

# EFFECT OF HEAT AND MECHANICAL TREATMENT OF THE SURFACE ON THE NUMBER OF IONS ADSORBED ON PLATINUM

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In using metal electrodes for electrochemical and adsorption measurements, diverse methods are employed for preliminary treatment of the surface, including mechanical and heat treatment of the metal.

The literature gives a number of indications of the effect of preliminary treatment of the metal surface on its adsorptive properties. Erbacher was the first to observe the change in the sorptive properties of platinum after treating it with emery and sandpaper [1]. It was shown for silver that polishing lowers, bending increases, and baking reduces exchange with ions of a solution [2]. The authors of [2] make the assumption of diffusion existing in the body 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 is explained by the heating effect on the metal during polishing, as a result of which the structure and adsorptive properties of the oxides formed is changed [4]. An explanation of the effect of preliminary treatment of platinum on the adsorption of ions on its surface, which is the purpose of the present paper, may throw light not only on the causes of the discrepancies in the results of experiments made on samples prepared by various methods, but also on the mechanism of absorption of ions by a metal.

In this work use was made of samples of commercial platinum sheet (0.1 mm thick) and of wires (0.3 and 0.6 mm in diameter) subjected to heat or mechanical treatment before the adsorption experiment. The heat treatment was carried out in an atmosphere of hydrogen, air, or nitrogen over the temperature range from 200° to the melting point of platinum (1773° C) in furnaces, or in a gas burner flame, after which microphotographs of the samples were taken. The mechanical treatment was done in air by bending, stretching, or forging of heated or unheated samples. The platinum sheet or wire was subjected to bending in opposite directions at an angle of about 50-60° several times (5-10). The forging was done by hand with two or three blows from a hammer on a sample placed between two platinum sheets. The stretching, which only the samples of wire heated to 1200° for one hour were subjected to, was done in a special apparatus. The adsorption was studied from a solution of sulfuric acid ( $5 \cdot 10^{-3}$  N), using radioactive S-35 as a tracer, from the  $\beta$ -radioactivity of the samples, which had been washed free of solution with water for different lengths of time.

The curve in Fig. 1 of the adsorption as a function of the temperature at which the platinum sheet had been preliminarily heated in an atmosphere of hydrogen shows that heating to 600° has relatively little effect on the sorptive properties of the platinum. In the temperature range 700-800°, a sharp drop-off in adsorption is observed, and with further increase in the temperature there is almost complete absence of change. Parallel with this, changes in the microstructure of the surface show up. The normal grain structure of the undeformed metal is visible only in the microphotographs of the samples which had been heated at temperatures above 700°. At this temperature, the changes in the microstructure apparently occur in the course of several minutes, which follows from the experiments on heating the platinum in the oxidizing flame of a burner. Simultaneously with the change in microstructure, healing of scratches and flaws occurs, but more slowly, so that the number and dimensions of these defects at 700°, where a sharp change in the sorptive properties is already occurring, is still very large.

The observed changes in the sorption properties and microstructure of platinum, which require a very short time and occur at temperatures 1000-1200° lower than the melting point, cause us to assume that a fundamental role is being played here by rapid recrystallization processes\*, which apparently occur as a result of surface migra-

\* According to Bochvar [5], the temperature at the start of the rapid recrystallization for platinum should be about 550°.

tion of metal atoms on the grain boundaries [6]. The rapidity of the recrystallization shows that ordinary commercial platinum has a considerable amount of internal stress.

As a result of the collective recrystallization, in which the intercrystalline surface is reduced because of enlarging of the grains, reduction of the number and dimensions of the spaces between crystals, and partly on account of healing of various kinds of defects, a reduction in the true sorbing surface occurs, which causes a drop in the

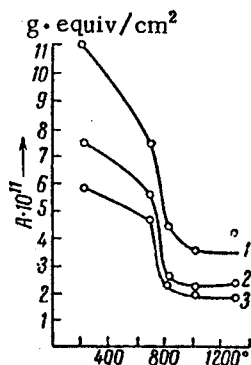


Fig. 1. Adsorption of sulfuric acid on platinum sheet as a function of preliminary heating temperature. 1) Samples washed 30 seconds, 2) 150 seconds, 3) 750 seconds.

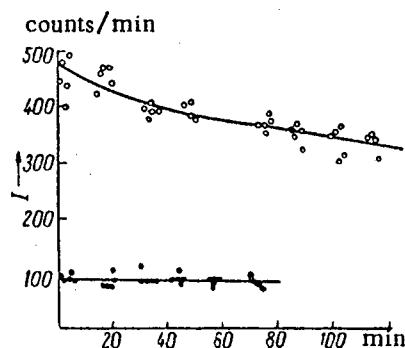


Fig. 2. Change in radioactivity of dried samples with time after adsorption. 1) Sample deformed by bending, 2) unbent sample.

measured amount of adsorption. If the platinum is first heated in an atmosphere of air or nitrogen, containing up to 0.5% oxygen, adsorption vs. temperature curves are obtained which are similar in form to the curves of Fig. 1. However under these conditions differences show up which are probably due to oxidation of the surface. The differences consist in the fact that, as the temperature is raised, definite grain boundaries appear at a higher temperature in an atmosphere of oxygen ( $1000^{\circ}$ ) than in an atmosphere of hydrogen ( $800^{\circ}$ ). This indicates that there is a difference between the recrystallization rate of pure platinum and its oxides. The presence of stable oxides on platinum at high temperatures was shown in [7], in which during oxygen adsorption at  $400^{\circ}$  it was observed that it went inside the metal at a comparatively small value of contact potential difference, and at  $800^{\circ}$  a large increase in the contact potential difference was observed, which remained constant in value with time. The amount of sulfuric acid adsorbed on the oxides of platinum is less than on unoxidized platinum independent of the temperature of the heat treatment.

As a result of the heat treatment, especially of undeformed commercial platinum, a change of several fold (sometimes of an order of magnitude) occurs in the amount of adsorption, and, consequently, in the amount of true sorbing surface, which depends on the uncontrollable extent to which defects are originally present in the metal. Changes in the amount of adsorption of the same order of magnitude, and sometimes even considerably greater, can be observed on platinum subjected to mechanical deformation before the adsorption. The results of experiments on wire samples 0.3–0.6 mm in diameter, washed free of solution for 10 seconds with water, show that bending increases the sorption on unannealed samples five or ten times. Subsequent heating of the same samples lowers the sorption approximately twenty times, and further bending of the heated wire brings about a restoration of the amount of sorption characteristic of deformed samples ( $3 \cdot 10^{-10}$  g-equiv/cm<sup>2</sup>). The table gives data on the change in the amount of sorption from bending and forging platinum sheet samples.

The forging was done on samples previously deformed by bending. The effect of the forging may be explained by the fact that the exit holes are closed up in the defects formed during bending, and the surfaces smoothed, so that the effective surface is reduced.

If a previously heated wire (0.2 mm diameter) was stretched by 5% of its original length, a 40–50% increase in sulfuric acid sorption was observed along with the appearance of the fibrous structure characteristic of deformed metal. Subsequent heating at  $1320^{\circ}$  restored the normal grain microstructure of the metal and reduced the sorption by 50% from the value existing before stretching. Bending of the heated wire again gave an increase in sorption of 50–60% measured against the value before stretching.

Adsorption on a metal surface not in direct contact with the solution (internal surface) is apparently possible as a result of migration of particles adsorbed on the external surface into the body of the metal along intercrystalline surfaces and lattice defects which arise in the course of deformation. This conclusion is supported by direct

| Sample<br>Nos. | Conditions<br>of treatment | Measured radioactivity<br>in counts/minute, cor-<br>rected for background |                        | Calculated adsorption,<br>g-equiv/cm <sup>2</sup> |                                  | $\frac{A_{in}}{A_{fin}}$ |
|----------------|----------------------------|---------------------------------------------------------------------------|------------------------|---------------------------------------------------|----------------------------------|--------------------------|
|                |                            | Before de-<br>formation                                                   | After de-<br>formation | Before defor-<br>mation $A_{in}$                  | After defor-<br>mation $A_{fin}$ |                          |
| 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              | Forging                    | 422                                                                       | 254                    | $4.0 \cdot 10^{-11}$                              | $2.4 \cdot 10^{-11}$             | 0.6                      |
| 6              | Forging                    | 787                                                                       | 220                    | $7.4 \cdot 10^{-11}$                              | $2.1 \cdot 10^{-11}$             | 0.3                      |

observations on the reduction in the measured  $\beta$ -radioactivity of dry samples deformed by bending while they are in the counter in air after several minutes adsorption of tracer sulfuric acid followed by 10–20 seconds washing with water. After washing, the samples were quickly dried with filter paper. All the operations after adsorption required not more than one minute. The results obtained are shown in the upper curve of Fig. 2. With an unbent sample in similar experiments, the activity remained constant (lower curve of Fig. 2). In unheated and undeformed samples of commercial platinum, these effects are smaller.

After adsorption lasting several hours, or after prolonged exposure to air following short adsorption of samples quickly washed free of solution, no changes in radioactivity were observed. After effective short-time desorption of these samples, on the other hand, an increase in the measured radioactivity was observed [8].

These phenomena may be explained in the following way: adsorption during a comparatively short interval of time manages to occur principally on the metal surface which is in direct contact with the solution, while a considerable part of the internal surface remains uninvolved. As a result, on the surface of samples which have been quickly washed free of tracer solution a concentration gradient of adsorbed particles appears after adsorption, directed toward the inside of the metal, and this is the reason why some of the particles leave the external surface. Since these particles contain S-35 tracer, which has soft  $\beta$ -radiation, a reduction in measured radioactivity is observed when they go inside because of adsorption of the soft  $\beta$ -radiation from the tracer. This should occur right up to the point where some kind of nominal saturation of the whole sorbing surface is reached. True sorption equilibrium between the external and all the internal surfaces is in general unattainable, and penetration of the sorbed particles into the metal is apparently an asymptotically decreasing process.

With prolonged exposure of the samples to air after adsorption, a uniform distribution of adsorbed ions is established over the whole accessible surface, which is disturbed only if ions are desorbed from the external surface. As a result, a concentration gradient appears which, in this case, is directed from the inside to the outside, which causes partial migration of the ions to the external surface, and this is what causes the increase in the measured radioactivity. Penetration of sulfuric acid anions in the experiments described, as well as iodine and bromine anions [8], probably occurs, along with cations from the solution adsorbed along with the anions on the external surface of the metal.

All the results presented show that previous treatment of the metal has considerable effect on the magnitude and microstructure of the surface, so that the adsorptive properties change along with the changes in the surface.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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