STUDIES ON THE EFFECT OF SOME ANIONS ON THE CORROSION AND ELECTRODIC BEHAVIOUR OF ALUMINIUM

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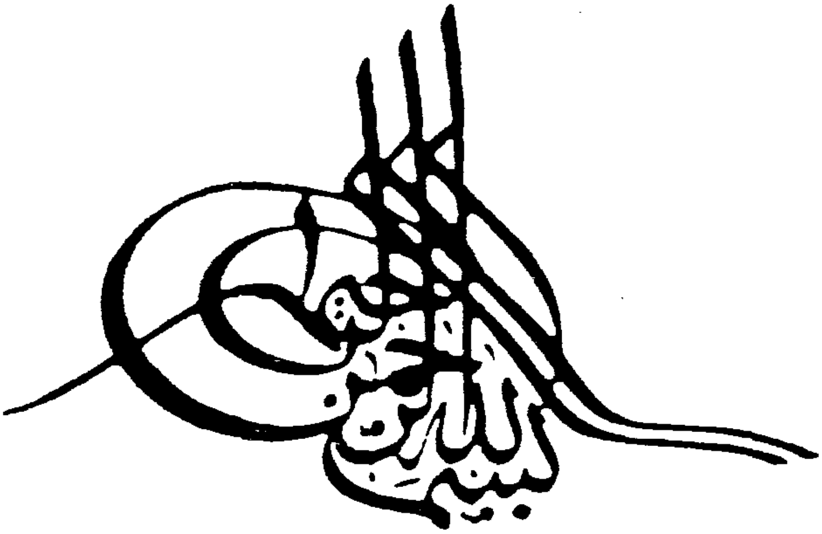
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NOTE

The candidate has attended postgraduate courses for two semesters in physical and inorganic chemistry, covering the following topics:

(1) Advanced electrochemistry and corrosion.
(2) Chemical kinetics.
(3) Quantum chemistry.
(4) Advanced surface chemistry.
(5) Photochemistry.
(6) Spectroscopy.
(7) Micro-analysis.
(8) Thermodynamics.
(9) Instrumental analysis

She has successfully passed a written examination in these courses.

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INTRODUCTION

INTRODUCTION

In studies connected with the corrosion of metals, the corrosion of iron and steel has drawn the attention of many workers in the field, because of the economic problems arising from the various uses of iron and steel in every day life. The corrosion of nonferrous metals, although it is so important as that of iron and steel, has yet occupied only a second place. Some of the earlier investigations of the electrochemical behaviour and corrosion of aluminium are reviewed below.

The effect of the anions on the potentials of aluminium in aqueous solutions was determined by Engang and Masing(1). Curves are given for Al in buffered and unbuffered solns. of NaBr, NaCl, KI, and Na_2SO_4 at temps. up to 80° show that the potential of Al depends upon the anion of the electrolyte, its concentration, and temperature.

Tomashov and Modestova(2) studied polarization curves and the neg. difference effect (increasing of the self-soln. rate with anodic polarization) of 99.935 % Al (I) (Fe 0.004, Si 0.02, Cu 0.03, Zn 0.009, Mg 0.002 %), tech. Al (II) (Fe 0.19, Si 0.11, Cu 0.01, Zn 0.04 %) and Duraluminium(III) (Fe 0.3, Si 0.48, Cu 4.17, Mg 1.5, Mn 0.64 %), in 0.5 N NaCl soln. at 25° at c.ds. up to 100 ma./sq. cm. The rate of soln. was measured by H evolution. The pH of the anodic compartment approached 4.2. The rate of self-soln. increased proportionally to the c.d. For I and II, the rate was const. with time and constituted 13-13.5 % of the anodic electrolytic soln. rate: For III, the rate first increased and then decreased, the max. rate of the self-soln. was 33.5 % of the electrolytic soln. The faster self-soln. of III was attributed to the less perfect oxide film and the presence of more microcathodes, mostly because of a secondary deposition of Cu on the cathodic areas, deposition was observed visually. In all cases pitting was observed. The no. of pits and their total area increased with c.d., but their depth decreased. The inside surface of the pits followed the crystal planes of the Al grains. The electrode potentials of all 3 metals changed temporarily with change of the anodic c.d., but then adjusted to values virtually independent of the c.d. The potential for III was more pos. than for I and II, and the potentials become more pos. with decrease of NaCl concn. These changes were explained in terms of changes in anodic areas. It was assumed that the end faces of incomplete raws of lattice cells in the inner surface of the pits form the anodes, but the cathodes were: (a) other flat portions of the crystal planes in the pits. (b) oxide films, (c) inclusions of impurities, (d) redeposited Cu, At low c.ds. the type (a) cathodes were not important.

Brouillet and Epelboin(3)found that anodic potential in electrolytic polishing is due primarily to the elec. field set up by the film of adsorbed anions. Potentials due to ohmic resistance at the anode are negligible. On interruption of the current, the potential due to the film of anodic products is negligible in comparison with the total anode potential in anhydrous paths such as fresh Ac_2O-$HClO_4$. Furthermore, this diffusion potential decays rapidly with Cu and Ni, but rises to a max. before decaying with the readily oxidized metals Zn and Al. This indicates that oxide films are not involved in polishing but form after the current is interrupted. In hydrated baths as H_3PO_4 or old aceto-perchloric solns., the anodic potential is diminished because the distance between the anionic film and the metal is increased. The value of the anodic potential is closely connected with polishing, where a max. potential is found (perchloric solns.). Polishing is obtained only on the level section of the i vs. E curve, but where the max. is not pronounced (alc. perchlorate solns.) or is nonexistent (H_3PO_4); polishing occurs even at c.d. higher than the level part of the curve. Variations in cathodic potential are negligible. Sundararajan and Rama Char(4) found that the corrosion rate of Al increases linearly with the conc. of NaOH, but the linearity does not persist at higher concns. The plot of corrosion rate against time gives a curve of the same shape as an adsorption isotherm. This indicates that the products of dissoln. inhibit the attack on certain areas of the surface after a given time.

Anderson and Hocking(5) studied the potentials of Al anodes in solns. of inhibitors in the presence of various concn. of KCl. The KCl concns. ranged from 10^{-2} to 10^{-5} M. The inhibitors were K_2CrO_4 and Na_2HPO_4 with inhibitor concns. ranging from 10^{-2} to 10^{-5} M. The current-potential curves show the existence of a crit. potential in each case corresponding to the breakdown of a protective film and the onset of the pit corrosion. The breakdown potentials increased with inhibitor concn. and decreased with chloride concn. It is concluded that the anions compete for positions on the surface and that this competition is connected with film formation and protection. Mechanisms of the action of corrosion inhibitors are discussed.

The static electrode potential behaviour of aluminium and the anodic behaviour of the pure metal and its alloys in chloride media were studied by Khairy and Hussein.(6) The electrode behaviour of Al in buffer solns. of pH 4-8 contg. varying concns. of Cl^- showed that the electrode potential does not respond to variations of pH. It changes linearly with pCl yielding a more or less const. E_o value (extrapolated) of -0.54 v. The corroding effect of the Cl^- supposedly is restricted to the adsorption of these ions on the surface and the electrode behaves as one of the second type. The oscillograms obtained both with the pure metal and with its alloys indicate that the surface oxide resists the corrosive effect up to 0.1 N (Cl^-). At higher concns,, the electrode surface is appreciably activated acquiring relatively high double-layer capacities, prominent passivity being achieved only on passing appropriate amts. of electricity.

Sundarajan and Rama Char(7) determined the corrosion rates and polarization values for 99.5 % and 92 % Al, in 0.3 N NaOH at 32° with and without dextrin as an inhibitor. Neither anodic nor cathodic protection of the Al is possible in the current range studied (0-1.87 amp./sq.dm of apparent surface area). The corrosion process occurs under cathodic as well as anodic control, with the predominance of inhibitor action on the anodic areas. Propagation of corrosion pits in metals were studied by Edeleanu(8). Pitting corrosion results from a quasi-autocatalytic anodic reaction. Expts. with the system Al-NaCl soln. show that the rate of corrosion per unit active area is const., and that changes in an external polarizing current, which alter the rate of pitting, influence only the area on which the attack occurs, and not the real rate of attack per unit of active area.

Dionis'ev and Antropov(9) studied the effect of albumin, casein, and alkali sulfites on the corrosion of Al in alkali by gravimetric and volumetric methods and by means of polarization curves. The corrosion rate of Al in 0.03-5.0 N NaOH was directly proportional to the square root of the NaOH concn. With an increase in the concn. of the NaOH, the cathodic process was retarded while the anodic process was accelerated. Admixts. retarded the corrosion rate of Al.

Hagyard(10) indicated that in aq. alkali metal chloride solns., there is continuous breakdown and reforming of the passive film. Oscillograph records of such occurrences are shown. Evidently the behaviour of oxide-coated Al is very complex. A means of eliminating the complication of oxide films and the unknown relative areas of anodes and cathodes on the normal electrode was found in an expt. which involves cutting a notch in an electrode completely coated with polythene and already immersed in the electrolyte. By suitable arrangements the cutting and wetting time has been reduced to about 10 μ sec., exposing about 10^{-3} cm of fresh Al to the soln. By using a cathode follower circuit of input impedance of 10^{9} ohms, the potential is then followed under substantially open-circuit conditions. It is presumed that the surface starts at the zero charge potential and that ionization of the surface atoms of Al charges the double layer, driving the potential in the neg. direction. The oscillograph trace shows that the peak is displaced by alteration in Al^{+++} concn. but not by pH, while the steady state, some 300 mV. less neg., is moved up and down by pH but not by Al^{+++} concn. The peak represents the equilibrium of Al with its ions in soln., and this equilibrium is reached in some 10-30 μ sec., whereas the steady mixed potential reached threreafter is controlled by H^+ ion discharge with H evolution. The value of the peak potential (-1.67 V) is higher than previously reported and is probably the reversible potential of Al, which cannot normally be observed. In the presence of dissolved oxygen, the potential falls slowly to ~ -0.5 V owing to the growth of the oxide film, with a time const. of several sec. Owing to the extreme rapidity with which the peak potential is reached, it may be assumed that all the surface is anodic. By the use of impressed currents from a transistor circuit the displacement of the peak by impressed current, with the electrode anodic, and by confining the observations to the first 30 μ sec., anodic polarization curves for Al free from oxygen and from H evolution and presumably with all the surface anodic, were obtained. By impressing a current in the opposite direction, of value sufficient to ensure that the potential is always more neg. than the peak potential, cathodic polarization curves are produced from a surface free from oxide and on which no anodic process is possible. Extrapolation and intrapolation of these 2 curves to the mixed potential of 1.3 V gives the ratio of anodic to cathodic surface areas (1:100) at the steady state.

Meyer(11) studied atm. corrosion products for some metals. In case of Al, the products are amorphous and not fully explained.

Distinction is made between (1) primary oxide layers (passivation layers) $\sim 10^{-7}$ cm thick. having a defined crystallographic (epitaxy) orientation and intergrown with the crystallites of the base metal, and (2) much thicker secondary layers whose compn. is largely defined by atm. impurities such as SO_2.

Inui, and co-workers(12) suggested that, the dissoln. of Al in N HCl is 1st order in the beginning, but gradually changes to 2nd order. The dissoln. in <0.5 N aq. HCl is $\frac{1}{2}$ order, but if atm. O is present, the dissoln. is 1st order. The reaction rate const., K, is proportional to the surface area. K depends on HCl concn., [HCl], as $K = k \exp.[HCl]$, where k is a const. K also follows the Arhenius equation. $K = k' \exp. (-E/RT)$. The activation energy, E, is $\sim$ 6 K cal./mole, so the reaction must be a diffusion reaction. The diffusion velocity of H^+ det. the reaction rate. It was also found by Inui, and Hosokawa(13) that, the dissoln. of Al in dil. NaOH follows the equation: $Al + NaOH + H_2O = NaAlO_2 + 3/2\ H_2$. The order of this dissoln. reaction is $\frac{1}{2}$. The activation energy is $\sim$ 13.7 K cal./mole, so this is also a diffusion reaction.

Corrosion of aluminum in alkaline solutions was also studied by Dionis'ev and Antropov.(14) The rate of corrosion of Al in NaOH solns. was proportional to the sq. root of its conc. Corrosion of Al in alk. solns. takes place with mixed cathode-anode control. Inhibition of the corrosion rate of Al can be carried out by inhibition of both the anodic and cathodic processes with equal effectiveness. For protection of Al from disintegration in alk. media, cathodic protection cannot be used.