ELECTROCHEMICAL STUDIES ON THE KINETICS OF ELECTRODE REACTIONS AND CORROSION OF METALS

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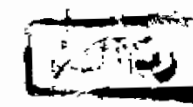

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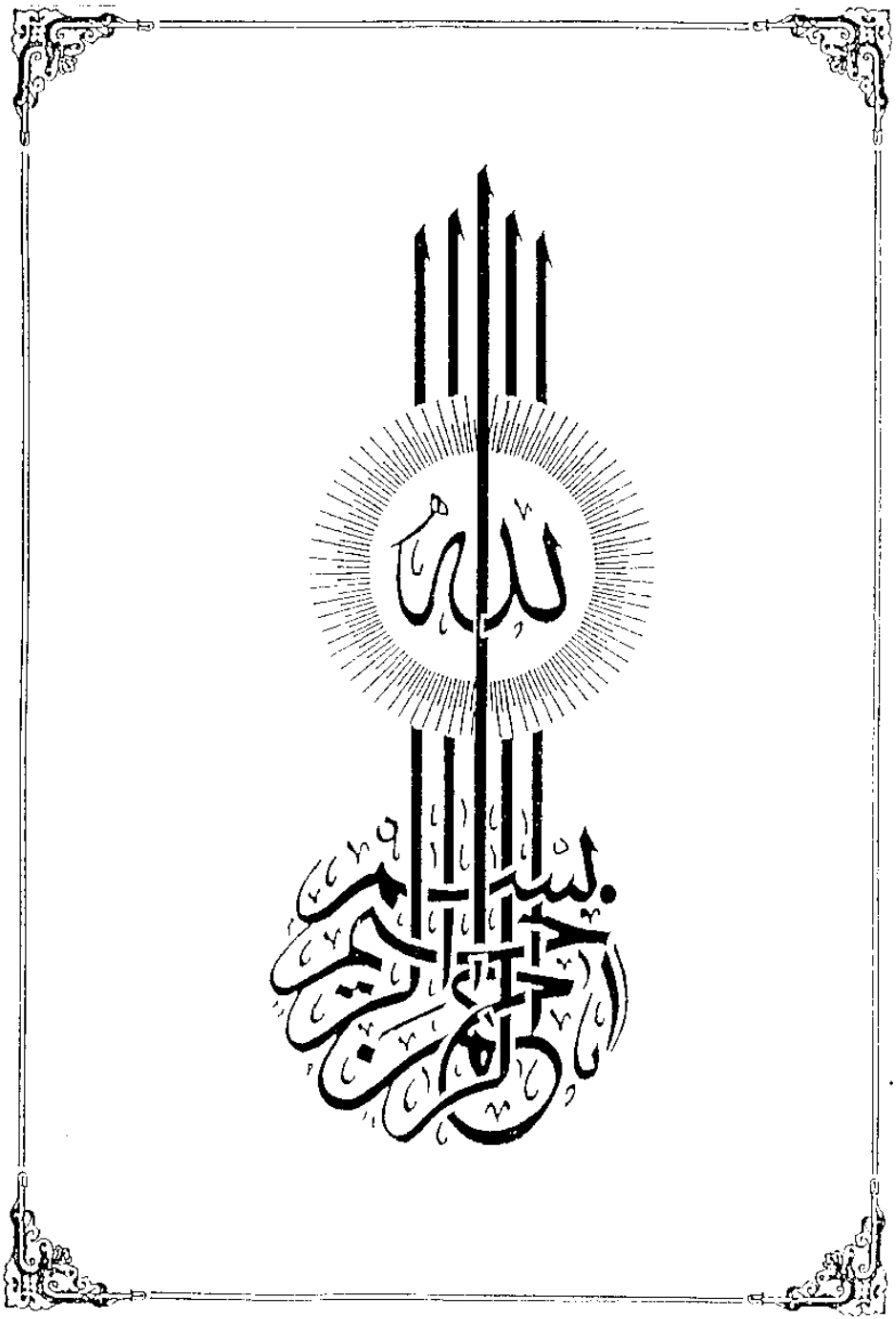

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INTRODUCTION

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 non-ferrous metals, although it is so important as that of iron and steel, has yet occupied only a second place . Some of the earlier investigation of the electrochemical behaviour and corrosion of copper and aluminium are reviewed below.

(I) Copper:

Krasil'Shchikov and Andreeva[1] found that when the polarisation voltage of Cu in air-saturated 0.1 N KCl is increased, the current density first rises then remains constant (reduction of O_2), and finally rises again (libration of H_2). In acidified solultions two horizontal regions are noticeable corresponding to reduction of O_2 and to catalytic titration of H_2. The current density D of the second horizontal region is proportional to N^2,N being the normality of HCl (0.001-0.01 N) in 0.1 N KCl. In K_2SO_4 solutions acidified with H_2SO_4, the two horizontal regions are also observed. The current density of the first region is almost independent of the concentration of H_2SO_4 (0.002-0.015 N) and is 0.8-1.1 x 10^{-5} A/cm^2. The rate of solution of Cu in air-saturated H_2SO_4 (without any current) is about 0.1 g/cm^2. hr, corresponding to a corrosion current of 0.8 x 10^{-5} A/cm^2. Hence, the rate of solution of Cu is equal to the rate of diffusion of O_2 to the Cu surface. This accounts for its independence of the concentration of the acid.

The solution of Cu in dilute acids in the presence of O_2 seems to be a purely electrochemical process.

A diffusion layer of approximately 0.1 mm thickness surrounding a stationary Cu anode with surface projections smaller than 1 micron and suspended in N H_2SO_4 was examined by Jean Mercadié[2] mathematically. The following conclusions were drawn: (a) the equipotential surfaces are those surrounded by an equal concentration of ions. (b) The lines of current are identical with the lines of the e.m.f. (c) There exits in the diffusion layer a positive electrostatic charge due to slight excess of Cu^{++} over SO_4^{--} ions. (d) There is a tendency towards equalization of current density of the surface of the anode.

Bockris and Pentland[3] studied the mechanism of hydrogen evolution at Cu cathodes in purified solutions of 0.0001-0.1 N HCl and 0.005 - 0.15 N NaOH, were used at 10 to 40°C over a current density range of 10^{-8} - 10^{-2} A/cm^2. The heat of activation at the reversible potential and the stiochiometric number of alkaline solutions have also been determined. The variances of these, and of the parameters of the Tafel lines were recorded.

The reaction $H_3O^+ + e \longrightarrow MH$, was rate determining on Cu in aqueous acid solution. Distinctions between slow discharge and electrochemical rate determining steps depended upon indirect methods of indicating degree of coverage of the surface with H_2. In alkaline solution, discharge from Na^+ was negligible under experimental conditions.

The desorption step was catalytic combination of H-atoms at low current density, at higher current density desorption by the electrochemical step may become important.

Pryor and Keir[4] compared the behaviour of Fe, Cu, Sn, Zn, Mg, and Pb cathodes with Al cathode in NaCl solutions at low current densities (1 μ A/cm^2). The Al clearly showed highly localizeds spots where true cathodic activity took place. The areas around the spots were inactive because of the very low conduction of Al_2O_3 films for electrons. Annealed Al also showed grain-boundary activity.

The relation between the amount of anodic dissolution and cathodic deposition in Cu plating was studied by Nobuteru Awa[5]. The experiments were made at a bath concentration of 10 % $CuSO_4 \cdot 5H_2O$, temperature 20 $\pm$ 0.5°, plating time 20 min., electrode thickness of 5 x 50 mm. or 10 x 50 mm. In the plating between 2 and 3 V, the amount of anodic dissolution is the same as that of cathodic deposition. But, plating below 2V, the amount is greater than the cathodic deposition, and above 3 V., is smaller. The gradient of the curve for the amount of anodic dissolution vs. Voltage and that of cathodic deposition vs. voltage are similar to ampare-voltage curves. The three curves differe remarkably when the anode takes a passive state. By assuming that a plating degree is expressed by 100 % (amount of cathodic deposition/amount of anodic dissolution), it becomes nearly 100 % between 2 and 3 V. However, it becomes 100 % after long-time plating only when the voltage is lower than 2 volts.

Sergeev[6] measured the Tafel constant (a) in H_2 overvoltage studies in 100 g/L H_2SO_4 solutions at 20° for various metal cathodes. The metals and the respective (a) values were: Zn 0.68, Cd 0.36, Co 0.25, Fe 0.21, Al 0.47, Cu 0.34, and Sb 0.445 V. At the higher part of the current density range of 1-800 A/m^2, with Pb anodes and Hg cathodes, the voltage was nearly independent of current density. The voltage component reflected in (a) is related to the electrode-electrolyte interaction and is independent of current density. The component of voltage which varies with amperage is related to concentration gradients in the diffusion layer adjacent to the cathode.

Ramoswamy and Patel[7] used stationary cathodes of Sn, Pb, Al, Zn, Fe, Ni, Cu, Pt and their amalgamated surfaces for reduction of N HNO_3 in 10 % Na_2SO_4. H_2 was evolved with Pt cathode. No NH_2OH was formed with Cu, Pt, and amalgamated Al electrodes. The current efficiency of NH_2OH formation was higher with amalgamated electrodes and varied from 21 to 63 %. The amount of NH_3 liberated decreased with amalgamation. They discussed the reduction mechanism.

The behaviour of different cathode materials in the electrolytic reduction of HNO_3 (in a solution of 60 g. HNO_3/L. 20 % H_2SO_4) was studied by Agladze and Kvaratskheliya[8] at a c.d. of 24 A/cm^2 and 18°. The overall cathodic current efficiency for 2-hr experiments showed that no reduction to NH_2OH or NH_3 takes place at the Cu cathode.

Changes of the direction of the current was observed by Songina and Studen Skaya[9] on cathodic polarisation of a relatively large Cu electrode coupled with a smaller Pt electrode (50 and 10 mm, respectively). The solution turns blue if the experiment is carried out in an NH_4OH solution. A still sharper change in the current direction is observed on cathodic polarisation in a solution of MnO_4^-. These phenomena are explained by Cu dissolution due to c.d. decrease on the large electrode and by the interaction of Cu with dissolved atomic oxygen and the simultaneous formation of an NH_4 complex.

Shams El Din and Abdel Wahab[10] suggested that the Cu oxidizes only to Cu_2O and $Cu(OH)_2$ in the first anodic half cycle and more to Cu_2O_3 at advanced cycles. Cu_2O_3 results from the oxidation of H CuO_2^-. The passivation of Cu follows the relation, $i T^{\frac{1}{2}} \simeq 80\ (OH^-)$, i being the current and T the time elapsing until atomic oxygen evolution starts. Cu_2O and $Cu(OH)_2$ are reduced at more negative potentials than their formation values. This is related to the semiconducting properties of these oxides.

Polarisation of copper in pyrophosphate electrolytes was suggested by Vagramyan and Yastrebova[11]. About 90 % of the polarisation curves taken by the rapid method consisted of concentration polarisation. Anodic polarisation was much lower than cathodic and was not affected by the rate at which it was measured. In the slow method, polarisation increased with dilution, whereas in the rapid method it increased with the concentration cathodic polarisation. A plot of φ vs. $\log i_o$ in 0.1 m $CuSO_4$ + 0.5 m $Na_4P_2O_7$, pH = 5.5, at 25-80°,

consisted of 2 intersecting straight lines. The slope at low φ was close to 2.3 RT/2F, whereas at high φ it was 4 times higher. The intersection of the 2-lines shifted to higher φ as the temperature increased. The anodic polarisation curves were not linear. The exchange curent of a Cu electrode increased from 0.26 to 6.3 mA/cm^2 as the temperature increased from 25 to 80°. At 25° it was 50 % of that in H_2SO_4. The activation energy, A, of the cathodic process decreased linearly as φ increased to the critical value beyond which it remained constant. At φ = 0, A = 14 kcal./mole. A of the anodic process was independent of φ, but it icnreased from 5.5 to 10.5 kcal./mole as the concentartion of $CuSO_4$ increased from 0.05 to 0.5 m; the concentration of $Na_4P_2O_7$ increased from 0.15 to 1.05 m. At high values of φ where A was independent of φ_c, A increased from 7.4 to 11.3 kcal./mole as the concentration increased from 0.05 to 0.5 m $CuSO_4$ and from 0.15 to 1.05 m $Na_4P_2O_7$.

Valiuliene and co-workers[12] observed that, on potentiodynamic cathodic polarisation curves of Cu in solutions of $K_6[Cu(P_2O_7)_2]$, both concentrated and diluted, at pH > 7.9, two external sections appear: the 1st at $-0.4 > \varphi_c > -0.55$ V and the 2nd at $-0.65 > \varphi_c > -0.8$ V. Thus, in the combined use of the cyclic voltammetric and rotating-disk electrode methods, transition sections on the polarisation curves can be identified which develop as a result of a decrease in the extent of passivation of the Cu cathode surface. These methods can probably also be used for solving analogous problems in other electrochemical systems.

Tsuru and co-workers[13] investigated the anodic and cathodic behaviour of the Cu electrode in acidic $CuSO_4$ solution (0.4 M $CuSO_4$ and 0.51 M H_2SO_4). The steady-state for anodic and cathodic polarisation depended on the concentration of iodide ion. With the increase of I^- concentration from 10^{-7} to 10^{-5} M, the overvoltage, especially for the cathodic process, increased considerably due to the formation of an insoluble CuI film on the electrode surface. On the other hand, this high polarisation disappeared at lower current densities in an electrolyte containing > 10^{-5} M I^-, because the CuI film dissolved into the solution to form CuI_2^-. At higher current densities, however, the cathodic overvoltage suddenly increased to reach the deposition potential of Cu from the insoluble CuI film.

Ezzat and El-Tantawy[14] reported that the galvanodynamic runs of Cu in 0.1 M Na_3PO_4 (pH 12.5) yielded 2 distinct anodic transients in addition to a 3rd ill-defined one, plus 2 well-defined cathodic potential arrests. A simple methode of calculation, from the galvanodynamic trace, of the quantity of electricity consumed along each process is proposed. The addition of Na_2SO_4 decreased to the total quantity of electricity needed to anodically passivate the electrode. Cl^- addition increased the quantity of electricity corresponding to each anodic process, but by different amounts. At $[Cl^-]$ = 1 M, the passivating film did not resist the Cl^- attack, and signs of rapid braekdown of passivity were observed. They also discussed a series of steps explaining the effect of Cl^-, involving adsorption, interaction with solution Cu-hydroxy intermediates and finally polarisation of the deposited oxide.

Asakura and Maehara[15] studied that the NO_2^- was determined by measuring the polarisation conductance of metallic Cu in aqueous solutions containing 10^{-5} - 10^{-1} M $NaNO_2$ at pH = 2-3. The method is simple but its sensitivity is only 0.6 ppm. The mechanism of oxidation of Cu in aqueous solutions of $NaNO_2$ is also discussed.

Šiška and co-workers[16] reported that nitrite NO_2^- is reduced by Na amalgam to $N_2O_3^{--}$, $N_2O_2^{--}$, and NH_3. Nitroxyl ion (NO^-) is assumed to be an intermediate in the formation of $N_2O_3^{--}$. The $N_2O_3^{--}$ ion is reduced to $N_2O_2^{--}$ and NH_3. At lower pH, the following equilibrium:

$$N_2O_3^{--} + H_2O \rightleftharpoons HNO + NO_2^- + OH^- \qquad (1)$$

is established. The presence of NH_2OH has not been proved, but NH_2OH is assumed to be present as an intermediate.

The behaviour of nitrate and nitrite ions in strongly acidic medium was measured by Masek[17]. The equilibria:

$$NO^+ + H_2O \rightleftharpoons H_2NO_2^+ \rightleftharpoons HNO_2 + H^+, \qquad (2)$$

$$NO_2^+ + H_2O \rightleftharpoons H_2NO_3^+ \rightleftharpoons HNO_3 + H^+, \qquad (3)$$

$$HNO_3 + H^+ \rightleftharpoons NO_3^- + 2\,H^+, \qquad (4)$$

were investigated in 10^{-1} to 18 M H_2SO_4. Both systems gave waves with the same $E_{\frac{1}{2}}$, even with the vibrating Pt electrode. The first wave occurred at 0.22 V versus saturated mercurous sulphate electrode. With nitrites this peak is due to the

$$NO^+ + e \longrightarrow NO\,, \qquad (5)$$

and with nitrates to the

$$HNO_3 + 3e + 3H^+ \longrightarrow NO + 2\,H_2O\,; \qquad (6)$$

this being the overall reaction involving 2 different reaction mechanisms depending on the activity of the solution. A second wave occurred in both cases and it tentatively explained by assuming that the product of the first electrode reaction is followed by a further chemical reaction at the electrode surface yielding a depolarizer which is in the same bivalent oxidation state as the N in NO, and which is reduced to hydroxylamine (I) with the uptake of 3-electrons. With nitrites, a third wave corresponds to the reduction of HNO_2 to I with the uptake of 4-electrons was observed.

Lyalikov and Mukhamednazarova[18] used 1 mm diameter microdisk Pt anode, rotating at the rate 190-1170 r.p.m., in the investigation of anodic waves of NO_2^-. The half-wave potentials $E_{\frac{1}{2}}$, measured vs. Pt cathode is 0.84-0.86 V in 0.1 N LiCl solution.

Starostenko and Starostenko[19] suggested that the neutral solutions of $NaNO_2$ (concentrations 0.003-3 M) were reduced at i = 0.01-1.0 A/cm^2 on a filtering Hg-cathode. After electrolysis, the catholyte had an alkaline reaction and reduced $KMnO_4$. The cathode process involved formation of hyponitrite :

$$2NO_2^- + 4\,e + 2H_2O = ONNO^{--} + 4\,OH^-. \qquad (7)$$

The current efficiency was 100 %.