CONTINUOUS DETERMINATION OF CORROSION RATES OF METALS BY MEANS OF TAGGED ATOMS AND MEASUREMENT OF QUANTITY OF ABSORBED OXYGEN

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The authors make a comparative assessment of the possibilities of continuous determination of metal corrosion rates by means of tagged atoms and by measuring the amounts of oxygen absorbed during corrosion. Using both these methods, they investigate the corrosion of copper with oxygen depolarization in solutions containing sulfuric or perchloric acids. They show that the results of the two methods agree and supplement one another. The results confirm that the corrosion mechanism of copper is catalytic.

In studies of the kinetics and mechanism of the corrosion process it is often necessary to make continuous determinations of the process rate. Since conjugate electrochemical reactions (ionization of metal and reduction of depolarizer) occur on the surface of a metal during corrosion, the development of the corrosion process with time can be followed by means of the loss of mass of the metal or of the amount of depolarizer, and also by means of the increase in the amount of solution products of the metal or reduction products of the depolarizer.

If the aggressive medium is a liquid and the corrosion products of the metal dissolve in it, then by measuring the rise in the concentration of metal ions in solution we can continuously determine the rate of corrosion. Losev et al. [1, 2] have described a similar method of continuous determination of the rate of solution of a metal, based on the use of radioactive isotopes; the apparatus permits simultaneous electrochemical and radiometric measurements (the ERM method). The essence of the method is that the metal is tagged with a radioactive isotope and the rise in radioactivity in the solution is measured and the rate of solution of the metal thus calculated [1, 2].

When the depolarizer is oxygen, the corrosion rate can be continuously determined with high sensitivity by means of the fall in the amount of depolarizer with time. This method, based on continuous registration of the amount of oxygen absorbed during corrosion (the OA method), was described by Kiss [3]. In this case, the principle of the measurement is that the oxygen expended on corrosion is compensated by oxygen obtained electrolytically, and the quantity of electricity used to liberate the electrolytic oxygen is used to calculate the amount of corroded metal per unit time [3].

The aim of our work was to compare and assess the possibilities of the ERM and OA methods. The corrosion of copper with oxygen depolarization was studied by both methods in solutions with perchloric acid or sulfuric acid. The choice of copper was dictated by the fact that its true corrosion rate in acid solutions with oxygen depolarization, determined by a direct method,* is higher than that found by extrapolation of the Tafel sections of the polarization curves at stationary potential [4], so that in this case an indirect electrochemical method gives too low a value for the corrosion rate. Since both the OA method and the electrochemical method

* By a direct method we mean one which gives direct kinetic information on the process, i.e., one which enables us to make direct measurements of the rate of consumption of a reagent, e.g., the metal, or of the rate of formation of the products.

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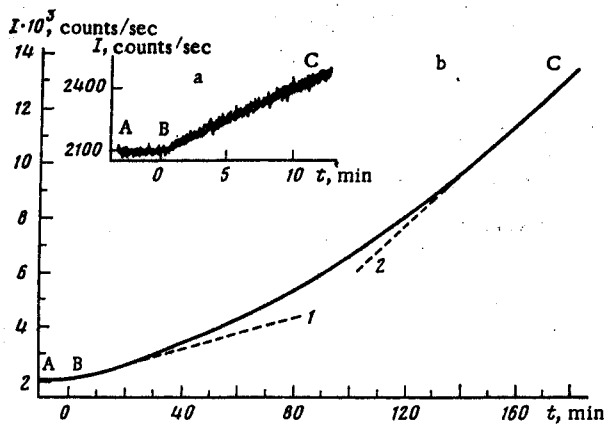

Fig. 1

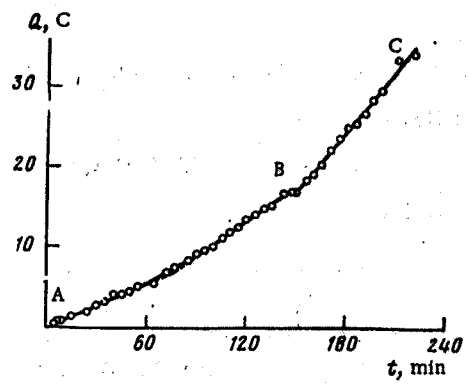

Fig. 2

Fig. 1. Variation of radioactivity of solution during corrosion of copper in sulfuric acid saturated with oxygen.

Fig. 2. Variation of quantity Q of electricity expended on oxygen during corrosion of copper in oxygen-saturated perchloric acid solution.

are indirect ways of determining the corrosion rate, to compare the ERM and OA methods it is necessary to compare the absolute corrosion rates of copper measured by the two methods in identical conditions.

From the principles and descriptions of the methods [1-3] we can distinguish their main possibilities and drawbacks.

The ERM method can be used with any depolarizer; in particular, it enables us to determine the solution kinetics of a metal at the very start of corrosion (within 1-2 sec). It enables us to determine the partial rates of solution of the components of an alloy and the true corrosion rate not only in the absence of polarization but also during passage of a current, in particular during cathodic protection. Moreover, the method enables us to find and compare the true corrosion rate and the rate determined from electrochemical measurements in identical conditions. It enables us to determine the kinetic parameters of the reaction of ionization of a metal (the rate constant, the transport coefficients, and the activation energy) [5]. However, the ERM method can be used only if the corrosion products of the metal go into solution from its surface and the metal itself has a suitable isotope for the measurement.

An important advantage of the OA method is that we can use it to obtain correct values of the corrosion rate even when the corrosion products remain on the surface of the metal in the form of insoluble compounds. It can also be used to study atmospheric corrosion. However, it gives correct results only in corrosion with oxygen depolarization, and the initial corrosion rate can be measured only after 1-3 min. A shortcoming of the apparatus [3] is that electrochemical measurements cannot be made simultaneously. To obtain correct results it is necessary to seal off the working volume of the cell, because access of air would lead to an underestimation of the corrosion rate.

A comparison between the possibilities of the ERM and OA methods shows that they can supplement one another.

The measurements were made in aqueous solutions of 3 M $HClO_4$ and 1.5 M H_2SO_4 saturated with air or oxygen at 22 ±2°C (for ERM) or 25 ±0.1°C (for OA). We used rolled electrolytic sheet copper OSCh-11-4 (99.999%) and Cu-ER copper (99.9%), and double-distilled (chemically pure grade) acid and water. The air and oxygen were purified by passing them through a cotton filter, concentrated solutions of sulfuric acid and caustic soda, double-distilled water, activated carbon, and double-distilled water. The details of the method and the apparatus were described in [1-3]. In the ERM method we used a cell similar to that described in [6], and the apparatus for continuous registration of the radioactivity of the solution was based on a PI-4 ratemeter, a USD-1 counter, a PV-2 supply unit, and an ÉPP-09 recording potentiometer. In the radiochemical experiments the copper was labeled with the isotope ^{64}Cu by neutron irradiation in a reactor. The gases were bubbled continuously through the working solution.

Spontaneous solution of copper was studied in solutions of pure acids and in solutions of acids with various concentrations of copper ions. In the ERM method, the concentration $[Cu^{2+}]$ of Cu^{2+} ions in solution varied

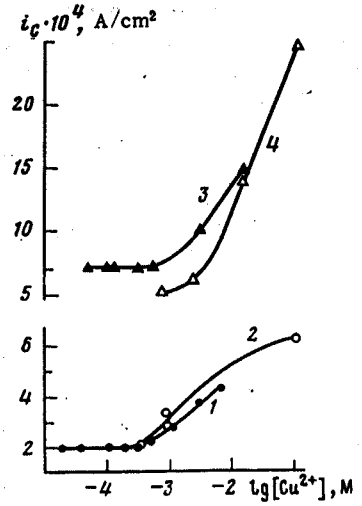

Fig. 3

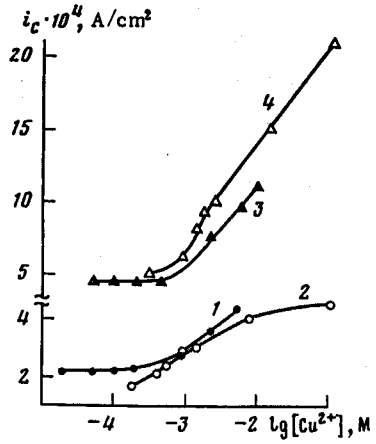

Fig. 4

Fig. 3. Corrosion rate of copper vs concentration of Cu^{2+} ions in 3 M $HClO_4$, saturated with air (1, 2) or oxygen (3, 4). 1, 3) ERM method; 2, 4) OA method.

Fig. 4. Corrosion rate of copper vs concentration of Cu^{2+} ions in 1.5 M H_2SO_4, saturated with air (1, 2) or oxygen (3, 4). 1, 3) ERM method; 2, 4) OA method.

either on account of spontaneous solution of the copper, or (in a study of the influence of high $[Cu^{2+}]$ values) by anodic solution of copper; in the case of the OA method, it varied on account of spontaneous solution of copper and on account of addition of chemically pure grade $CuSO_4$ to the electrolyte.

Figures 1 and 2 illustrate the main feature of the methods – continuous registration of the corrosion rate. Figure 1 plots the results obtained by the ERM method. Section AB corresponds to the background count. In recording the background level, the copper electrode was cathodically protected at −0.6 V relative to an S. H. E. The start of corrosion (point B) corresponds to time t = 0. After subtraction of the background count, the quantity I (the number of radioactive decays registered per second in the solution) is proportional to the concentration of copper in the solution. In the initial period (Fig. 1a) the rate of corrosion of copper, i_c, determined from the slope of BC, is nearly equal to $4 \cdot 10^{-4}$ A/cm² (point C corresponds to a Cu^{2+} concentration of $1.5 \cdot 10^{-5}$ M in the solution). The corrosion rate found in the same experiment (by extrapolation of the Tafel section of the cathodic polarization curve of reduction of oxygen to the stationary potential) was equal to $i_e = 4 \cdot 10^{-5}$ A/cm². Thus, in agreement with the previous results [4], the true corrosion rate of copper is higher than that determined by the indirect electrochemical method, and is independent of the Cu^{2+} concentration in the range 0-$1.5 \cdot 10^{-5}$ M.

In a long-term experiment (Fig. 1b), there is a marked rise in the Cu^{2+} concentration in the solution (at point C it is equal to $6 \cdot 10^{-3}$ M). In the figure the curve is smoothed and corrected for decay of the isotope ^{64}Cu (half-life 12.8 h). We see that at the start of the experiment i_c is less than at the end (the corresponding figures are $4 \cdot 10^{-4}$ and 10^{-3} A/cm²). Thus an increase in the Cu^{2+} concentration leads to a rise in the corrosion rate.

Figure 2 shows the results obtained by the OA method. Note that the first experimental point (value of Q) does not correspond to time zero, because 1-3 min are required after the start of the experiment for oxygen to be absorbed in the corrosion process and for the electrolyzer to start to replace it. In this time $6 \cdot 10^{-6}$ g-atom of copper can be corroded away. In section AB, on account of corrosion the copper concentration in the solution gradually rose to $1.3 \cdot 10^{-3}$ M, and there was some rise in the corrosion rate. At point B, $CuSO_4$ was added to make the total Cu^{2+} concentration $1.1 \cdot 10^{-2}$ M. As we see from the figure, this led to a marked increase in the corrosion rate.

Thus, both methods permit continuous study of the corrosion rate of copper and give qualitatively concordant pictures of the development of the corrosion of copper with time and of the influence of the Cu^{2+} concentration.

Figures 3 and 4 compare the results obtained by the ERM and OA methods. We give the mean values of i_c for 2-4 measurements. The maximum deviation from the mean is close to ±20% for both methods. Since

the values of i_c for OSCh 11-4 and Cu-ER agree within the experimental error,* in Figs. 3 and 4 we give the mean values of i_c for the two grades of copper. We see that within the error of measurement the two methods give equal values for the rate of spontaneous solution, and consequently continuous determination of the rate of corrosion from the quantity of absorbed oxygen gives reliable results.

The above laws of corrosion of copper agree with the idea that this process has a catalytic mechanism [4, 7].

According to this mechanism, the metal dissolves mainly on account of two conjugate electrochemical reactions according to the scheme

$$M \rightarrow M^+ + e \quad (1)$$

$$\frac{M^{2+} + e \rightarrow M^+}{M + M^{2+} \rightarrow 2M^+} \quad (2)$$

and the oxidant (Ox) is reduced in the layer next to the electrode on account of a chemical reaction involving intermediate low-valence ions,

$$Ox + M^+ \rightarrow Ox^- + M^{2+}, \quad (3)$$

regenerating M^{2+} ions.

As we see from scheme (1)-(3), in this mechanism an important part is played by the capability of the metal of forming intermediate low-valence particles in the course of the discharge–ionization process [8]; in this case they are Cu^+ ions. In the course of chemical reaction (3), these reactive particles donate an electron to the oxidant more easily than the electrode does in the electrochemical reaction, and thus they promote (catalyze) the reduction of the oxidant. This ultimately leads to an increase in the corrosion rate. An important feature of this mechanism is that the true corrosion rate should be greater than the value found by extrapolation from electrochemical measurements [4]. This was indeed observed in the experiments.

Moreover, as shown by a kinetic analysis of scheme (1)-(3), during corrosion in a solution with finite volume we should observe autocatalytic acceleration of the corrosion process with rise of the M^{2+} concentration. The data in Figs. 1-4 confirm the presence of the autocatalytic effect during corrosion [7, 9-11]. As seen from Figs. 3 and 4, in the experiments with air i_c starts to increase at $[Cu^{2+}] \approx (2\text{-}3)\cdot 10^{-4}$ M, but in the experiments with oxygen, at $[Cu^{2+}] \approx 10^{-3}$ M; in the latter case, the absolute value of i_c is 2-4 times higher than in the experiments with air.

Evidently the above corrosion behavior of copper is consistent with mechanism (1)-(3).

Judging by the experimental data (Figs. 3 and 4), there is no marked difference between the corrosion behavior of copper in solutions of perchloric and sulfuric acids: In both cases corrosion follows scheme (1)-(3).

Thus, the experimental data obtained by the two independent methods agree, and confirm that the corrosion of copper with oxygen depolarization in acidic aqueous solutions follows a catalytic mechanism.

It follows that the ERM and OA methods supplement one another, and by using them together we can obtain additional information on the corrosion process. Thus, the ERM method can determine low corrosion rates (in the given conditions, the sensitivity of the ERM method is about 10^{-6} A/cm^2, that of the OA method $5\cdot 10^{-4}$ A/cm^2), and can measure the corrosion rate at the start of the process. In particular, this enabled us to study the influence of very small values of $[Cu^{2+}]$ on i_c and to elucidate the region in which i_c is practically independent of $[Cu^{2+}]$ (see Figs. 3 and 4). On the other hand, the OA method has advantages. Although both methods can measure very high rates of solution of metal (up to $5\cdot 10^{-2}$ A/cm^2 for the OA method and up to several A/cm^2 for the ERM method), in some cases the ERM method has a limitation at relatively low values of i_c. This occurs when an appreciable amount of radioactive corrosion products has accumulated in the solution, creating a high level of radioactivity, so that against this background it is difficult to reliably determine a low corrosion rate. Therefore, the ERM method could not determine i_c in solutions with $[Cu^{2+}] > 10^{-2}$ M, for which, according to the OA method, $i_c \leq 2.5$ mA/cm^2. At the same time, the OA method gives good results at higher $[Cu^{2+}]$ values (Figs. 3 and 4).

* This shows that in these conditions impurities in the copper have little effect on its corrosion.

In conclusion, we must mention another possibility which appears when we compare the results obtained from the two methods. If insoluble corrosion products are formed, the value of i_c found by the ERM method must be less than that found by the OA method; so on the basis of the corrosion rates determined by the two methods we can estimate what fraction of the corrosion products consists of insoluble compounds. Since the ERM method is direct in relation to ionization of the metal, and the OA method is direct in relation to reduction of the oxidant, their combination is a direct method of studying the corrosion of metals with oxygen depolarization as a whole, enabling us to obtain complete and direct information on the kinetics of the conjugate reactions of the corrosion process.

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CORROSION AND MECHANICAL PROPERTIES OF VERY PURE HIGH-CHROMIUM FERRITIC STEELS ALLOYED WITH MOLYBDENUM AND PALLADIUM

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The authors investigate the mechanical properties, cold-brittleness temperature, and corrosion properties of high-chromium (25% Cr) steel, very free from interstitial impurities (C + N), and study the influence of 2% Mo and 0.3% Pd, added to the steel, on these properties. They find that Pd improves the corrosion resistance of the steel in hot acids for wide ranges of concentrations of sulfuric acid and dilute hydrochloric acid. The simultaneous presence of 2% Mo increases the stability of the passive film.

In the production of stainless steels there is a tendency to develop and adopt high-chromium ferritic steels of high purity, obtained by special methods of melting [1-3]. They have high corrosion resistance and improved technological properties – e.g., they can be welded. However, like standard high-chromium steels,

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