V. P. Maksimchuk and I. L. Rozenfel' d

1960

SovietRxiv

V. P. Maksimchuk and I. L. Rozenfel' d

Investigation of the Mechanism of the Activating Action of Chloride Ions by Means of Labeled Atoms

(Presented by Academician A. N. Frumkin, November 21, 1959)

The chloride ion is the most active anion capable of activating most metals that are in the passive state. The mechanism of this phenomenon has not been finally established, and on this question there are two theories: the film theory ([1,2]) and the adsorption theory ([3–5]).

In one of our works ([6]) it was established that the activating action of chloride ions on stainless steels can be completely suppressed not only by typical oxidizing agents, but also by sulfate ions. The interpretation of these results from the standpoint of the film theory of passivity encountered considerable difficulties, and therefore the suggestion was made that the processes occurring on the surface of alloys in the presence of various anions are of an adsorption character. In this case the passive state of the alloy surface should depend on which anions are preferentially adsorbed.

To confirm this point of view, measurements were carried out of the adsorption of chloride ions by a method using a radioactive indicator (Cl^{36}), with a half-life of $4 \cdot 10^5$ years and a specific activity of 0.058 mCu/g. The amount of adsorbed NaCl was determined from the change in the activity of a 0.01 N NaCl solution, samples being taken before and after adsorption. In order that these changes in NaCl concentration be significant, a porous electrode with a large surface area (about 10^4 cm^2), obtained by pressing chromium powder ([7]), was used. The use of a chromium electrode instead of a stainless-steel electrode is in principle possible, since it has been shown that it is precisely the presence of chromium in the composition of stainless steels that chiefly determines the passivating action of SO_4^{2-} ions. Adsorption was expressed as the amount of chloride ions absorbed from the solution by one specimen. In the electrolytic cell the cathode and anode compartments were separated by a tube with a ground joint, in order to prevent diffusion of the products of the cathodic reaction to the anode.

Into the anode compartment were poured 15 cm^3 of a 0.01 N solution of nonradioactive NaCl; the chromium electrode was immersed in it and its cathodic polarization was carried out at a potential of -1.2 V for 30 min. Then the inactive solution was replaced by a radioactive one with the same NaCl con-

centration. To establish equilibrium, the chromium electrode was kept in the active solution for one hour without polarization. Its stationary potential by this time was equal to −0.14 V. Then a sample of the solution was taken and the potential of the electrode was shifted by 100 mV in the positive direction, held for 30 min, another sample was taken, and the potential was again changed by 100 mV, and so on.

Figure 1 gives the curves of the dependence of chloride-ion adsorption on the electrode potential; on one electrode four measurements were carried out successively. Before each measurement the electrode was polarized cathodically in an inactive 0.01 N NaCl solution (potential −1.2 V, time 30 min).

It is characteristic that, despite identical conditions for carrying out all the experiments, the amount of adsorbed chlorine is different. In the first experiment, carried out on a fresh electrode after the preliminary treatment described, adsorption of chloride ions is observed only at large positive values of the potential (Fig. 1, 1), beginning at +1.3 V. But if after this the electrode is again subjected to cathodic polarization and the experiment is repeated

Fig. 1. Adsorption of Cl^- ions on one and the same chromium electrode. 1 —during the first measurement, 2 —during the repeated measurement, 3, 4 — during the third and fourth measurements.

Fig. 2. Dependence of adsorption of chloride ions from 0.01 N NaCl on time at $\varphi = 1.0$ V

in a fresh active NaCl solution, the absorption of Cl^- ions increases strongly; in this case it begins not at +1.3 V, but at +0.8 V. Thus, during the first measurement there occurs, as it were, an "activation" of the surface—a lowering of some barrier that hinders the adsorption of chloride ions on chromium. In the second experiment the maximum adsorption values are observed at all potentials. In subsequent experiments (Fig. 1, 3, 4) the number of adsorbed Cl^- ions decreases. This decrease can be explained by the fact that chloride ions irreversibly adsorbed in the preceding measurements hinder further absorption of Cl^-.

The irreversibility of the adsorption of chloride ions on chromium is directly evident from the fact that their desorption cannot be caused even by prolonged cathodic polarization at a potential of −1.2 V. The lack of reproducibility of the data obtained on one and the same electrode made it necessary to use a new electrode for each measurement; this electrode was preliminarily "activated" at a potential of +1.3 V for 20 min in a 0.01 N solution of nonradioactive NaCl, then subjected to cathodic polarization and to the other operations described above.

Figure 2 shows the change in adsorption of chloride ions with time at a constant potential equal to 1.0 V. As can be seen, the amount of adsorbed anions increases continuously during the first 2 hours; then saturation occurs and the curve proceeds with a slight upward slope.

Fig. 3 and Fig. 4 graphs

Figure 1: Fig. 3 and Fig. 4 graphs

Figure 3 presents the dependence of the amount of adsorbed chloride ions on the potential of the chromium electrode in NaCl solutions containing various concentrations of Na_2SO_4. Curve 1 corresponds to adsorption of Cl^- from a pure 0.01 *N* NaCl solution and coincides with curve 2 of Fig. 1. From a solution of 0.01 *N* NaCl +0.01 *N* Na_2SO_4 (Fig. 3, 2), a considerably smaller amount of chloride ions is adsorbed than from pure 0.01 *N* NaCl. In addition, the value of the potential from which Cl^- ions begin to be adsorbed in noticeable quantities is shifted somewhat in the positive direction.

If Na_2SO_4 is added in such an amount that the ratio $C_{Na_2SO_4} : C_{NaCl} \geq 10$ is satisfied, then no noticeable adsorption of chloride ions occurs even at large positive potentials (Fig. 3, 3).

Fig. 4 shows the influence of hydroxyl ions in a NaCl solution on the magnitude of adsorption of Cl^-. It should be noted that OH^- ions, in comparison with sulfate ions, hinder the adsorption of Cl^- ions much more strongly. Thus both SO_4^{2-} and OH^- ions have the ability to hinder the adsorption of chloride ions on chromium. On the other hand, it is known that these same ions are inhibitors of pitting corrosion of stainless steels containing chromium as an alloying element. Obviously, one may

Fig. 3. Adsorption of chloride ions on chromium:
1–from a 0.01 *N* NaCl solution; *2*–from a 0.01 *N* NaCl + 0.01 *N* Na_2SO_4 solution; *3*–from a 0.01 *N* NaCl + 0.1 *N* Na_2SO_4 solution

Fig. 4. Adsorption of chloride ions on chromium:
1–from a 0.01 *N* NaCl solution;
2–from a 0.01 *N* NaCl + 0.002 *N* NaOH solution

conclude that the indicated anions hinder the adsorption of chloride ions on the surface of chromium and of solid Fe–Cr solutions, thereby suppressing the pitting corrosion of stainless steels.

It may therefore be concluded that the first stage of the activating action of Cl^- on stainless steels is the chemisorption of Cl^- on the metal surface. If the chemisorption of chloride ions is prevented by introducing into the NaCl solution a sufficient quantity of foreign anions, such as SO_4^{2-}, OH^-, then the activating action of Cl^- will be suppressed, and consequently the cause of pitting corrosion will be eliminated.

The irreversibility of the adsorption of chloride ions, which follows from these experiments, casts doubt on the hypotheses of some authors ([2]) concerning a possible mechanism of the activating action of chloride ions on passive metals.

The data presented do not contradict the adsorption theory of the action of

chloride ions ([3], [4]).

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
5 XI 1959

REFERENCES

1. Yu. R. Evans, *Corrosion, Passivity and Protection of Metals*, 1941, p. 99.
2. T. P. Hoar, U. R. Evans, *J. Chem. Soc.*, 1932, 2476.
3. B. V. Ershler, *ZhFKh*, **18**, 131 (1944); Proceedings of the II Conference on Corrosion of Metals, 1943, p. 52.
4. L. V. Vanyukova, B. N. Kabanov, *ZhFKh*, **28**, 1025 (1954).
5. H. H. Uhlig, *J. Electrochem. Soc.*, **97**, 11, 215 (1950).
6. I. L. Rozenfeld, V. P. Maksimchuk, *DAN*, **119**, 986 (1958).
7. S. V. Tkachuk, N. N. Voronin, *ZhFKh*, **32**, 201 (1958).

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