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Abstract

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ON THE ROLE OF THE PRIMARY PROTECTIVE FILM IN THE PROCESS OF OXIDATION OF METALS IN AQUEOUS SOLUTIONS

The role of the primary—mostly oxide—protective film in the process of oxidation of metals in water and aqueous solutions can be explained in different ways. In a number of cases it may be assumed that, in the presence of a film, one cannot judge the interaction of the metal with the components of the solution, since the process is completely regulated by their diffusion through its thickness. Thus, when studying the mechanism of oxidation of the metal under investigation by a solution, it becomes necessary to apply special methods of preparing the metal surface, i.e., to remove the film before the experiment.

One may also put forward the proposition (see, for example, (ˆ1)) that a protective film is never continuous, and that the interaction of the metal with the surrounding medium (solution + gas) breaks down into two independent processes: one proceeding through the film, for example by the type of processes in vapors or gases, and another process—the direct interaction at exposed sites. Finally, one may assume that a more or less rapid destruction of the native film by the given liquid or liquid solution occurs. In this case the initial stages of the process must, naturally, differ from the subsequent ones, which proceed under a more or less established regime. The delay in the oxidation of metals by acids, observed in a number of cases at the initial stage of the process, can often be reduced to the presence of a gradually disintegrating protective oxide film.

Whether such destruction can also occur during the oxidation of metals in solutions of neutral electrolytes (neutral salts) and in pure water can be established only after studying the kinetics of the initial and subsequent stages of the process, and also by studying the processes of interaction of the presumed oxide compounds of metals with water and with the aqueous solutions under study, in order to judge the stability of these compounds. It is natural to suppose that, since under ordinary conditions of storage of metal specimens a native film of one thickness or another is formed under the action on the metal of air (oxygen and moisture, carbon dioxide and other gaseous or vaporous substances), it will not, in the general case, be in equilibrium with respect to the given solution, and interaction of the film with the solution should follow, changing its properties. The only exceptions may be cases of complete inertness of films with respect to

electrolytes, i.e., cases of films that passivate the metal (for example, films of complex composition on stainless steels).

Most metals form oxides and hydroxides that differ not only in their chemical composition but also in their phase composition. Studies of the processes of their interaction with electrolyte solutions show that the structure of the crystal lattice of an oxide or hydroxide is of very great importance, and that, with one and the same chemical composition, forms may be observed ranging from highly reactive to completely inert. We have such a series, for example, in the case of aluminum hydroxides, beginning with boehmite, which is very active with respect to solutions of salts (γ-AlOOH), and ending with the almost completely inert hydrargillite (γ-$Al(OH)_3$), which does not react with and does not adsorb even salts of aluminum itself from their

aqueous solutions, which react so vigorously with bayerite (α-$Al(OH)_3$) (2). The various crystalline modifications of iron oxides and hydroxides also differ in their reactivity and adsorption capacity. Goethite (α-FeOOH), for example, is hydrated to a greater extent than lepidocrocite (γ-FeOOH), which, moreover, is more basic. The rate of the indicated processes of interaction of oxides with the electrolyte and the attainment of an equilibrium state depend on the concentration of the electrolyte and on the temperature (other conditions being equal). It should therefore be expected that the influence, on the process of metal oxidation, of oxide or hydroxide films formed on the metal surface before its immersion in the solution will likewise depend to a high degree on these factors.

[Figure 1 and Figure 2 graphs]

Fig. 1. Kinetics of iron oxidation in the initial stage (first 60 min.) at 0 and 90°: 1 –4.0 (2.0) N KCl; 2 –1.0 N KCl; 3 –0.01 N KCl; 4 –0.001 N KCl; 5 – H_2O

Fig. 2. Change in the rate of oxidation of iron in water as a function of time

We studied the kinetics of oxidation of iron (steel) in the presence of air in water and in aqueous potassium chloride solutions at temperatures from 0 to 90° in the initial stage (minutes) and in subsequent stages (hours and days) (3). Visual observations already showed that the process in its initial stage is clearly topochemical in character, and that the pattern of change of the metal surface, on which corrosion centers appear and insoluble oxidation products are deposited, depends on the concentration of the solution, the residence time of the plates in the liquid, and the temperature. In water and dilute solutions at low temperatures the process has a more local character, only gradually passing into general corrosion; in more concentrated solutions at high temperatures the entire surface is subjected to oxidation at once.

The reaction was studied quantitatively by colorimetric and volumetric determination of the amount of oxidized metal*. Analysis of the curves obtained, $g - t$ (g –loss of weight, t –time), shows that at all temperatures, in the initial stage,

Figure 3

Figure 1: Figure 3

covering minutes, the reaction follows, at concentrations $N < 2.0$, a parabolic law ($g^2 = kt$), and at higher concentrations a cubic law ($g^3 = kt$) (see Fig. 1), i.e., from the very be–

* And at more remote stages, gravimetrically.

the process of oxidation is at first regulated by diffusion, and the rate constant k increases with temperature.

One might think that the whole matter lies precisely in the unremoved native film on the metal surface. However, in the present case this conclusion is incorrect. Study of the subsequent stages shows that the native (evidently oxide) film is destroyed the more rapidly, the higher the concentration and the higher the temperature; the diffusion process, however, is connected mainly with the formation of new deposits, already of another chemical and phase composition, which appear on the surface as it is gradually freed from the native film. This process is especially easy to observe at low temperatures in more dilute solutions. In Fig. 2 are given curves of the change with time of the rate of oxidation of iron in water, on which a minimum is found, the more distinct and embracing the larger time interval, the lower the temperature. This minimum indicates that at the very beginning (during minutes) the process proceeds at a constant value of the active surface (open), and then the reacting area begins gradually to increase owing to destruction of the film.

Fig. 3. Verification that the kinetics of oxidation of iron in water at 20 and 40° obey equations (1) and (2). $1, 2$ –experimental curves $g(t)$; $1_1, 2_1$ –curves obeying the quadratic equation $g_1(t)$; $1_2, 2_2$ –calculated curves $g_2(t)$ ($g_2 = g - g_1$); $1_3, 2_3$ –verification that the curves $g_2(t)$ obey equation (2).

Thus, the entire surface of the specimen may be divided into two parts: open (S_1) and occupied by the native film (S_2). The amount of oxidized metal g by time t in this case is expressed by

$$g = g_1 + g_2 = k_1 S_1 t^{1/n'} + k_2 S(t) t^{1/n}, \tag{1}$$

if it is assumed that, on the gradually opening surface as well, owing to the deposition of new insoluble products, the oxidation process obeys the same law as on the areas S_1 (k_1 and k_2 are kinetic constants referred to unit area).

The form of the function $S(t)$ must, evidently, be determined by the character of the interaction of the native film with the electrolyte. It may be assumed, for example, that this interaction obeys the same kinetic law as many chemisorption processes. If the native film is ultimately completely destroyed, then the surface

S_2 is also completely freed from it. And then, evidently, the function $S(t)$ must have the form of a hyperbola,

for example,

$$S = S_2 \frac{t - t'}{a \pm (t - t')}, \tag{2}$$

where a is the rate constant of the chemisorption process, and t' is the period of time during which the film has not yet begun to break down.

Depending on the ratio S_1/S_2 and the value of the constant, different forms of the curves $\Delta g/\Delta t - t$ should be obtained. At $S_2 \ll S_1$ the rate minimum should be shifted to the very beginning of the curve, and the oxidation rate should rise to a certain maximum. At $S_2 \lesssim S_1$ the maximum is shifted to later stages of the process.

The applicability of equations (1) and (2) was tested by us in the following manner.

If, for the initial stages of oxidation, a quantitative dependence has been found between the weight of oxidized metal (g_1) and time (the first part of equation (1)), then, obviously, the difference between the experimentally determined total amount of oxidized metal (g) and the calculated value of g_1 (according to the equation found) for more advanced stages should be equal to g_2 for the given time t; moreover, equation (2) is readily checked by reducing it to the linear form

$$\frac{(t - t')^{1+1/n}}{g - g_1} = \frac{1}{k_2 S_2 a} + \frac{1}{k_2 S_2}(t - t') \tag{3}$$

and plotting a graph in the corresponding coordinates. In Fig. 3 graphs are given which illustrate the applicability of the quadratic equation for g_1 and the validity of equation (2) for the case of oxidation of iron in water at temperatures of 20 and 40°. Similar results were obtained for 0 and 30°.

It follows from the data obtained that the native film on steel in water and in KCl solutions at temperatures below 50° is not destroyed immediately, but after some time—different in different cases—with variations from 1/4 to 2 h. The destruction of the film itself also occurs after different intervals, ranging from 6-8 h (0°, H_2O) to 2-3 h at higher temperatures. These variations are an obvious result of the nonidentical states of the surfaces of the specimens, and they could have been avoided (and more constant characteristics obtained) with carefully unified surface preparation.

In addition, it should be borne in mind that it is evidently not always possible to follow the destruction of the film to completion when the metal specimen is in a vertical position in the liquid, since the newly formed products may fail to

remain completely on the metal surface. This is precisely what occurs in the case of oxidation of iron under the indicated conditions. Ultimately the thickness of the layer reaches a certain definite value, which then remains constant. The curve $g(t)$ becomes a straight line, as do both of its components $g_1(t)$ and $g_2(t)$.

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