THE ADSORPTION AND CORROSION BEHAVIOR OF A PLATINUM ANODE IN SOLUTIONS CONTAINING THIOUREA

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During anodic polarization of platinum in perchloric acid solutions containing thiourea (TU), the electrode becomes covered with the oxidation products of the latter, which effectively inhibit the reaction of solution of platinum (RSP) and the reaction of separation of oxygen (RSO) [1]. Some observations indicate that the surface of the platinum has regions with increased adsorption and corrosion activity.

It seemed of interest to test these conclusions by direct experimental observation of the products of adsorption of TU on platinum and by investigating the character of their distribution over the surface.

The adsorption of the oxidation products of TU was determined by means of radioactive indicators "with respect to the electrode" with TU preparations marked with the beta isotopes S^{35} and C^{24}. For comparison, some experiments were performed with preparations of Na_2S and KSCN marked with the isotope S^{35}. The conditions of polarization by means of the P-5848 potentiostat (retention at constant potentials until the rate of solution becomes stable) are similar to those used in corrosion tests [1, 6]. The experiments were performed in a small (5 ml) flow-type cell without a diaphragm with a thermostated (50 ± 1°) platinum anode in the shape of a cowl sealed to the end of the funnel of the ground-glass joint. The concentration of sulfur-containing additives was usually two orders of magnitude less than in corrosion joints. The outer surface of the anode was first mechanically polished and treated with concentrated solutions of alkali and acids. The visible surface of the anode was 0.78 cm^2; the roughness factor, determined by the potentiodynamic method by adsorption of hydrogen, was close to two. As a reference electrode we used a palladium-hydrogen half-cell filled with perchloric acid.

With the current (potentiostat) switched on, the electrode was introduced into the cell filled with electrolyte, kept at constant potential for 1-90 min, and removed from the cell with the current still on. It was washed with water for 3 min, * and dried with filter paper; then its radioactivity was determined by a specially-devised method: a thin plastic scintillator without a lightproof coating was fastened at a strictly fixed distance (0.3 mm) from the electrode, which was then introduced via the light trap into the measurement chamber of a USS-1 beta spectrometer. In the measurement conditions there was no self-absorption of the registered radiation. The sensitivity of the measurements to sulfur was $3 \cdot 10^{-13}$ g-mole/cm^2, and that to carbon $1 \cdot 10^{-11}$ g-mole/cm^2.

After the measurements the electrode was subjected to cathodic–anodic treatment in perchloric acid, by the method used in corrosion measurements in order to reproduce the original state of the surface [1, 6]; this treatment ensured complete removal of adsorbed radioactive products from the surface.

After the electrode had been kept in the solutions with TU, we did in fact observe on its surface products containing sulfur and carbon (which we shall call S- and C-particles), and that their concentrations

*This washing ensured constancy of the radioactivity.

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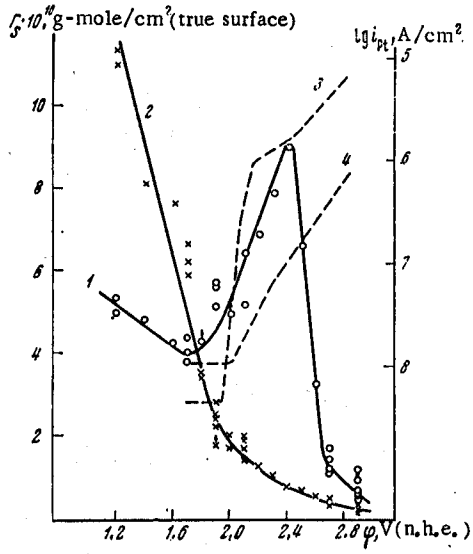

Fig. 1

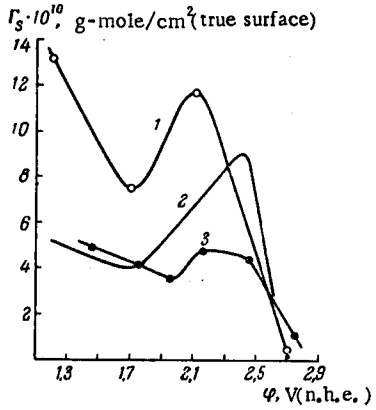

Fig. 2

Fig. 1. Surface concentrations of S-particles (1) and C-particles (2) as a function of potential. The electrode was kept for 10 min in 3N $HClO_4$ + $1 \cdot 10^{-4}$ M/TU. The dashed curves denote the partial curves of solutions of platinum in 3N $HClO_4$ (3) and in 3N $HClO_4$ + $1.5 \cdot 10^{-2}$M TU (4) [1].

Fig. 2. Surface concentration of S-particles as a function of potential. The electrode was kept for 10 min in 3N $HClO_4$ to which was added $1 \cdot 10^{-4}$ M Na_2S (curve 1), TU (curve 2, identical with curve 1 in Fig. 2), or KSCN (curve 3).

and relative amounts depend markedly on the potential, the retention time, and the solution composition. Accumulation of particles on the surface occurs mainly in the initial period of polarization (the first few minutes). At the chemisorption potentials of oxygen on platinum, a roughly steady particle concentration in the surface layer is established in a time which decreases when the potential is higher, and which is usually less for C-particles than for S-particles. The C- and especially the S-particles are tightly bound to the platinum surface, and are only removed to a small extent when it is washed in water. A much more effective desorption process occurs when the electrode undergoes anodic polarization in perchloric acid (base electrolyte); in the region φ = 1.2-2.9 V, the relative rate of removal of particles increases with the desorption potential and with decrease in the potential of formation of an adsorbed layer.

As we see from Fig. 1 (where for comparison we also give in schematic form the partial curves of solution of platinum [1]), the surface concentration of C-particles decreases monotonically with rise of potential, whereas the concentration of S-particles passes through a maximum at φ = 2.1-2.4 V (the potential of the maximum depends on the duration of polarization of the electrode).

The increase of adsorbability of various compounds on platinum in this potential range, and its influence on the kinetics of the electrochemical reactions, have been discussed by several authors [2]. The noncoincidence between the surface concentrations of the S- and C-particles, and their different adsorption and desorption kinetics in identical conditions, show that throughout the investigated range of potentials, adsorption (oxidation) of TU is destructive and at least partly involves rupture of the C–S bond.

Comparison of the adsorption and corrosion data (Fig. 1) shows that the inhibiting action of TU on RSP in 3N $HClO_4$ is manifested in the same potential region in which we observe preferential accumulation of S-particles on the electrode surface. Between the adsorption of S-particles and the degree of retardation of RSP [1] there is a definite relation, which is illustrated by the dependence of the coefficient of inhibition of RSP at φ = 2.7 V on the surface concentration of S-particles, measured after polarization of the electrode in solutions with various TU contents (Fig. 3). On transition to a dilute solution (0.3N $HClO_4$) the inhibiting action of the TU is augmented and there is a corresponding rise in the surface concentration of S-particles; for more concentrated solutions (7N and 10N $HClO_4$) we observe the opposite effects.

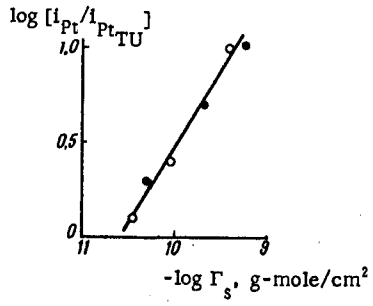

Fig. 3. Coefficient of inhibition (γ) of RSP in 3N $HClO_4$ to which is added $1 \cdot 10^{-4}$M TU (●) or Na_2S (○), vs surface concentration of S-particles. Potential, 2.7 V. Values of $i_{Pt}/i_{Pt_{TU}}$ are equal to the ratio of the RSP current without additive to the RSP current in the presence of additive.

Although the available data are insufficient to enable us to judge the composition of the S-particles (elementary sulfur [3], platinum sulfides [4], etc.), there is no doubt that their formation in conditions of anodic polarization involves splitting off of sulfur from TU molecules. In addition to the above proofs, this is also demonstrated by the fact that when the TU in 3N $HClO_4$ is replaced by some other compounds of divalent sulfur (Na_2S, KSCN), the shapes of the graphs of the surface concentration of S-particles vs the potential are not essentially altered (Fig. 2), while the coefficient of inhibition of RSP (at $\varphi = 2.7$ V) is determined by the surface concentration of S-particles, and is independent of their source (Fig. 3).

There are various possible distributions of S-particles over the anode surface; in particular, concentration of sulfur in individual most active regions until "islands" are formed with polyatomic coatings [5]. This model enables us to explain certain features of the corrosion-electrochemical behavior of platinum [1].

The distribution of S-particles over the surface was investigated by x-ray spectral microanalysis with an MS-46 instrument (electron probe diameter about 1 μ).

The morphology of the surface after anodic polarization of the electrode in perchloric acid solutions with or without TU was studied with the aid of an ISM-2 scanning electron microscope.

After polarization in 3N $HClO_4$ plus TU, on the surface of the anode we see areas from a few microns to a few tens of microns in diameter, covered with a weakly-conducting porous sulfur-containing film.* These areas are found near nonmetallic inclusions present in the platinum (silicon and aluminum oxides); the thickness of the film decreases with increasing distance from the inclusions. After polarization of the electrode in 10N $HClO_4$ with TU, these areas are seen very rarely: most of the inclusions are "free" from film. Thus there is a definite correlation between the inhibiting action of TU on RSP and the formation of a film on parts of the surface adjoining inclusions. We can suppose that in the absence of TU, when no protective sulfur-containing film is observed, these regions possess reduced corrosion resistance in $HClO_4$ solutions which are not concentrated, and their solution makes a marked contribution to the RSP [1]. This hypothesis agrees with the observations of L. I. Freiman and G. S. Raskin on the possibility of accelerated corrosion of passive stainless steel near an inclusion. It is not impossible that similar effects of local solution might take place on a platinum electrode also. In fact, after prolonged anodic polarization of platinum in 3N $HClO_4$ with added HF, which accelerates RSP [6], on the electrode surface we sometimes see etch pits of regular crystallographic shape, which occasionally contain trapped inclusions.

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*The sensitivity of the electron probe method is insufficient to determine the elements in coatings a few atoms thick. Therefore the data do not exclude the possibility of the presence of S-particles in the adsorption layer on the rest of the surface.