ANODIC SOLUTION OF PLATINUM IN ALKALI GALLATE ELECTROLYTES

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Using the radioisotope method in conjunction with electrochemical measurements, the authors investigate the corrosion behavior of a platinum anode in alkali gallate electrolytes, in conditions simulating the electrorefining of gallium. They show that the corrosion losses of platinum increase with the gallium content of the electrolyte. They study the electrode surface by means of the scanning electron microscope and by x-ray spectral microanalysis: They conclude that anodic solution of platinum may be localized near nonmetallic inclusions.

Concerning the anodic solution of platinum in alkaline electrolytes there is only indirect information which indicates that this process takes place at an appreciable rate at surface oxidation potentials in the conditions of steady [1] or pulsed [2] polarization, and also that the anode oxide films formed in acid electrolytes are unstable [3]. Information on the corrosion behavior of platinum is not only of theoretical interest but is also necessary to solve the problem of using Pt anodes in industrial electrolysis, in particular, to make certain of very pure substances which must not be contaminated by anode solution products. In the electrorefining of gallium in alkaline solutions, platinum can be used as an additional "insoluble" anode to stabilize the electrolyte composition [4].

We have studied the anodic solution of platinum in alkali gallate electrolytes in conditions simulating the industrial process of electrorefining. In connection with the problem of choosing a material for the current leads to a gallium electrode, we also investigated the contact solution of platinum in liquid gallium.

The solution of platinum was studied by means of a combination of electrochemical and radioisotope measurements with gamma spectrometers, by a method similar to that described by us in [5]. The three-electrode cell, with no diaphragm, had an electrolyte duct and a thermostated anode at 50 ± 0.5°C. The electrodes (platinum foil of grade Pl 1, 0.02 and 0.05 mm thick, and plate 0.3 mm thick, effective area 1-2 cm^2) were first irradiated for 20 h in a nuclear reactor by a flux of $1.2 \cdot 10^{13}$ neutrons/$cm^2 \cdot$ sec, and immediately before the experiment were subjected to special treatment with concentrated acids (HNO_3, HCl, and aqua regia). The cathode was of platinum; the anode potential was measured with respect to a hydrogen electrode in 3N NaOH. The solutions were prepared from double-distilled water, NaOH of very pure grade, and metallic gallium of grade G1-VCh; we also used an industrial electrolyte (from refining baths). The gallium and sodium contents of the solutions were monitored by volumetric titration. The electrodes were polarized by P-5827 and P-5848 potentiostats.

In our experiments on the corrosion of the current leads, radioactive specimens of platinum (foil and 1-mm-diameter wire) were kept in liquid gallium (contact area 0.01-0.5 cm^2) for periods ranging from 5 min to a few days without polarization or with anodic (0.05 A/cm^2) or cathodic (0.1 A/cm^2) current supplied to the gallium electrode. In the latter case, the electrolyte contained 70 g/liter of gallium and 200 g/liter of alkali. The gallium electrode (15-17 g) was then completely dissolved and the content of radioactive platinum was determined.

In another series of experiments we determined the character of the surface damage and the elementary composition of the surface layer on nonradioactive Pt anodes polarized in similar conditions. After polarization the specimens were carefully washed free of electrolyte with water and dried with filter paper. We took

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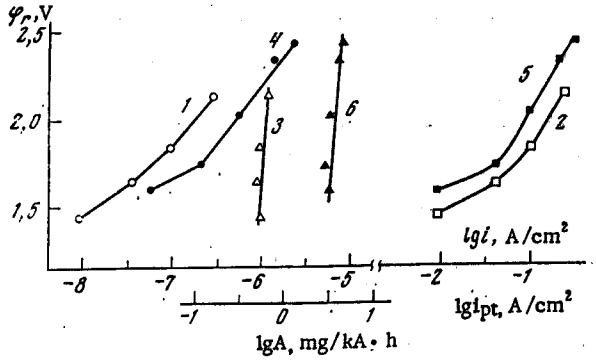

Fig. 1. Steady rates of solution of platinum (1, 4) and of emission of oxygen (2, 5) and expenditure of platinum (3, 6) as a function of anode potential. Gallium contents of electrolyte (200 g/liter NaOH): 1-3) 0; 4-6) 70 g/liter.

photomicrographs with a JSM-2 scanning electron microscope, and determined the local composition of the surface layer with an MS-46 x-ray spectral microanalyzer. In certain cases we used the "Camebax" combined instrument made by the Cameca firm, enabling us to photograph the specimen surface in electron beams* and in characteristic x rays, with registration of the surface relief and of the distribution of a given element along the scanning lines of the microprobe.

RESULTS AND DISCUSSION

Anodic solution of platinum in acid nonactivated electrolytes involves the formation of labile oxygen compounds of a metal, arising on the anode surface as a result of discharge of water [6]. This might be expected in alkali also because when hydroxyl ions are discharged intermediate particles of the same nature ought to be formed. Experiment confirms this assumption. As in acid electrolytes, solution of platinum in 5N NaOH occurs at a measurable rate ($> 10^{-9}$ A/cm^2) only at the surface oxidation potentials of the metal. Up to the start of visible separation of oxygen at constant potential, the rate of solution gradually decreases, not reaching steady values for 2h or more. At high anodic polarizations, steady solution conditions are established fairly rapidly: the rate of corrosion† is approximately proportional to the rate of emission of O_2 (Fig. 1, curves 1 and 2). As a result, the expenditure of platinum per unit quantity of electricity is practically the same over a broad range of potentials (3).

Addition of gallate to the electrolyte retards the emission of oxygen and accelerates the solution of platinum (Fig. 1, curves 4 and 5). The expenditure of platinum increases; however, for each given solution composition it maintains an approximately constant value over the given range of potentials (curve 6). In view of this, and owing to the practical aims of our work, further measurements were made with the electrodes galvanostatically polarized.

To assess the influence of the fundamental parameters of electrolysis on the corrosion behavior of a platinum anode, we performed a series of experiments by means of the mathematical design of experiments with statistical processing of the results by the method of Ridge analysis [7]. As independent variables we chose the anode current density (interval of variation 0.01-0.110 A/cm^2), the gallium concentration in the electrolyte (47-123 g/liter), and the NaOH concentration (156-233 g/liter). The calculations revealed that the expenditure of platinum depends only weakly on the polarizing current density (see Fig. 1, curves 1, 3 and 4, 6); however, it does increase appreciably with rising gallium concentration and with falling alkali concentration. From the viewpoint of solution of platinum anodes and with allowance for other requirements of electrolysis, we find that the optimum electrolytes contain 50-80 g/liter of gallium and 200-220 g/liter of alkali.

In further experiments with constant NaOH content (200 g/liter), we varied the gallium concentration in the electrolyte over a wide range (0-155 g/liter). The method was as follows. The electrode was polarized

*The resolving power at maximum magnification was 100 Å.

†Calculated on the assumption that platinum goes into solution in the tetravalent form.

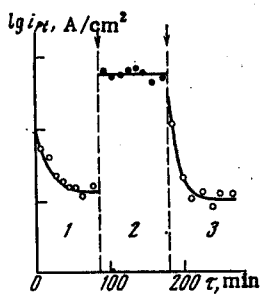

Fig. 2

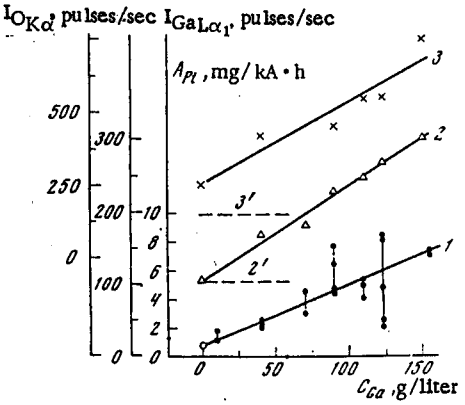

Fig. 3

Fig. 2. Time dependence of rate of solution of platinum when composition of solution is changed (as shown by arrows). Anode current 0.1 A/cm^2. Gallium contents of electrolyte (200 g/liter NaOH): 1, 3) 0; 2) 90 g/liter.

Fig. 3. Expenditure of platinum A_{Pt} (1) and averaged values of intensity of characteristic radiation of gallium $Ga_{L\alpha}$ (2) and oxygen $O_{K\alpha}$ (3) from anode surface (after electrolysis) as function of gallium concentration in electrolyte (200 g/liter NaOH). Anode current density 0.1 A/cm^2. Dashed lines: intensity of lines $Ga_{L\alpha}$ (2') and $O_{K\alpha}$ (3') for original electrode surface.

anodically in a base electrolyte of pure alkali (200 g/liter) with a current density of 0.1 A/cm^2 until a steady rate of solution was reached. Then, without interrupting the electrolysis, we added to the cell a solution with gallate, which after stabilization of solution was again replaced by base electrolyte. The agreement between the rates of solution in the base electrolyte before and after polarization in the gallate solution (Fig. 2) indicates that the observed acceleration of the corrosion process is reversible. The data on the influence of the gallium concentration on the platinum expenditure are summarized in Fig. 3 (curve 1).

The decrease in the corrosion stability of a platinum anode in the presence of gallate might be attributed to the lower content of free alkali in the gallate solutions in comparison with the base electrolyte of the same concentration with respect to NaOH. However, preliminary calculations based on the data for solutions differing only in NaOH content showed that this explanation is clearly inadequate. As we have shown, the influence of the anode potential can practically be neglected (Fig. 3). The main cause of the increase in corrosion rate may lie in a change in the state of the electrode surface.

In the base electrolyte the solution of platinum occurs relatively uniformly, but in solutions with high gallium contents, etching occurs preferentially near nonmetallic inclusions (silicon and aluminum oxides) and also the inclusions themselves in the metallic matrix. This type of localization of solution has been described for stainless steels [8] and has been observed by us on platinum in acid solutions [9]. In alkali gallate solution, the etched places on the platinum sometimes include etch pits of regular crystallographic shape, several micrometers in diameter. In some cases, fine inclusions can be seen within the etch pits. Furthermore, in gallate solution a layer rich in gallium and oxygen forms on the anode; its mean thickness increases with the gallium content of the electrolyte (Fig. 3, curves 2 and 3). Round the residues of the inclusions, the etched parts of the surface are covered with the products of solution of the inclusions and are enriched with gallium (Fig. 4a). * To judge by the character of the oxygen and gallium distributions, the latter is in oxidized form.

The local rise in the surface gallium concentration is difficult to explain by the presence of traces of unwashed electrolyte or gallium oxide, formed by hydrolysis of gallate during washing of the electrolyte with water, in hollows round the inclusions. The first possibility is rejected owing to the absence of sodium at the sites of accumulation of gallium, and the second is improbable in view of the absence of high quantities of

* The dimensions of the inclusions in the original specimen did not exceed 5-10μ, whereas the zones of local etching reached 20-25μ.

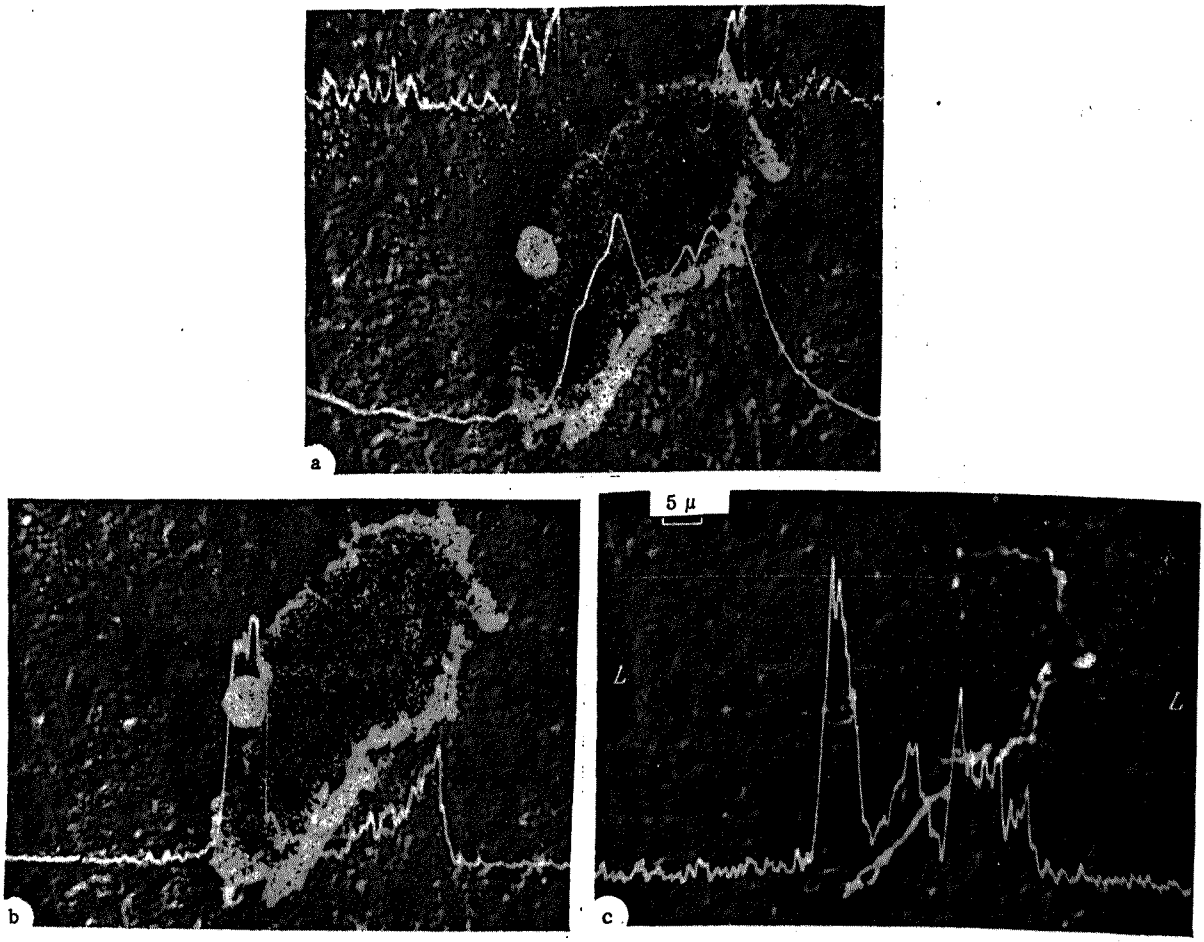

Fig. 4. Photomicrographs of part of platinum surface (× 1200) and distribution of radiation of elements along scanning line L—L (inclusion—pit). Gallium content of electrolyte (200 g/liter NaOH) is 155 g/liter. Anode current density is 0.1 A/cm^2. Duration of polarization, 8.5 h. a) $Ga_{K\alpha}$ (1) and profilogram of surface (2); b) $Si_{K\alpha}$; c) $O_{K\alpha}$. Frames a and b were photographed simultaneously in electrons and characteristic radiation.

gallium in the many grooves, traces of rolling, narrow hollows, and other depressions on the unpolished surface of the anode. *

Gallium in the form of the oxide is apparently deposited on the anode surface as a result either of direct discharge of negatively charged gallate ions, or of their precipitation as oxides in the electrode layer of the solution where the pH is lower on account of the reaction of oxygen evolution. If the latter reaction occurs more rapidly on more active parts of the anode near inclusions, then the greatest decrease in the alkalinity of the solution at these places should lead to the greatest deposition of gallium oxides.

Thus the process of anodic solution of platinum in a solution of pure alkali, as in acid electrolytes, can include an intermediate stage involving the formation of surface oxygen compounds which also play an important part in the process of evolution of O_2. It is possible that, as in acid electrolytes [9], places with nonmetallic inclusions are more active in the processes of corrosion and oxygen evolution. However, owing to the extremely low overall rate of solution, we were unable to detect localization of corrosion at inclusions in alkali by the methods in question.

When the electrolyte contains gallate, a gallium-containing layer forms on the surface, with reduced protective properties and lower catalytic activity with respect to the main electrochemical process. It is possible that this layer includes mixed oxides of gallium and platinum. Such a layer forms particularly quickly on active sites near inclusions, leading to development of a local corrosion process. The observed rise in the

* To avoid the possibility of additional inclusions getting into the surface layer of the platinum, the electrode was not mechanically polished before the experiment.

measured rate of solution (the mean over the surface) must depend on the concentration, and possibly the nature, of the inclusions on the specimen surface. This may be connected with the large scatter of values of platinum expenditure in gallate electrolytes, in some cases showing threefold or fourfold discrepancies (Fig. 3, curve 1). In the base electrolyte the scatter did not exceed 30% (13 measurements on 5 specimens of foil or sheet).

When a platinum specimen is oxidized in air and immersed in pure gallium, an amount of metal equivalent to the removal of about one monolayer from the contact surface is quite rapidly (within 5 min) transferred into the gallium. Further accumulation of platinum in the liquid phase occurs exceedingly slowly. The kinetics of solution of platinum are practically independent of whether the gallium is polarized or not.

We can conclude that platinum current leads do not appreciably contaminate gallium electrodes and can be recommended for use in electrorefining processes.

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EFFECT OF RUTHENIUM ON THE ELECTROCHEMICAL AND CORROSION BEHAVIOR OF TITANIUM AND TITANIUM—NICKEL ALLOYS IN ACID CHLORIDE SOLUTIONS

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The corrosion and anodic behavior of titanium—nickel alloys (0.5-8%), modified with small additions of ruthenium (0.2%), in acid (to pH 0) 2 N NaCl solutions at 100°C was studied. It was established that a higher corrosion resistance and significantly greater efficiency exists for Ti—Ni—Ru alloys in relation to the anodic evolution of chlorine in comparison with Ti—Ni alloys and Ti—0.2% Ru alloy.

The discovery of the phenomenon of self-passivation of metals and alloys by cathodic modification is finding wider application in increasing the corrosion resistance of titanium and a number of its alloys in acids [1-3]. Cathodic modification of Ti—Ni alloys by ruthenium provides alloys with increased corrosion resistance

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