Physical Chemistry

1961

SovietRxiv

Abstract

Full Text

Physical Chemistry

Ya. M. Kolotyrkin and V. A. Gil’ man

The Influence of Chlorine Ions on the Electrochemical and Corrosion Behavior of Zirconium

(Presented by Academician A. N. Frumkin on 20 X 1960)

Judging from the available data ($^{1-4}$), zirconium and many alloys based on it possess good corrosion resistance both in solutions of alkalis and in solutions of many mineral acids, including solutions of HNO_3 and moderately concentrated solutions of H_2SO_4. The stability of Zr in solutions containing chlorine ions depends substantially on the nature of the other components of the solution. Thus, for example, Zr has good corrosion resistance in pure solutions of HCl and chlorides of many metals ($^{1-3}$), whereas in mixed solutions of $HCl + HNO_3$, and also in solutions of $FeCl_3$ and $CuCl_2$, appreciable dissolution of this metal is observed (^{2,3}).

On the basis of the results of works ($^{1-4}$), it does not appear possible to establish the true causes of such a difference in the corrosion properties of zirconium in the indicated solutions. Unfortunately, the authors of these investigations limited themselves to determining the magnitude of the corrosion losses, without taking into account the electrode potential of the corroding metal. At the same time, the noted difference in the behavior of Zr is apparently due to the difference in the potentials established on it in these solutions. This is confirmed, in particular, by the results of works (^{5,6}), according to which the good corrosion resistance noted above in pure solutions of HCl and chlorides of alkali metals can be disturbed by applying anodic polarization and shifting the electrode potential to a certain critical value.

To understand the observed influence of the composition of the solution and other experimental conditions on the corrosion behavior of Zr in chloride solutions, in the present work a more detailed study was made of the dependence of the dissolution rate of this metal on the potential.

To solve this problem, the potentiostatic method described earlier (^{7,8}) was used, with the aid of which measurements were carried out in 1.0, 0.1, and 0.01 N solutions of HCl, and also (for comparison) in 1.0 N solutions of H_2SO_4, KBr, and KJ. The electrodes were plates of zirconium sheet with a visible surface area of 1 and 3 cm^2. The Zr used had a purity of 99.8% (0.065% hafnium). Before the experiment the plates were degreased in sulfuric ether and then subjected to brief etching in 5% HF, followed by washing in tap water and in twice-distilled

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

water. For preparing the solutions, twice-distilled water and chemically pure HCl and H_2SO_4, distilled three times, were used. Before the experiment the solution was saturated for a long time with purified nitrogen, which was also passed through during the experiment itself.

The results of the measurements showed that in a 1.0 N H_2SO_4 solution the stationary potential and the rate of spontaneous dissolution of zirconium have values equal, respectively, to $-0.16 \div -0.18$ V* and $5 \cdot 10^{-7}$ A/cm^2**.

---

* Here, as everywhere below, potentials are given relative to the potential of the normal hydrogen electrode.

** These results are fairly close to the data obtained by Balashova and Kabanov (15).

The potentiostatic curve measured on Zr in a 1 N H_2SO_4 solution (Fig. 1, curve 1) shows that in this solution Zr is in the passive state even before anodic polarization is applied, and that this passivity is further preserved over the entire investigated range of potentials.

Transition to HCl solutions does not lead to any noticeable change either in the value of the stationary potential or in the rate of self-dissolution of zirconium. The dependence of the dissolution rate on the potential in these solutions at first follows the same curve as in the H_2SO_4 solution. However, such agreement is observed only up to a certain critical potential φ_{cr}, upon reaching which unrestricted dissolution of Zr begins, in the sense that, under stationary conditions, the value of this potential practically does not change with increasing current density. In galvanostatic measurements, however, this is manifested in the fact that an increase in the anodic current is accompanied only by a brief shift of the potential in the positive direction, after which it rather quickly returns to the initial value φ_{cr} (Fig. 2). Fig. 2 also shows that, in the process of decreasing the current density from high values, at φ_{cr} only a brief shift of the potential in the negative direction is observed, followed by its rapid return to the initial value.

Fig. 1. Potentiostatic curves for Zr in solutions: 1 –1 N H_2SO_4; 2 –1 N HCl; 3 –1 N KBr; 4 –1 N KJ

Fig. 2. Change of potential with time during successive increase and decrease of the anodic current density in 0.1 N HCl

Fig. 3

Figure 3: Fig. 3

The data obtained are confirmed by the results of measurements of charging curves (Fig. 3), which show that in the initial periods of time Zr is polarized to potentials lying appreciably more positive than φ_{cr}. It was found that the maximum magnitude of the deviation of the potential from φ_{cr} increases with increasing current density (at constant Cl^- concentration) and with decreasing Cl^- concentration (at constant current density). The value of φ_{cr} depends substantially on the Cl^- concentration and is completely independent of the pH of the solution. Increasing the chloride concentration by a factor of 10 is accompanied by a shift of φ_{cr} toward negative values by an amount close to 65 mV. This result is in good agreement with data obtained earlier in works (5, 6).

The behavior of Zr in bromide and iodide solutions does not differ in principle from its behavior in chloride solutions. As can be seen from Fig. 1, the only result of passing along the series Cl^-—Br^-—J^- is a shift of φ_{cr} toward positive values. Special experiments established that the addition of a ferric salt to an HCl solution has the same effect on the behavior of Zr as the application of anodic polarization, i.e., it leads to a shift of the potential in the positive direction, and at a certain concentration of added—

of the salt being added, the potential reaches the critical value φ_{cr} and then does not change with an increase in the content of Fe^{3+} ions in the solution.

Visual observations showed that, upon reaching φ_{cr} (as a result of imposing anodic polarization or introducing Fe^{3+} ions into the solution), the dissolution of zirconium does not occur uniformly over the entire surface, but has a clearly pronounced local character and leads to the formation of pits. In this case, the number of pits increases with increasing density of the polarizing current; a decrease in the current, in turn, leads to passivation of some of the previously formed pits.

Fig. 3. Charging curves at $i = 5.0 \cdot 10^{-6}$ A/cm^2 in an HCl solution:
1—1.0 *N*; 2—0.1 *N*; 3—0.01 *N*.

On the basis of the data obtained, it may be concluded that the aggressive action of chlorine ions is associated in this case with depassivation of part of the metallic surface; moreover, the observed effect depends substantially on the density of the polarizing current and is fully reversible in the sense that, when the causes producing activation of the metallic surface are removed, the latter again passes into the passive state. The existence of such reversibility can be understood and explained if it is assumed that, under the conditions considered, two mutually competing processes proceed on the metal surface: passivating adsorption of water oxygen and displacement of this oxygen by halide ions.*

The fact that halide ions begin to displace oxygen only upon reaching a definite potential gives grounds for concluding that pitting corrosion can develop only in those cases in which the corroding metal under normal conditions has a higher affinity for oxygen than for the corresponding halide. The imposition of anodic polarization and the associated increase in the positive charge of the metallic surface, accompanied by polarization of the halide ions, apparently also leads to an increase in their chemical activity. For this reason, when a certain potential is reached, conditions are created at the surface under which the affinity of the metal for the halide begins to exceed its affinity for oxygen.

It is obvious that the possibility of adsorption displacement of passivating oxygen by halide ions is determined not only by the magnitude of the electrode potential, but also by the concentration of halide ions at the metal surface, which in each case must reach some critical value. As was recently shown by Engell and Stolica[9], the stimulating effect of chlorine ions on the corrosion of passive iron is observed only when a certain critical concentration of these ions in the solution is reached.

Naturally, the question arises: why, in this case, is not the entire metal surface depassivated, but only individual, comparatively small areas, the number of which increases with increasing current density? In our opinion, this is connected with the fact that the supply of halide ions to the metal surface is effected predominantly by their transport by the current. In favor of this assumption is the observed dependence of the effectiveness of the action of chlorine ions on the nature and concentration of the supporting electrolyte. The results of our measurements showed, for example, that the above-noted influence of Cl^- ions on the anodic dissolution of zirconium in a solution sulfates disappears completely when the ratio of the sulfate concentration to the chloride concentration becomes close to 5. If, however, perchlorate is used as the supporting electrolyte, the anion of which is singly charged, then the critical concentration ratio is practically doubled, i.e., becomes close to 9–11.

Taking into account that dissolution of a solid metal always proceeds with a certain nonuniformity and that, consequently, a nonuniform distribution of the anodic current over the surface always occurs, it is natural to expect that the concentration of halide ions reaches the critical value first of all at those few areas that dissolve at the highest rate. It is evident that the activation of these areas, once begun, causes an even more nonuniform current distribution and an even more directed supply of halide ions to them. Taking into account that φ_{cr} of zirconium in chloride solutions of ordinary concentrations lies at a potential appreciably more positive than the passivation potential of this metal, one may expect that dissolution of the active areas will proceed under diffusion limitation, owing to which an increase in the polarizing current must inevitably lead to an increase in the size or number of pits. For this reason the true current density always remains constant, which apparently accounts for the constancy

* A similar mechanism for the anodic behavior of Fe in alkaline chloride solutions was proposed earlier by Vanyukova and Kabanov[14].

of the potential observed experimentally over a broad range of current densities calculated with respect to the apparent surface.

It is natural to assume that halide ions, after displacing passivating oxygen, take direct part in the elementary act of ionization of zirconium atoms ([10,11]) by forming, as the primary dissolution products, complexes of the type $ZrCl_n^{(4-n)+}$. Under these conditions, however, one might expect inhibition of the process caused by the slowness of the supply of halide ions to the reaction zone. Measurements carried out by us showed that this conclusion is not consistent with experiment, since even at a comparatively low concentration of Cl^- an increase in the current density up to 100 ma/cm^2 does not cause a noticeable deviation of the potential from the critical value (see Fig. 1), but this result can be explained if one takes into account what was said above about the higher affinity of the metal for oxygen than for chlorine; for under these conditions the complex ions of the indicated type must inevitably hydrolyze as they diffuse from the metal surface into the solution, with the formation of oxygen-containing metal complexes and free halide ions, which can again take part in the process. Thus, without entering into the composition of the chemical products, the halide ions play the role of peculiar catalysts of zirconium corrosion.

Judging from the available data, the proposed mechanism of formation and development of pits on Zr is also applicable to a whole series of other metals, such as Mg ([12]), Al ([13]), Fe ([14]), and others.

Physical-Chemical Institute
named after L. Ya. Karpov

Received
13 X 1960

CITED LITERATURE

1. E. A. Gee, L. B. Golden, W. E. Lusby, Ind. and Eng. Chem., **41**, 1668 (1949).
2. D. F. Taylor, Ind. and Eng. Chem., **42**, 639 (1950).
3. L. B. Golden, I. R. Lane, W. L. Acherman, Ind. and Eng. Chem., **44**, 1930 (1952); **45**, 782 (1953).
4. I. R. Lane, L. B. Golden, W. L. Acherman, Ind. and Eng. Chem., **45**, 1067 (1953).
5. N. Hackerman, O. B. Cecil, J. Electrochem. Soc., **101**, 419 (1954).
6. M. Maraghini, G. B. Adams, P. Van Rysselberghe, J. Electrochem. Soc., **101**, 400 (1954).

7. Ya. M. Kolotyrkin, V. M. Knyazheva, ZhFKh, **30**, 1990 (1956).
8. V. M. Knyazheva, Ya. M. Kolotyrkin, DAN, **114**, 1265 (1957).
9. H. J. Engell, N. D. Stolica, Zs. Phys. Chem., N. F., **20**, 113 (1959).
10. Ya. M. Kolotyrkin, L. A. Medvedeva, ZhFKh, **29**, 1477 (1955).
11. V. V. Losev, A. I. Molodov, DAN, **130**, 111 (1960).
12. D. V. Kokoulina, B. N. Kabanov, DAN, **112**, 682 (1957); **120**, 558 (1958).
13. N. D. Tomashov, V. N. Modestova, *Studies on the Corrosion of Metals*, Publishing House of the Academy of Sciences of the USSR, 1951, p. 75.
14. L. V. Vannokova, B. N. Kabanov, DAN, **59**, 917 (1948).
15. N. A. Balashova, B. N. Kabanov, DAN, **121**, 126 (1958).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.