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Abstract

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ON THE CONDITIONS FOR DESTRUCTION OF THE PRIMARY FILM DURING THE OXIDATION OF ALUMINUM IN NEUTRAL SOLUTIONS

It is generally known that many metals, functioning as electrodes in aqueous solutions of neutral salts, under ordinary conditions are characterized by values of the electrode potential corresponding not to a pure metallic electrode, on which the reaction $Me \rightleftarrows Me^{n+} + ne$ proceeds unhindered, but to an electrode covered with an oxide film, with a substantially reduced reaction activity with respect to the transition of the metal into solution in the form of aqua-, aquoacido-, or aquohydroxo-ions. Aluminum also belongs to such metals; it is known for its relatively high passivity, precisely due to the phase film present on its surface, with low permeability for ions, electrons, or molecules (H_2O).

In work ([1,2]) on the kinetics of oxidation of aluminum in water and aqueous solutions under static conditions with access of air, it was shown that at low temperatures ($t^\circ \leq 25$), even in chloride solutions (KCl) at pH from 4.0 to 10.0, aluminum oxidizes slowly, following a linear law with a rate constant dependent on concentration. With an increase in temperature, however, the picture changes sharply, and in solutions of lower concentrations other regularities are observed than in more concentrated ones. In a narrow temperature range—$25 < t^\circ < 35$—in dilute solutions, and especially sharply in water, the reaction rate in its initial period, covering 8-10 days, increases rapidly with time. A parabolic law is obeyed ($\Delta g = kt^2$, where Δg is the loss of weight, k is a constant, t is time), which, however, is subsequently replaced by a logarithmic one ($\Delta g = k_1 \lg t + k_2$), and the reaction begins gradually to die out. In concentrated solutions ($N \geq 2$), the former regularities are obeyed.

The linear relationships are determined by the fact that the process during the period of observation (up to 360-720 hr) proceeded, first, with an undestroyed primary film and, second, with only an insignificant and constant-in-amount accumulation of secondary deposits that do not adhere firmly to the surface (amorphous aluminum hydroxide ([3])). The parabolic law, however, is clearly connected with the fact that the process is in the kinetic region of heterogeneous reactions, proceeding on the metal surface freed from the primary film

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

(cf. (4)). The subsequent attenuation already depends on new deposits separating out on the surface under the specified conditions. To trace the kinetics of the destruction itself of the primary film on aluminum, however, is considerably more difficult than can be done, for example, in the case of iron (5).

It was therefore of interest to establish the relationships between the kinetic regularities found for the oxidation of aluminum under the specified conditions and the changes with time of its electrode potential, as a function both of the solution concentration and of the temperature.

The experiments were carried out with the same grade of metal as in the kinetic studies (Al 99.6, with a surface preliminarily degreased with ether, etched with hydrochloric acid until the crystalline structure appeared, then thoroughly washed and dried over anhydrous calcium chloride). The potential was measured with a PPTV-1 potentiometer.

The reference electrode was a saturated calomel electrode, kept in the same thermostats at temperatures of 20, 25, 28, and 30°. The concentration of the solutions tested varied from 0.001 N to saturation ($\sim 4.0\ N$).

Figures 1 and 2 present the results of these experiments for 20 and 30°. The left-hand parts of the figures show the experimental data (averages of 5–6 experiments) for the initial stage, covering 3–5 hours; the right-hand parts show data for the subsequent stages, followed for up to 25–30 days. It is evident from the figures that

Fig. 1. Electrode potentials of aluminum in KCl solutions at 20°. The dashed lines show the potentials of individual specimens in a 0.001 N KCl solution

Fig. 2. Electrode potentials of aluminum in KCl solutions at 30°

after the first irregular fluctuations, potential values become established which, in all solutions, remain practically constant during the indicated period.*

Within the measurement errors, these values are related to the chloride concentration by a logarithmic dependence

$$\varepsilon = \varepsilon_0 + k \lg C_{\mathrm{KCl}} \tag{1}$$

where $\varepsilon_0 \sim 500$ mV (20°) and 520 mV (30°), and $k \sim 60$–70 mV. Similar relationships were obtained in work (6) in the region of high concentrations.

Such con– the concentration dependence indicates that, in the indicated temperature interval, the aluminum electrode at the initial stage functions as a complex electrode with an undestroyed primary film, partially transformed in its surface layer into a complex oxychloride, whose structure could be represented by the formula

$$(\mathrm{Al_2O_3})_n(\mathrm{Al(OH)_3})_m \cdot \mathrm{Al}_x(\mathrm{OH})_{3x-1}\mathrm{Cl} \tag{2}$$

or, in the absence of hydrated forms of the oxide,

$$(\mathrm{Al_2O_3})_n \cdot \mathrm{Al}_x\mathrm{O}_x\mathrm{Cl}_x. \tag{3}$$

Upon further observation of the state of aluminum electrodes in KCl solutions, however, differences are found in their behavior in solutions of different concentrations as the temperature and observation time increase.

At 20° (see Fig. 1, its right-hand part), in solutions of all concentrations, with time there is a relatively uniform change of potential to a definite, somewhat more negative value; moreover, the indicated dependence on concentration is retained, although the constants of equation (1) change somewhat. However, in individual specimens in dilute solutions sharp deviations are sometimes observed, as is clearly seen from Fig. 1.

At 30° (see the right-hand part of Fig. 2), in dilute KCl solutions, after approximately a day, a very sharp displacement of the potential in the negative direction occurs, and after 2–3 days it reaches values comparable with the value of the potential of a bare metallic aluminum electrode (1.2 V). This sharp rise is followed by a decline in the opposite direction.

Comparing these data with the kinetic regularities indicated above, one can indeed speak of the destruction of the primary oxide film that has occurred, accompanied by intense hydrogen evolution. Since the described changes are observed mainly in highly dilute solutions, whereas in more concentrated ones ($N = 2.0$–4.0) no special changes, in contrast to those observed at 20°, are recorded, the conclusion in work (^{1}) may be considered valid: the destruction of the film is mainly of a hydration character; this distinguishes the primary film on aluminum from the film on iron (^{5}) and requires certain favorable conditions. In subsequent stages the rapid increase in the oxidation rate also leads to the rapid accumulation of secondary insoluble products, giving new surface deposits (for their chemical and phase composition, see (^{3})) and again creating an obstacle to the diffusion of the reaction components.

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* For this period no kinetic data are available: the rate of metal oxidation is small and cannot be accounted for by ordinary measurement methods. In the works cited in the text, the first kinetic data refer to days.

Fig. 3. Kinetics of oxidation and electrode potentials of aluminum in 0.001 and 2.0 N KCl solutions at 30°

Figure 3: Fig. 3. Kinetics of oxidation and electrode potentials of aluminum in 0.001 and 2.0 N KCl solutions at 30°

The intermediate temperature interval 25-28° may be called transitional: at 25° the processes taking place are closer in character to those observed at 20°, while the processes at 28° differ little from those observed at 30°. In this narrow interval, random irregular shifts of potential are also observed more often, apparently associated with the beginning "weakening" of the film. A transitional region of salt concentrations is also indicated, lying within the limits from 0.1 to 1.0 *N* KCl.

As is seen from Fig. 2, the fall of the potential after reaching the maximum proceeds considerably more slowly than the rise, which is evidently connected with the formation of a new complex electrode, considerably more negative than the initial one, of a polyoxychloride type. The concentration dependence of the potential on the solution composition at this stage remains undefined because of the continuous change of the potential with time (as also of the oxidation rate: logarithmic law). Apparently, in this region the potential generally becomes independent of the chloride concentration, since the composition of the deposits on the metal surface changes. According to the X-ray and thermographic data of work (^{3}), under the indicated conditions bayerite (α-Al$(OH)_3$)—boehmite-type deposits are formed on the aluminum surface.

(γ-AlO(OH)) precipitates, with a ratio of components changing with time, and consequently with a changing solubility product.

From a comparison of the results of the present study with kinetic data it follows that the relative constancy with time of the electrode potential of aluminum, established in KCl solutions, is also matched by the constancy of the rate of oxidation of the metal in these solutions (linear law). Changes in the potential values, however, correspond to definite changes in the rates of oxidation. In Fig. 3 these relations are presented for 0.001 and 2.0 *N* solutions at 30° (the kinetic data are taken from (1)).

Fig. 3. Kinetics of oxidation and electrode potentials of aluminum in 0.001 and 2.0 *N* KCl solutions at 30°.

It does not follow from this correspondence, of course, that the rate of oxidation is unambiguously determined by the electrochemical behavior of the metal under the conditions studied. In the region of applicability of the linear law of oxidation kinetics, the electrode potentials of aluminum increase with the concentration of KCl (equation (1)), whereas the rate constants of the linear equations (see (1)) pass through a maximum as the chloride concentration changes, the position of which depends on temperature: at 20—25° this maximum lies in the region of 1.0—2.0 *N*, while at 28° it shifts to 0.1 *N*. This fact, one must suppose, is connected with the mixed mechanism of aluminum oxidation (which proceeds at the expense of oxygen and water), as well as with the conditions that arise for diffusion through the thickness of the deposits. The question requires further study. Experiments at higher temperatures are in progress.

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