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Abstract

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THE INFLUENCE OF THERMAL AND MECHANICAL SURFACE TREATMENT ON THE MAGNITUDE OF ION ADSORPTION ON PLATINUM

(Presented by Academician A. N. Frumkin, 11 XII 1961)

When metallic electrodes are used for electrochemical and adsorption measurements, various methods of preliminary preparation of their surface are employed, including mechanical and thermal effects on the metal.

The literature contains a number of indications of the influence of preliminary preparation of a metal surface on its adsorption properties. Erbacher was the first to observe a change in the sorption properties of platinum after treating it with emery and sandpaper (^{1}). In the case of silver it was shown that polishing decreases, bending increases, and annealing decreases exchange with ions of the solution (^{2}). The authors of work (^{2}) suggest the presence of diffusion into the interior of the metal. Polishing changes the adsorption of phosphorus on steel (^{3}). On iron, treatment with emery paper increases the adsorption of sulfuric acid, which was explained by the influence of heating of the metal during polishing, as a result of which the structure and adsorption properties of the oxides formed are altered (^{4}). Clarifying the influence of preliminary preparation of platinum on the adsorption of ions on its surface, which is the aim of the present work, may shed light not only on the reasons for discrepancies in the results of experiments carried out on samples prepared in different ways, but also on the mechanism of ion uptake by the metal.

In the work, samples of commercial platinum foil (0.1 mm thick) and wire (0.3 and 0.6 mm in diameter) were used; they were subjected to thermal or mechanical treatment before the adsorption experiment. Thermal treatment was carried out in an atmosphere of hydrogen, air, or nitrogen in the temperature range from 200° to the melting temperature of platinum (1773° C), in furnaces or in the flame of a gas burner, after which microphotographs of the samples were taken. Mechanical treatment was carried out in air by bending, stretching, or forging annealed or unannealed samples. Platinum foil or wire was bent in

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

opposite directions at an angle of about 50-60° several times (5-10). Forging was performed by hand by means of two or three hammer blows on a sample placed between two platinum plates. Stretching, to which only samples of wire annealed beforehand (up to 1200°, 1 hour) were subjected, was carried out on a special apparatus. Adsorption was studied from a sulfuric acid solution ($5 \cdot 10^{-3} N$), labeled with the radioactive isotope sulfur S-35, by the magnitude of the β-radioactivity of the samples washed with water from the solution for various periods of time.

The curve shown in Fig. 1 for the dependence of adsorption on the temperature of preliminary annealing of platinum foil in an atmosphere of hydrogen shows that annealing up to 600° changes the sorption capacity of platinum relatively little. In the temperature range 700-800° a sharp drop in adsorption is observed, and with a further increase in temperature it remains almost completely unchanged. In parallel with this, microstructural changes of the surface are revealed. The normal granular structure of undeformed metal is visible only in microphotographs of samples annealed

at temperatures above 700°. At such a temperature, changes in the microstructure apparently occur within several minutes, as follows from experiments on calcining platinum in the oxidizing flame of a burner. Simultaneously with the change in microstructure, cracks and scratches are healed, but more slowly, so that the number and size of these defects at 700°, when a sharp change in sorption capacity is already taking place, are still very large.

Fig. 1. Dependence of the adsorption of sulfuric acid on platinum foil on the temperature of preliminary calcination. **1** —samples washed for 30 sec.; **2** —150 sec.; **3** —750 sec.

Fig. 2. Change in the radioactivity of dried samples over time after adsorption. **1** —sample deformed by bending; **2** —fused sample.

The observed changes in the sorption capacity and microstructure of platinum, which require very little time and occur at temperatures 1000-1200° lower than the melting temperature, make it possible to assume that the main role here is played by processes of rapid recrystallization,* which apparently occur as a result of surface migration of metal atoms at grain boundaries (^{6}). The rapidity of recrystallization indicates that ordinary commercial platinum has considerable internal stresses.

As a result of coalescence recrystallization, in which intercrystalline surfaces are reduced owing to grain coarsening, the decrease in the number and size of voids between crystals, and partly owing to the healing of various kinds of defects, there is a decrease in the true sorbing surface, leading to a decline in the measured adsorption value. When platinum is preliminarily calcined in an atmosphere of air or nitrogen containing up to 0.5% oxygen, curves of the dependence of adsorption on temperature are obtained that are analogous in shape to the curves in Fig. 1. Under these conditions, however, differences appear, probably connected with oxidation of the surface. These differences consist in the fact that, with increasing temperature, distinct grain boundaries appear in an oxygen atmosphere at a higher temperature (1000°) than in a hydrogen atmosphere (800°). This indicates a different rate of recrystallization of pure platinum and its oxides. The presence of stable oxides on platinum at high temperature was shown in work ([7]), in which, during adsorption of oxygen at 400°, its penetration into the metal was observed at a comparatively small value of the contact potential difference, whereas at 800° a large increase in the contact potential difference was observed, the value of which remained constant with time. The magnitude of sulfuric acid adsorption on platinum oxides is smaller than on unoxidized platinum, independently of the annealing temperature.

* According to Bočvar ([5]), the temperature at which rapid recrystallization begins for platinum should be about 550°.

As a result of the thermal treatment of specially undeformed commercial platinum, the change in the amount of adsorption and, consequently, in the magnitude of the true sorbing surface occurs by several times (sometimes even by an order of magnitude) and depends on the degree of the uncontrolled initial defectiveness of the metal. Changes in the amount of adsorption of the same order, and sometimes considerably greater, can be observed on platinum subjected to mechanical deformation before adsorption. The results of experiments with wire samples (diameter 0.3–0.6 mm), washed free of solution with water for 10 sec, show that bending increases sorption on unannealed samples by 5–10 times. Subsequent annealing of the same samples reduces sorption by approximately 20 times, while further bending of the annealed wire leads to restoration of the sorption value characteristic of deformed samples ($3 \cdot 10^{-10}$ g-eq/cm^2). Table 1 gives data on the change in sorption upon bending and forging samples of platinum sheet.

Table 1

Sample Nos.	Treatment conditions	Measured radioactivity, imp/min, background subtracted: before def.	Measured radioactivity, imp/min, background subtracted: after def.	Calculated ads., g-eq/cm^2: before def. A	Calculated ads., g-eq/cm^2: after def. A	$A\,/A$
1	Bending (5 times)	124	787	$1.2{\cdot}10^{-11}$	$7.4{\cdot}10^{-11}$	6.2
2	Bending (5 times)	222	1057	$2.1{\cdot}10^{-11}$	$1.0{\cdot}10^{-10}$	5.0
3	Bending (10 times)	290	15357	$2.8{\cdot}10^{-11}$	$1.5 \cdot 10^{-9}$	53.0
4	Forging	369	176	$3.5{\cdot}10^{-11}$	$1.8{\cdot}10^{-11}$	0.5
5	»	422	254	$4.0{\cdot}10^{-11}$	$2.4{\cdot}10^{-11}$	0.6
6	»	787	220	$7.4{\cdot}10^{-11}$	$2.1{\cdot}10^{-11}$	0.3

Samples previously deformed by bending were subjected to forging. Its effect can be explained by the fact that the exits of defects formed during bending are closed and the surface is smoothed, as a result of which the effective magnitude of the surface decreases.

When a previously annealed wire (diam. 0.2 mm) was stretched by 5% of its initial length, an increase in the sorption of sulfuric acid by 40–50% and the appearance of a fibrous structure characteristic of deformed metal were observed. Subsequent annealing at 1320° led to restoration of the normal granular microstructure of the metal and to a decrease in sorption by 50% of the value present before stretching. Bending of the annealed wire again gave an increase in sorption by 50–60% compared with the value before stretching.

Adsorption on the surface of the metal not directly in contact with the solution (the internal surface) is apparently possible as a result of migration of particles adsorbed on the external surface into the depth of the metal along intercrystalline surfaces and lattice defects arising in the process of deformation. This conclusion is confirmed by direct observations of a decrease in the measured β-radioactivity of dry samples deformed by bending over the time they remained in the counter in air after brief (several minutes) adsorption of labeled sulfuric acid, then washed (10–20 sec) with water. After washing, the samples were rapidly dried with filter paper. All operations after adsorption took no more than one minute. The results obtained are shown by the upper curve in Fig. 2. On a fused sample, in analogous experiments, the value of the activity remained constant (lower curve in Fig. 2). On unannealed and undeformed samples of commercial platinum these effects are smaller.

After many hours of adsorption or prolonged exposure in air after brief adsorption of samples rapidly washed free of solution,

no changes in radioactivity were observed. After effective short-term desorption of such samples, on the contrary, an increase in the measured radioactivity was observed (8).

These phenomena may be explained as follows: adsorption over a comparatively short interval of time has time to occur mainly on the surface of the metal directly in contact with the solution, while a considerable part of the internal surface still remains unoccupied. As a result, on the surface of samples rapidly washed free of the labeled solution after adsorption, there arises a concentration gradient of the adsorbed particles directed into the metal, and this is the cause of the departure of some of them from the outer surface. Since these particles are labeled with the isotope S-35, which has soft β-radiation, their departure is accompanied by a decrease in the measured radioactivity as a result of absorption of the indicator’ s soft β-radiation. This should occur up to the onset of a certain conditional saturation of the entire sorbing surface. True adsorption equilibrium between the outer and the entire internal surface is in general unattainable, and the penetration of the sorbing particles into the metal is, apparently, an asymptotically decaying process.

With prolonged exposure of the samples to air after adsorption, a uniform distribution of adsorbed ions over the entire accessible surface is attained; this distribution is disturbed only upon desorption of ions from the outer surface. As a result, a concentration gradient arises, in this case directed from within outward, which leads to the partial migration of ions to the outer surface, determining the increase in the measured radioactivity. The penetration of sulfuric acid anions in the experiments described, as well as of iodine and bromine anions (8), probably occurs together with solution cations coadsorbed with the anions on the outer surface of the metal.

All the results presented demonstrate the considerable influence of preliminary treatment of the metal on the magnitude and microstructure of the surface, in connection with changes in which its adsorption properties change.

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