THE CORROSION OF METALS UNDERGOING STEPWISE DISSOLUTION. THE CORROSION MECHANISM OF INDIUM IN ACIDIC SOLUTIONS

A. P. Pchel'nikov and V. V. Losev

UDC 620.193.01:669.87

A theoretical analysis is carried out of the corrosion mechanism of a metal which undergoes stepwise dissolution involving the formation of unstable particles of low valency. It is shown that in this case, corrosion follows a complicated electrochemical and chemical mechanism, which involves electrochemical and chemical steps in the formation of the final corrosion product. It is established by comparing experimental corrosion rates with extrapolated hydrogen ion discharge rates that in pure perchlorate solutions, indium corrosion follows an electrochemical and chemical mechanism, while in chloride solutions it occurs via an electrochemical mechanism.

Where the anodic dissolution of a metal, $M \rightleftharpoons M^{n+} + ne$, occurs stepwise and with the formation of unstable, low-valency metal particles, e.g., of ions M^+:

$$M \xrightarrow{v} M^+ + e, \tag{1}$$

the latter may become oxidized to stable ions of higher valency M^{n+}, not only at the anode:

$$M^+ \xrightarrow{v_1} M^{n+} + (n-1)e, \tag{2}$$

but also via reactions with solution components (hydrogen ions, oxygen, etc.) [1]:

$$M^+ + (n-1)Ox \xrightarrow{v_2} M^{n+} + (n-1)Ox^-, \tag{3}$$

or may diffuse into the bulk of the solution with a rate $v_3 = (D/\delta)[M^+]_S$.

In the general case, reactions (1)-(3) can occur in the absence of external polarization, too, whereupon the corrosion rate of the metal must rise above the value corresponding to the usual electrochemical corrosion mechanism [2]. Thus, the corrosion of a metal which during its dissolution produces unstable, low-valency particles, must proceed via a complex electrochemical and chemical mechanism involving several stages:

(i) transition of ions M^+ into solution via an electrochemical mechanism, via the anodic reaction (1) and a coupled cathodic reaction

$$Ox + e \xrightarrow{v_4} Ox^-; \tag{4}$$

(ii) the electrochemical oxidation of ions M^+ by (2), compensated by reaction (4);

(iii) the chemical oxidation of ions M^+ by solution components, reaction (3).

Without external polarization, the sum of the rates of the anodic reactions (1) and (2) must equal the rate of cathodic reduction of the oxidizing agent via [4]:

$$Fv + (n-1)Fv_1 = Fv_4, \tag{5}$$

where the rates v, v_1, and v_4 are expressed in g-atom/cm^2 · sec.

L. Ya. Karpov Physicochemical Scientific-Research Institute, Moscow. Translated from Zashchita Metallov, Vol. 8, No. 6, pp. 673-678, November-December, 1972. Original article submitted June 11, 1971.

In the stationary state, the rate of formation of M^+ ions (v), which represents the corrosion rate of the metal, equals the sum of the rates of subsequent oxidation ($v_1 + v_2$) of these ions and of their diffusion into the bulk of the solution (v_3)*:

$$v = v_1 + v_2 + v_3. \tag{6}$$

From (5) and (6) we obtain a relation linking the corrosion rate with the rates of cathodic reduction of the oxidizing agent, of chemical oxidation of the M^+ ions, and of their diffusion into the bulk of the solution:

$$nFv = Fv_4 + (n-1)F[v_2 + v_3], \tag{7}$$

whence we find the corrosion rate in g-atom/$cm^2 \cdot$ sec as

$$v = \frac{v_4 + (n-1)[v_2 + v_3]}{n}. \tag{8}$$

In the general case, the M^+ ions may become oxidized, not only by the Ox particles but also by other solution components. For a metal with high hydrogen overvoltage, the transition of M^+ ions into solution may occur at the expense of cathodic oxygen reduction, while its chemical oxidation can occur, on the whole, via interaction with hydrogen ions or water molecules.

The following limiting cases are possible, depending on the ratio of the rates of the parallel reactions (2) and (3) as well as of the diffusion of M^+ ions into the bulk of the solution:

A) $v_1 \gg v_2 + v_3$; here the M^+ ions are oxidized practically wholly electrochemically at the metal surface. For these conditions we find from (6) that $v = v_1$, and from (7) that

$$nv = v_4. \tag{9}$$

In this case the dissolution of one g-atom of metal is accompanied by reduction of n g-atoms of oxidizing agent. Therefore, the rate of corrosion i_c, now expressed in electrical units, equals that of the coupled cathodic process which is measured, e.g., by extrapolation of the cathodic polarization curve to the stationary potential (i_c^e):

$$i_c = nFv = Fv_4 = i_c^e, \tag{10}$$

i.e., corrosion occurs via the usual electrochemical mechanism.

B) $v_1 \ll v_2 + v_3$; here the M^+ ions are oxidized practically wholly chemically via reaction (3) at the metal surface and in the bulk of the solution. Hence, we obtain $v = v_2 + v_3$ from (6), and we find on inserting the sum $(v_2 + v_3)$ into (7) that

$$v = v_4. \tag{11}$$

In this case the dissolution of 1 g-atom of metal is accompanied by the reduction of only 1 g-atom of oxidizing agent. When the corrosion rate i_c is calculated as for case A, viz., from the relation $i_c = nFv$ (which means that the M^{n+} ions as the final corrosion product are assumed to be formed electrochemically), we obtain with (11)

$$i_c = nFv = nFv_4 = ni_c^e. \tag{12}$$

Hence the corrosion rate i_c thus found is n times as high as the rate of the coupled process i_c^e which has been calculated by extrapolating the cathodic polarization curve to the stationary potential. †

* In the general case, the quantities v and v_1 represent the differences in the rates of reactions (1) and (2) in the anodic and cathodic direction [2]. However, consideration of this fact is of no consequence for the results obtained when analyzing the effect of various parameters upon the corrosion rate of the metal. It is assumed, moreover, that there are no M^{n+} ions in the starting solution, and that their accumulation during corrosion can be neglected. In so far as reaction (3) occurs in the bulk of the solution and not only at the metal surface, the concentration of M^+ ions in the bulk of the solution may be assumed to be zero.

† In case B the M^+ ions are only oxidized via reaction (3), and are in essence the final product of a one-electron electrochemical reaction. Strictly speaking one should therefore assume n = 1 when calculating the corrosion rate in electrical units, and then the usual relation $i_c = i_c^e$ is obtained. However, in the general case, i.e., when the rates of steps (2) and (3) are comparable, one must know the ratio between the rates of these steps in order to calculate i_c, which requires additional experimental data; therefore, the conventional way for calculating i_c which is shown above is more convenient.

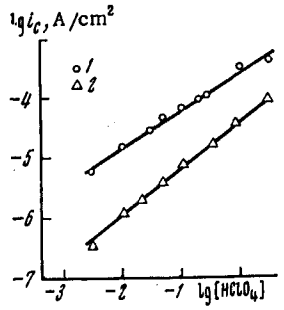

Fig. 1

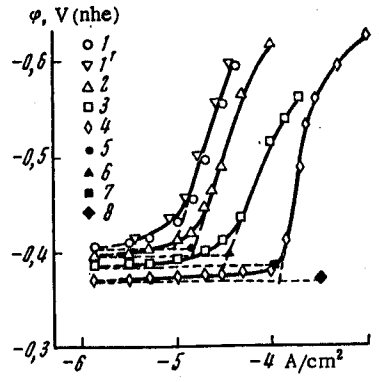

Fig. 2

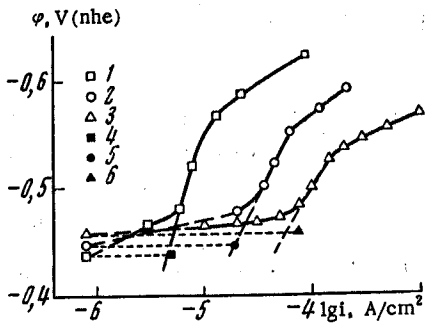

Fig. 3

Fig. 1. The corrosion rate of indium as function of $HClO_4$ concentration for the solutions: xM $HClO_4$ + (3 − x) M $NaClO_4$ (1) and xM $HClO_4$ + (2.8 − x) M $NaClO_4$ + 0.2 M NaCl (2).

Fig. 2. Cathodic polarization curves on indium for solutions: xM $HClO_4$ + (3 − x) M $NaClO_4$ with x values of: 1) $1 \cdot 10^{-2}$ M; 2) $6 \cdot 10^{-2}$ M; 3) 0.27 M; 4) 1 M. 1') The partial curve for hydrogen ion discharge at x = 0.01 M; 5-8) the corrosion rates of indium as calculated from the radiochemical data for x values of $1 \cdot 10^{-2}$ M, $6 \cdot 10^{-2}$ M, 0.27 M, and 1 M, respectively.

Fig. 3. Cathodic polarization curves for solutions: x M $HClO_4$ + (2.8 − x) M $NaClO_4$ + 0.2 M NaCl with the x values: 1) $5 \cdot 10^{-2}$ M; 2) 0.27 M; 3) 2.8 M; 4-6) the corrosion rates of indium as calculated from radiochemical data for the x values: $5 \cdot 10^{-2}$, 0.27, and 2.8 M, respectively.

Thus, if there is a discrepancy between the experimental corrosion rate i_c of a metal and the rate i_c^e of the coupled cathodic process as extrapolated to the stationary potential, this is an indication that the metal corrodes via the complex electrochemical and chemical mechanism discussed. The extent to which the ratio i_c/i_c^e deviates from unity can serve as a quantitative measure for the contribution of the electrochemical/chemical mechanism to the overall corrosion rate. In the general case this ratio obeys the condition $1 \leq i_c/i_c^e \leq n$.

Indium is a convenient material for experimentally detecting and studying corrosion occurring by this mechanism. It has been shown previously [3] that in acidic perchlorate solutions, the anodic dissolution of indium occurs stepwise and involves the formation of unstable In^+ ions:

$$In \rightarrow In^+ + e, \tag{13}$$

which can be oxidized further both at the electrode

$$In^+ \rightarrow In^{3+} + 2e, \tag{14}$$

and by hydrogen ions (H^+) in the solution

$$In^+ + 2H^+ \rightarrow In^{3+} + H_2. \tag{15}$$

The effective valency of the indium ions going into solution, which depends on the ratio of the rates of reactions (14) and (15), tends toward unity in strongly acidic solutions and also when the potential of indium is shifted to the negative side [1, 3]. The effective valency increases up to a value of 3 when chloride ions are present, which accelerate reaction (14) [3, 4]. One can suggest on the basis of these data that in sufficiently acidic perchlorate solutions, the oxidation of univalent indium ions by hydrogen ions will lead to a marked increase in the corrosion rate of indium relative to the value which is calculated by extrapolating the cathodic polarization curve.

It is the aim of the present work to elucidate the corrosion mechanism of indium in acidic perchlorate solutions and to study the effect of chloride ion additions upon this reaction.

The corrosion rate of indium was determined radiochemically in nitrogen atmosphere at 20° on a rotating electrode in the cell described before [5], using $HClO_4$ + $NaClO_4$ solutions of different acidities but constant ionic strength (μ = 3 M). The electrode was prepared by electrodepositing indium onto platinum. The indium electrode was cathodically prepolarized in weakly acidic solution at $i = 3 \cdot 10^{-6}$ A/cm²

TABLE 1. The Corrosion Rate of Indium in Solutions of Different Composition (μ = 3 M)

Solution composition	i_c, A/cm^2	i_c^e, A/cm^2	i_c/i_c^e
$1 \cdot 10^{-2}$ *M* $HClO_4$	$1{,}42 \cdot 10^{-5}$	$9{,}55 \cdot 10^{-6}$	1,49
$6 \cdot 10^{-2}$ *M* $HClO_4$	$3{,}4 \cdot 10^{-5}$	$1{,}38 \cdot 10^{-5}$	2,46
0,27 *M* $HClO_4$	$1{,}05 \cdot 10^{-4}$	$3{,}3 \cdot 10^{-5}$	3,18
1 *M* $HClO_4$	$3{,}15 \cdot 10^{-4}$	$1{,}2 \cdot 10^{-4}$	2,64
$5 \cdot 10^{-2}$ *M* $HClO_4$ + 0,2 *M* NaCl	$4{,}9 \cdot 10^{-6}$	$4{,}47 \cdot 10^{-6}$	1,1
0,27 *M* $HClO_4$ + 0,2 *M* NaCl	$1{,}86 \cdot 10^{-5}$	$1{,}86 \cdot 10^{-5}$	1
2,8 *M* $HClO_4$ + 0,2 *M* NaCl	$7{,}25 \cdot 10^{-5}$	$5{,}63 \cdot 10^{-5}$	1,29

until it attained $\varphi = -0.42$ V (nhe) before the corrosion rate was determined. The corrosion rate v (in g-atom/cm^2 · sec) found from the radiochemical measurements was converted to electrical units using the usual relation $i_c = 3Fv$, inasmuch as trivalent indium ions are the final corrosion product. The cathodic polarization curve was recorded right after the corrosion rate measurement.

Figure 1 shows the corrosion rate of indium as function of acidity for pure perchlorate solutions (curve 1) and for the same solutions also containing NaCl (curve 2). The i_c increase in both cases with acidity, but are lower in the presence of Cl^- ions than in pure perchlorate solutions.

The data for direct determinations of the self-dissolution rate of indium were compared with polarization measurements (Fig. 2). It can be seen that the cathodic curves are displaced toward higher current densities as the acidity increases, and that they are very steep.* It was shown by radiochemical measurements which were performed while recording the cathodic polarization curve that even in 0.01 M $HClO_4$, the part of the current spent on cathodic deposition of indium (which had gone into solution during prior corrosion) was no more than 3-10% (cf. curve 1' in Fig. 2), and it was still less in more acidic solutions. Therefore, the cathodic curves represent practically only hydrogen ion discharge, and by extrapolating them to the stationary potential one can find the rate of the coupled cathodic reaction of hydrogen evolution, i_c^e, in the corrosion of indium.

Values for the corrosion rate of indium in the corresponding solutions which were determined radiochemically (i_c) are shown together with the polarization curves in Fig. 2. It can be seen from this figure as well as from Table 1 that the ratio i_c/i_c^e substantially exceeds unity, and approaches three with increasing acidity. This result shows that the univalent indium ions forming during corrosion with hydrogen depolarization at $HClO_4$ concentrations above 0.1 M are practically not further oxidized at the electrode but are transformed into stable In^{3+} ions via the chemical reaction (15).† In fact, when the univalent ions are oxidized entirely by solution components, one must have according to (12)

$$i_c = 3i_c^e, \tag{16}$$

which is in good agreement with our experimental data.

Thus, indium corrosion in acidic perchlorate solutions occurs via the above complex electrochemical / chemical mechanism.

The electrochemical oxidation of the In^+ ions (14) is strongly accelerated in the presence of chloride ions [3, 4]. It could be suggested in this connection that in acidic chloride solutions, indium corrosion will occur via the electrochemical mechanism. It can in fact be seen from Fig. 3‡ and from Table 1 that the corrosion rate of indium measured radiochemically in such solutions practically coincides with that found by extrapolating the hydrogen evolution curve. Thus, in this case one has

$$i_c = i_c^e, \tag{17}$$

corresponding to the usual electrochemical corrosion mechanism (10).

* The slope of these curves decreases at potentials more negative than −0.6 to −0.7 V, and Tafel sections with the usual slopes (0.115-0.12 V) are observed, in harmony with literature data [6, 7].

† It has been shown previously [8, 9] that the oxidation of In^+ ions (15) is a first-order reaction with respect to H^+ ions.

‡ The addition of NaCl accelerates the discharge of indium ions in perchlorate solutions [4]. Therefore, cathodic polarization curves for hydrogen ion discharge were recorded in a separate experiment in order to avoid any noticeable accumulation of indium ions in solution during the radiochemical measurements of corrosion rate.

The corrosion rate of indium in sufficiently acidic solutions would have to be lowered upon chloride addition by a factor of 3 relative to pure perchlorate solutions of the same acidity if chloride ions had no effect on the kinetics of cathodic hydrogen evolution and of reaction (15). It is apparent from Fig. 1 in the meanwhile that at acidities above 0.1 M, the corrosion rate of indium decreases by almost one order of magnitude upon the addition of chloride. This divergence is caused by the increase in hydrogen overvoltage on indium when chloride is present. In fact, at constant potential ($\varphi = -0.5$ V) and given acidity, the hydrogen evolution rate on indium is lower in the presence of chloride (Fig. 3) than in pure perchlorate solutions (Fig. 2), e.g., by a factor of 2.5 in 0.27 M $HClO_4$. The overall reduction in indium corrosion rate, given as the ratio i_c/i_c^e for pure perchlorate solutions multiplied with the corresponding figure for the above drop in hydrogen evolution rate when NaCl is present, is in satisfactory agreement with the drop in indium corrosion rate observed experimentally in the presence of chloride ions.

Thus, it follows from the analysis given and from the experimental data that the corrosion of indium in pure perchlorate solutions occurs via a complex electrochemical and chemical mechanism, while in chloride solutions it occurs via an electrochemical mechanism.

We express our gratitude to Academician Ya. M. Kolotyrkin and to A. I. Molodov for their valuable advice during the discussion of the results of the present work.

CONCLUSIONS

A theoretical analysis is carried out of the corrosion mechanism of a metal which undergoes stepwise dissolution involving the formation of unstable particles of low valency. In this case, corrosion follows a complex electrochemical and chemical mechanism, which involves electrochemical and chemical steps in the formation of the final corrosion product.

The rate of indium corrosion was measured radiochemically in pure perchlorate solutions and in the same solutions containing NaCl (0.2 M) covering a wide range of $HClO_4$ concentrations ($3 \cdot 10^{-3}$ to 3 M). It is established by comparing experimental corrosion rates with hydrogen ion discharge rates extrapolated to the stationary potential that in pure perchlorate solutions, indium corrosion follows an electrochemical and chemical mechanism, while in chloride solutions it occurs via an electrochemical mechanism.

LITERATURE CITED

1. A. I. Molodov, G. N. Markos'yan, and V. V. Losev, Élektrokhimiya, 5, 918 (1969).
2. V. V. Losev and A. P. Pchel'nikov, Elektrokhimiya, 4, 264 (1968).
3. A. P. Pchel'nikov and V. V. Losev, Zashchita Metal., 1, 482 (1965); Proceedings of the Third International Congress on Metal Corrosion [in Russian], Mir, Moscow (1968).
4. A. P. Pchel'nikov and V. V. Losev, Élektrokhimiya, 5, 284 (1969).
5. A. P. Pchel'nikov and V. V. Losev, Élektrokhimiya, 1, 1058 (1965).
6. J. N. Butler and M. Dienst, J. Electrochem. Soc., 112, 226 (1965).
7. A. L. Rotinyan and E. D. Levin, Élektrokhimiya, 6, 328 (1970).
8. A. P. Pchel'nikov and V. V. Losev, Zh. Fiz. Khim., 41, 971 (1967).
9. R. E. Visco, J. Phys. Chem., 69, 202 (1965).