

DETERMINATION OF THE RATE OF CORROSION OF PASSIVE METALS BY A RADIOCHEMICAL METHOD

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Existing methods for determining the corrosion resistance of metals and alloys are not sufficiently sensitive for estimating the corrosion of specimens with a very high corrosion resistance and this makes it necessary to increase considerably the duration of experiments on the determination of corrosion losses (in some cases up to several thousand hours). It is of interest to use the tracer atom method to determine corrosion resistance, since this method has an extremely high sensitivity. The aim of the present work was to develop a radiochemical method for determining the rate of corrosion of passive metals and alloys for the case of platinum anodes in hot concentrated sodium chloride solutions, i.e., under the conditions of the industrial preparation of chlorine by the diaphragm method. According to the literature data [1], the rate of corrosion of platinum anodes under these conditions is extremely low and its determination by ordinary methods is difficult.

EXPERIMENTAL

The proposed method is based on the preliminary activation of the test specimens by neutron irradiation with subsequent determination of the concentration of radioactive products in the solution (in which the corrosion test is carried out) by measuring the radioactivity of specimens of the solution by means of a scintillation γ -spectrometer [2].* The studies were carried out with platinum specimens with a thickness of 0.2 mm.† For an accurate determination of the specific activity of the irradiated specimen, which is necessary for calculating the rate of corrosion, we simultaneously irradiated a standard specimen prepared from the same platinum. Both specimens were sealed into a quartz ampoule which was placed in a pure aluminum container and irradiated in a reactor with a beam of $(1-2) \cdot 10^{13}$ neutrons per $1 \text{ cm}^2 \text{ sec}$ for 1-5 days. After irradiation, a platinum wire was spot-welded to the test specimen (visible surface area 0.6 cm^2), the other end of the wire was sealed into the lid of the measuring cell (Fig. 1), and the specimen A was placed in the anode compartment of the cell, separated from the cathode compartment by a tap B cooled internally with running water. The potential of the anode was measured relative to a saturated calomel electrode via the bridge C. The anode compartment of the cell was fitted with double walls (not shown in the diagram) to keep the temperature constant. When immersed in the solution, the specimen was subjected to anodic polarization at constant current strength; after definite time intervals (from 30 min to 5-6 h depending on the rate of corrosion of the anode) the whole of the anolyte was poured rapidly through the lower tap D, which had a wide opening, the cell and electrode were washed with the same hot solution, and a fresh portion of solution was then poured into the cell through tap E (the replacement of the solution took 1-2 min). The anolyte which had been poured off was brought to a standard volume (200 ml) and its radioactivity was determined on the γ -spectrometer. The experiments were carried out simultaneously with two identical cells connected in series (while the current in one of the cells was switched off for the removal of the anolyte the cell was shunted by means of a specially chosen resistance and this made it possible to avoid interrupting the polarization process in the other cell during this operation).

The standard specimen was dissolved in hot aqua regia and the resulting solution, after the necessary dilution, was examined on the γ -spectrometer and used as a calibration solution for calculating the rate of corrosion. To

* The use of a γ -spectrometer makes it possible to record the radioactivity of the individual γ -isotopes without preliminary radiochemical separation of the latter and makes it possible to decrease the background by approximately two orders of magnitude, which is particularly important in work with specimens of low activity.

† It is advisable that the specimens be as thin as possible in order to decrease their total radioactivity for a given surface area.

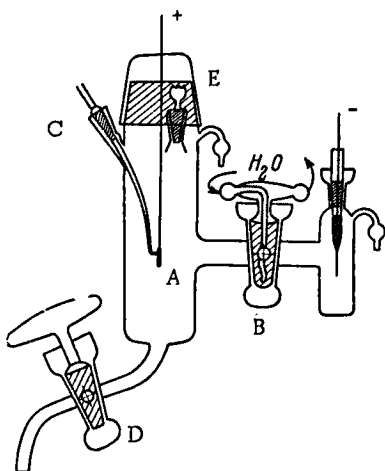


Fig. 1. Diagram of measuring cell.

magnitude of the background was 20 impulses for 30 min in the channel.* In the quantitative treatment of the γ -spectra we usually used the sum of the impulses in 10 channels arranged symmetrically about a given peak on the spectrum.

determine the extremely low rates of corrosion of the platinum anodes it was necessary to use comparatively high total levels of radioactivity (several tenths of a millicurie per specimen at the start of the experiment), so that all the operations with the specimens were carried out behind a protective screen and the cells were placed behind a lead wall. The γ -radioactivity of the specimens was measured by means of a single-crystal 100-channel scintillation γ -spectrometer [2]. To ensure that the sensitivity of the γ -spectrometer and the energy scale remained constant, we carried out periodic measurements with the radioactive isotopes Cr^{51} , Hg^{203} and Am^{241} . A single crystal of NaI(Tl) (diameter 40 mm, height 50 mm) was used as γ -radiation detector. The scintillation counter was screened by means of a lead wall (thickness 50 mm), which weakened the external γ -background and also acted as a thermostat. The radioactivity of the solution was measured with a cylindrical glass cell with a ground glass lid and a recess in the lower part, into which the crystal was placed. The measurement of the activity of the specimens took 2-30 min. Before each measurement we recorded the γ -background of the cell filled with water; the average

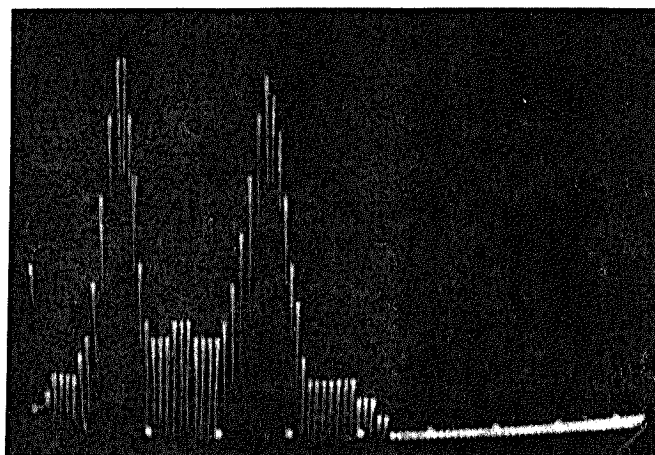


Fig. 2. Histogram for the solution after the anodic polarization of radioactive platinum.

A photograph of the histogram for the spectrum of sodium chloride solution in which a radioactive platinum specimen was subjected to anodic polarization is shown in Fig. 2. The energy corresponding to the left-hand peak amounts to 0.07 MeV and that of the right-hand peak to 0.16 MeV. To identify the isotopes corresponding to these peaks, their decay curves were recorded. The decay curve for the right-hand peak is linear and corresponds to a half-life period $T = 3.1$ days; the decay curve for the left-hand peak is complex: in the first few days after irradiation is stopped, its activity is due chiefly to a short-lived isotope, apparently Pt^{197} with $T = 18$ h, whereas after five days it corresponds to a half-life period $T \approx 3$ days. Analysis of the literature data [3-5] indicates that the right-hand peak corresponds not to radioactive platinum, as Japanese workers have assumed [6, 7], but to the isotope Au^{199} formed from the short-lived isotope Pt^{199} with $T = 30$ min, whereas the left hand peak corresponds to the platinum isotopes Pt^{191} , Pt^{193} , Pt^{195} and Pt^{197} , which have similar energies. Because of the complex nature of the decay curves corresponding to the left hand peak, it is better, instead of introducing a correction for the decay of radioactive plat-

* The background can be observed visually in the form of the histogram (the representation of the collected spectrum on the oscilloscope) when not less than 50 impulses are counted in the channel.

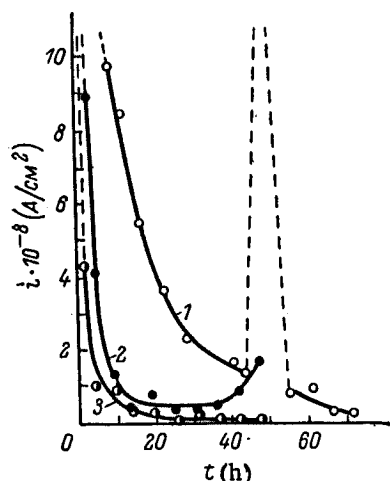


Fig. 3. Time dependence of the rate of dissolution of a platinum anode at a current density of 100 mA/cm². 1) Without preliminary treatment; preliminary treatment of specimen: 2) cathodic polarization for 35 min in NaCl solution; 3) treatment for 40 min in hot concentrated HNO₃.

fers to a specimen which was kept beforehand for 40 min in hot concentrated nitric acid. For the first 5-6 h after the start of electrolysis the rate of dissolution of the platinum anodes is relatively high and decreases rapidly with time. Thus, for curves 2 and 3 in the first 30-60 min after the start of electrolysis the rates of dissolution amounts to $5 \cdot 10^{-6}$ and $1 \cdot 10^{-6}$ A/cm² respectively (not shown in Fig. 3). This effect, which was also observed earlier [8], is not related to the predominant transfer of radioactive impurities to the solution during the initial stage of the electrolysis, since in the calculation of the rate of dissolution we used only the peak corresponding to platinum isotopes. The immersion of the platinum anode in the solution apparently leads to the gradual dissolution of the surface oxide film [9], which has no passivating properties, and the extremely slow attainment of the passive stationary state characterized by the stable low rate of dissolution. It can be seen from Fig. 3 that in the case of platinum anodes which were not subjected to preliminary treatment the stable stationary rate of corrosion is attained only 60-70 h after the start of electrolysis (curve 1). The rapid attainment of the stationary rate of corrosion of the platinum specimen is facilitated by preliminary cathodic polarization (curve 2) and also by preliminary passivation in hot concentrated nitric acid (curve 3). When the anodes are treated in this way, 20-30 h are sufficient for the attainment of the stable low rate of corrosion, which lies in the range $2 \cdot 10^{-9}$ to $5 \cdot 10^{-9}$ A/cm² ($3.6 \cdot 10^{-6}$ to $9.1 \cdot 10^{-6}$ mg/cm² · h). It should be noted that the stable rate of corrosion lies in the same range for the anode which was not subjected to preliminary treatment.

A distinguishing feature of the corrosion behavior of platinum anodes is the marked effect of interruption of electrolysis on the rate of corrosion. For example, in the experiment corresponding to curve 1, in the time interval from 47 to 52 h, the electrolysis was interrupted for approximately 20 min, the platinum specimen remaining in the same solution at a high temperature (after the current was interrupted, the electrode was subjected to anodic polarization for a further period of approximately 30 min, after which the solution was replaced). As a result of this interruption, the average rate of dissolution of the anode after 6 h increased to $1.4 \cdot 10^{-7}$ A/cm² (broken section of curve 1) and the rate of corrosion, referred to the time interval after the interruption, was naturally still higher. Analogous activation of a platinum specimen is observed if a specimen in the stable passive state is subjected to anodic polarization in hot hydrochloric acid and afterwards used as anode in a solution of sodium chloride under ordinary conditions.

* The rate of dissolution refers to the middle of the time interval for which the anode was immersed in the given portion of solution.

inum, to measure the activity of the calibration solution at intervals as well as that of the main specimens of solution and to use these measurements for the calculations.

In the measurements on specimens of radioactive solutions whose activity exceeded that of the background by one order of magnitude or more, the statistical errors were fairly small; under these conditions the error in the measurements was determined chiefly by the accuracy of operation of the counting assembly and did not exceed 10%. In the case of specimens with low activities, when the measured values exceeded the background by a factor of approximately three, the error in the measurements was due chiefly to static scatter and did not exceed 25%.

Results of Experiments and Discussion

We used the above method to determine the rate of corrosion of platinum anodes during continuous electrolysis for 60-80 h in NaCl solution (270 g/liter) at a current density of 100 mA/cm² and a temperature of 80° with periodic rapid replacement of the anolyte at intervals of 3-6 h. The pH of the solution was 4-5 and remained almost unchanged during the experiment.

The time dependence of the rate of dissolution of the platinum anode is shown in Fig. 3.* Curve 1 refers to a specimen which was not subjected to preliminary treatment; curve 2 refers to a specimen which before the start of the experiment was subjected to cathodic polarization ($i = 100$ mA/cm²) for 35 min in the same solution; and curve 3 refers to a specimen which was kept beforehand for 40 min in hot concentrated nitric acid. For the first 5-6 h after the start of electrolysis the rate of dissolution of the platinum anodes is relatively high and decreases rapidly with time. Thus, for curves 2 and 3 in the first 30-60 min after the start of electrolysis the rates of dissolution amounts to $5 \cdot 10^{-6}$ and $1 \cdot 10^{-6}$ A/cm² respectively (not shown in Fig. 3). This effect, which was also observed earlier [8], is not related to the predominant transfer of radioactive impurities to the solution during the initial stage of the electrolysis, since in the calculation of the rate of dissolution we used only the peak corresponding to platinum isotopes. The immersion of the platinum anode in the solution apparently leads to the gradual dissolution of the surface oxide film [9], which has no passivating properties, and the extremely slow attainment of the passive stationary state characterized by the stable low rate of dissolution. It can be seen from Fig. 3 that in the case of platinum anodes which were not subjected to preliminary treatment the stable stationary rate of corrosion is attained only 60-70 h after the start of electrolysis (curve 1). The rapid attainment of the stationary rate of corrosion of the platinum specimen is facilitated by preliminary cathodic polarization (curve 2) and also by preliminary passivation in hot concentrated nitric acid (curve 3). When the anodes are treated in this way, 20-30 h are sufficient for the attainment of the stable low rate of corrosion, which lies in the range $2 \cdot 10^{-9}$ to $5 \cdot 10^{-9}$ A/cm² ($3.6 \cdot 10^{-6}$ to $9.1 \cdot 10^{-6}$ mg/cm² · h). It should be noted that the stable rate of corrosion lies in the same range for the anode which was not subjected to preliminary treatment.

The rate of corrosion of platinum anodes depends to a marked extent on the potential. The above values for the stable stationary rate of dissolution of platinum are observed at potentials of 1.4-1.5 V (relative to a normal hydrogen electrode), whereas, when the potential is displaced to more positive values, the rate of corrosion increases considerably. This effect is illustrated by curve 2 in Fig. 3: in the time interval from 15 to 35 h the platinum anode had a potential of 1.40-1.55 V, after which the potential began to be displaced gradually towards more positive values* and after 48 h reached a value 1.75 V; it can be seen that this displacement of the potential is accompanied by an increase in the rate of corrosion by a factor of more than three. If the current density is decreased from 100 to 10 mA/cm² after the stationary stable rate of dissolution of the platinum anode is attained, its potential is displaced towards more negative values and the rate of corrosion decreases considerably. The stable rate of dissolution of the platinum anodes in the range of high anodic potentials is apparently determined primarily by the value of the potential.

Although the results which we have obtained in the study of the corrosion of platinum anodes are of a preliminary nature, they show that the stable constant rate of dissolution of the anodes is attained after comparatively short time intervals not exceeding 1-2 days, so that the above radiochemical method can be used for the accelerated quantitative estimation of the corrosion resistance of platinum anodes. The use of platinum isotopes with a half-life period of approximately three days for the determination of the rate of corrosion, together with the high sensitivity of the proposed method, make it possible, when necessary, to carry out corrosion tests over a more prolonged period (up to 10 days). It should be noted that the sensitivity of the method may be increased considerably, not only by increasing the specific radioactivity of the specimens but also by increasing their surface area and decreasing the volume of solution, and also by using scintillators with a special shape ensuring much more favorable geometrical conditions for measuring the radioactivity (crystals with a pit).

It is of interest to compare the above method with the analogous method used by Japanese workers [6, 7] to study the dissolution of platinum electrodes in dilute hydrochloric acid. Since in this work the platinum specimens were irradiated with a beam of comparatively low intensity ($5.1 \cdot 10^{11}$ neutron/cm²·sec) for a short time interval (2 h) while the radioactivity was determined by means of a single-channel γ -spectrometer,† the sensitivity of the determination of the rate of dissolution of platinum was smaller by several orders of magnitude than that for our experiments. The first paper [6] contains only qualitative conclusions regarding the corrosion of platinum; in the second paper [7] the rate of dissolution of a platinum anode in 0.1 N HCl solution at a current density of $4.5 \cdot 10^{-5}$ A/cm² (anode potential 1.9 V) was estimated quantitatively by carrying out the electrolysis for 95 h, after which the volume of the solution was decreased by a factor of 20 by evaporation and its activity was measured for a period of 60 min. In the calculation of the rate of corrosion the authors made use of calibration from a Co⁵⁷ standard instead of the more accurate method involving relative measurements with a calibration solution. During the experiment, approximately 13 layers of platinum were transferred to the solution, which corresponds to an average dissolution current of the order of 10^{-8} A/cm² and lies outside the limit of sensitivity of the method, since the measured activity exceeded the background by only 25%. For comparison it may be noted that in our experiments, at a rate of corrosion of $5 \cdot 10^{-9}$ A/cm² (curve 2 in Fig. 3), after dissolution of the anode for 6 h, the measured activity (without concentration of the solution) exceeded the background by a factor of five.

Since the sensitivity of their method was comparatively low, the Japanese workers were unable to detect the increased rate of dissolution of the platinum electrodes in the initial stage of the electrolysis; it is also doubtful if their conclusion that no dissolution of platinum takes place during cathodic polarization is correct.‡

Mention must also be made of the possibility of using a more simple radiometric apparatus for the radiochemical determination of the rate of corrosion of platinum anodes. In earlier work [8] we used for this purpose an ordinary end-face counter and B-2 radiometric apparatus. Naturally this recorded not only the radioactivity of the

* We were unable to determine the reason for this displacement; it is possibly due to a slight increase in the value of the pH [8].

† In a single-channel spectrometer the different sections of the γ -spectrum are passed in sequence, whereas in the multichannel spectrometer which was used in our work the impulses are recorded in all channels simultaneously. Thus, other conditions being equal, the use of a multichannel spectrometer makes it possible to increase considerably the sensitivity of the measurements.

‡ Preliminary data indicate that with cathodic polarization (100 mA/cm²) under the conditions of our experiments for 10 h after the start of electrolysis, transfer of radioactive platinum to the solution is observed, the rate of this transfer decreasing with time (the measurements were not continued until a stationary rate of corrosion of the platinum cathode was attained). This phenomenon, like the increased rate of dissolution of the platinum anodes in the initial stage of the electrolysis, is apparently due to breakdown of the oxide film on the platinum surface [9].

platinum isotopes but also that of their decay products (radioactive gold and iridium isotopes) and also that of possible radioactive contaminants, so that correct results can be obtained only if the transfer of all the radioactive components of the anode to the solution takes place in uniform fashion. Our preliminary data indicate that the chief radioactive impurity (Au^{199}) goes into solution at the same rate as the radioactive platinum isotopes. The radiation from the long-lived iridium isotopes (products of the radioactive decay of platinum isotopes) in the first few days after the irradiation of the platinum specimens is stopped and can be neglected and surface radioactivity contaminant can apparently distort the results only in the initial stage of the electrolysis. Thus generally speaking it is possible to determine the rate of corrosion of platinum by means of a radioactive assembly with an end-face counter and it is not necessary, before the measurement of the activity of the specimens, to separate the radioactive platinum isotopes from the daughter Au^{199} isotope. The chief advantage of the method involving the use of the γ -spectrometer is the much higher sensitivity (by approximately two orders of magnitude) and also the fact that no additional operations with radioactive samples (evaporation, preparation of targets, etc.) are required.

In conclusion it should be noted that, thanks to the high sensitivity of the above radiochemical method involving the use of a γ -spectrometer, it can be used for the accelerated estimation of the rate of corrosion of various metals and alloys with a high corrosion resistance, both with anodic polarization and for the case of dissolution without the application of an external current, so long as the corrosion products do not remain on the specimen but pass into solution. In particular, this method appears extremely promising for solving the problems of the rate of dissolution of the different components of alloys (e.g., stainless steels) both in the initial stage of the corrosion process and under conditions of stationary dissolution.

SUMMARY

1. Examination of a radiochemical method developed for determining the rate of corrosion of passive metals, based on the preliminary neutron activation of the test specimens with subsequent determination of the concentration of radioactive corrosion products in the solution by means of a 100-channel scintillation γ -spectrometer, has shown that the proposed method can be used for the quantitative estimation of the corrosion resistance of platinum anodes in hot concentrated sodium chloride solutions.

2. It has been shown that in the initial stage of the electrolysis the rate of corrosion of platinum anodes is comparatively high and decreases rapidly with time; 1-2 days after the start of electrolysis a stable constant rate of dissolution of the anodes, amounting to $2 \cdot 10^{-9}$ to $5 \cdot 10^{-9}$ A/cm², is attained. It has been concluded that the stationary passive state of a platinum anode is attained extremely slowly and is readily broken down when the electrolysis conditions are changed (by interrupting the electrolysis or displacing the potential); the stable rate of dissolution of a passive anode is determined chiefly by its potential.

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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.
