the ones obtained under chlorine atmosphere. The perfection of this texture decreases as the temperature is increasing. The texture of ruthenium (hcp lattice) layers depends on the temperature, cathodic current density, ruthenium ions concentration in the melt, and mainly the concentration of oxygen-containing impurities. The texture changes in the row (10 $\bar{1}$ 0)-(11 $\bar{2}$ 1)-(0001) as the concentration of oxygen-containing impurities in the melt is decreasing.

The morphology of the dendrites of relatively low-melting platinum metals (*Pt*, *Rh*, *Pd*) is mainly the same as that of any other metal with the fcc lattice (for example, *Ag*, *Cu*, *Au*) (Fig.3). The directions of the dendrite stem axes of *Pt*, *Rh*, *Pd* were, depending on the nature of the metal, temperature and composition of the melt, 2D<110>, 2D<112>, 2D<112>-<110>, 3D<110> (needles), 3D<100>. At 700-800 °C, the dendrites 3D<100> were always obtained for all these metals (Fig.3f). Platinum was preferably deposited in the form of the dendrites 2D<110>, whereas in the case of *Rh* and *Pd* the needles 3D<110> were the main type of dendrites. *Pt*, *Pd*, *Rh* dendrites had perfect faced tops, strictly straight edges and regular crystallographic angles between them. The stem and the branches of the two-dimensional dendrites 2D<110> and 2D<112> lay in the plane (111), which was predominating in the faceting of dendrites. These dendrites were twinned having several parallel twinning planes (111). The morphology of the ruthenium dendrites obtained in the melt *NaCl-KCl-CsCl* was described in details [12].

The co-deposition of alloy components always resulted in the depolarization effect. *Ir-Pt*, *Ir-Ru* and *Pt-Rh* alloys were produced in the form of solid solutions in the whole range of composition. *Pt-Rh* alloys were deposited as dendrites only. *Ir-Pt* alloys were obtained in the form of compact coherent layers in the composition range up to 80 at. % of platinum. If the platinum content exceeded 80 at. %, dendrites were deposited. *Ir-Ru* alloys were electrodeposited in the form of coherent layers in the whole range of composition. It was established that in some cases the phase composition of electrodeposited alloys did not correspond to the phase diagram. In such cases, *Ir-Pt* and *Ir-Ru* alloys were in the form of supersaturated solid solutions. One-phase alloys as well as two-phase ones were observed but the composition of these phases did not always correspond to the phase diagram.

Ir-Pt alloys (both one-phase and two-phase) had the fcc lattice. In the *Ir-Ru* system, one-phase alloys had the fcc or hcp lattice. The two-phase *Ir-Ru* alloys consisted of either phase with the same lattice types differing in the values of lattice parameters, or phases with the fcc and hexagonal lattices. In the case of alloys, the texture of compact coherent layers is determined by the conditions of electrolysis and type of the lattice. Depending on the conditions of electrodeposition, the layers (coatings) had columnar, “bush”, stratum, spiral (dissipative) structures (Fig.1,2). The stratum and dissipative structures were observed only in the alloys (Fig.1e,f, Fig.2f).

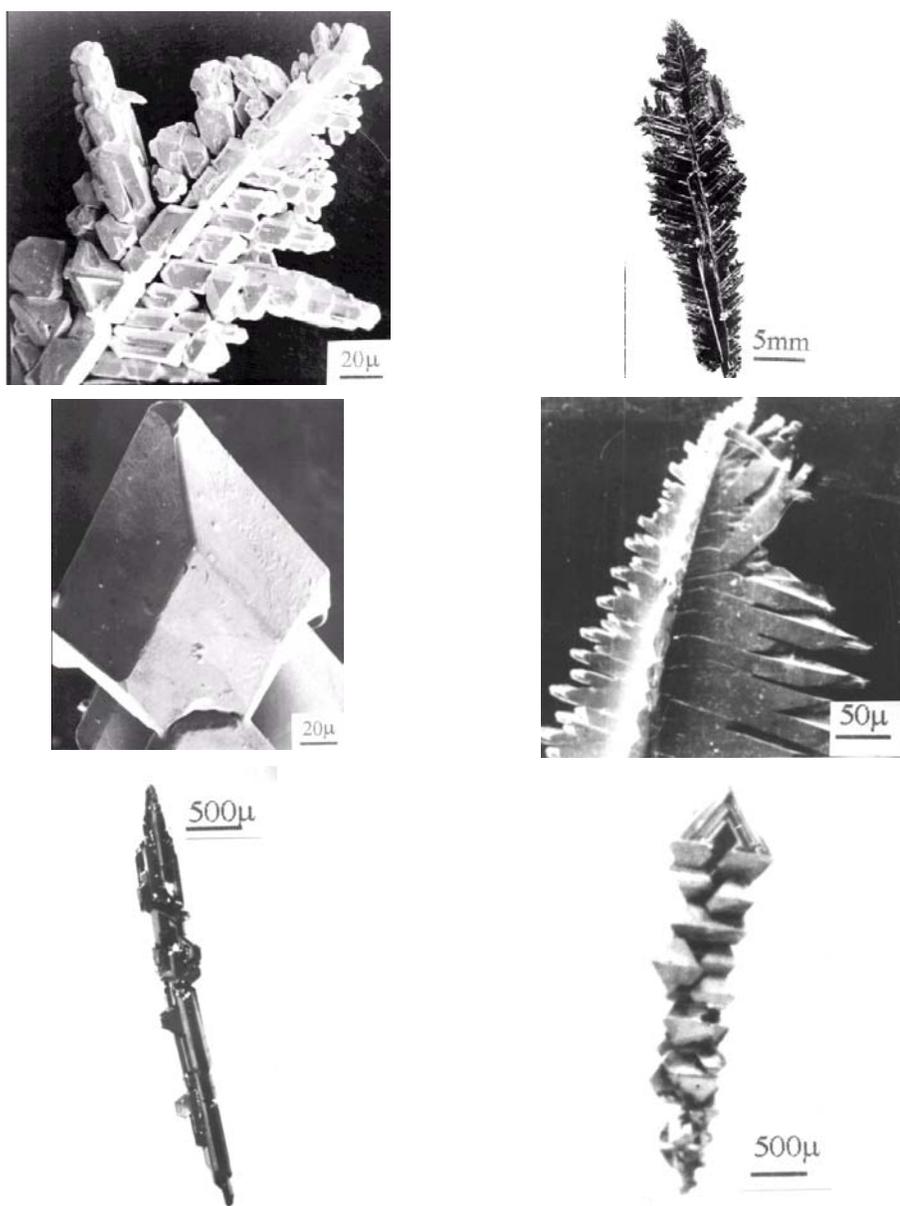


Figure 3. Types of the metal and alloy dendrites: a - $2D\langle 110 \rangle$ (Pt-Ir alloy),
 b - $2D\langle 110 \rangle$ (Pt-Rh alloy), c - $2D\langle 112 \rangle$ Pd (top), d - $2D\langle 112 \rangle$ - $\langle 110 \rangle$
 Pt, e - $3D\langle 110 \rangle$ Rh, f - $3D\langle 100 \rangle$ Pt.

The layers of the stratum structure were parallel to the growth front, and there were as many as 20 layers 3-10 μm thick each. The distribution of alloy components changed periodically in accordance with the number of layers. There was no difference in the distribution of components in the one-phase and two-phase alloys of the stratum structure. The surface of stratum deposits was fairly smooth (Fig. 2e). The dissipative structure was observed only in the case of *Ir-Ru* alloys (Fig. 2f). This structure appeared at low ruthenium concentration in the electrolyte when the cathodic current density exceeded the limiting diffusion current density for the deposition of pure ruthenium. These alloys when forming coatings of the dissipative structure always had two phases both in the bulk and on the surface. One of these phases (light and convex) had a higher ruthenium content and the other (dark) had a higher iridium content (Fig.2f). *Ir-Ru* alloys of the dissipative structure had very small crystals and the surface was mirror-like.

The component microdistribution in the cross-section of compact coherent layers is monotonous, homogeneous for one-phase columnar alloys, whereas for the stratum and spiral structures it is always periodic.

Coherent metal (*Ir* or *Ru*) and alloy (*Ir-Pt*, *Ir-Ru*) layers of the columnar structure with a thickness of up to 3000 μm can be deposited. Crucibles, tubes, disks etc. have been produced using the method of galvanoplastics.

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