STUDIES OF ELECTROCHEMICAL BEHAVIOUR OF SOME METALS

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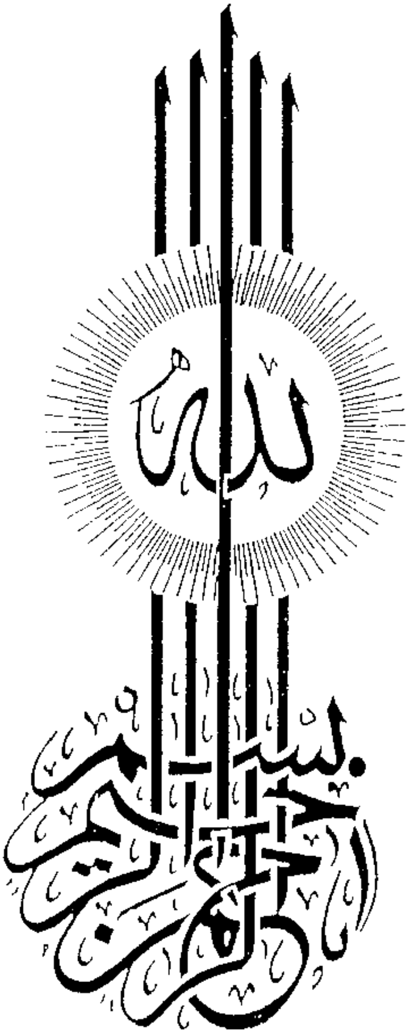
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STUDIES OF ELECTROCHEMICAL BEHAVIOUR OF SOME METALS

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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) Thermodynamics;

(8) Instrumental analysis.

She has successfully passed a written examination in these courses.

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(II) EXPERIMENTAL TECHNIQUES

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ABSTRACT

The first part was devoted to the mechanism of reaction and corrosion of 5 % Mg-Al alloy in alkali solutions containing Na_2MoO_4.

The effect of MoO_4^{-2} ions were related to the change of the thickness of space charge region, as well as the change of OH^- ion concentration in the double layer.

The second part of the present work was devoted to the study of the anodic dissolution of 5 % magnesium-aluminium alloy in NaOH solutions containing $NaNO_2$. As well as the mechanism of hydrogen evolution from alkaline solutions containing $NaNO_2$ at magnesium-aluminium cathodes.

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 investigations of the electrochemical behaviour and corrosion of aluminium and aluminium-magnesium alloys are reviewed below.

Jangg and Meissner(1) developed a new technique. They determined the so called break down potential V in the pitting corrosion of Al and its alloys in NaCl solutions containing various additives. NO_3^- ions addition to chloride solutions lowers the pitting susceptibility of Al shifting V to more positive values, while SO_4^{-2} ions and NO_2^- ions bring about no shift to V, but appear to form a protective layer which inhibits the initiation and progress of attack. Addition of CrO_4^{-2} ions have a similar effect but shift the potential especially in case of Zn containing Al alloy.

The pitting mechanism of Al and its alloys was studied by Wood and Co-workers(2) using transmission electron microscopy, scanning electron microscopy, corrosion potential measurements and capacitance determination.

Hisamatsu and Co-workers(3) showed that a single pit was developed by using a diamond indenter. By measuring the growth rates of the single pits, corrosion rates of 1080 Al[39418 - 82 - 1], Al - Mn and Al-Mg alloys were determined. The growth rate of pit depth was lower than that of the periphery. For 1080 Al the effect of H_2O content in CCl_4 was studied. H_2O accelerated the growth of the pit periphery but not the depth.

Ford and Hoar(4) measured the fatigue cracke propagation rates of a cold-worked and stabilized Al- 7 % Mg alloy [12678-96-5] immersed in an aqueous solution, as a function of the stress intensity amplitude testing frequency, electrode potential and anion content, these results were compared with the bare surface dissolution, hydrogen [1333-74-0] evolution rates and the passivation rates obtained from scratching electrode experiments. The environment controlled propagation rate in aqueous solutions is governed by an enhanced electrode reaction rate due to the protective oxide rupture at the advancing crack edge and by the interaction between the stress intensity dependent oxide rupture rate and the passivation rate.

Mukhina and Yu(5) observed that the corrosion resistance increased with increasing atomic number of solid solution region and decrease in the stability of the corresponding intermetallic compounds with decreasing m.p of the intermetallic compounds. They also concluded that the cathode potential of the binary alloys became more negative and their hydrogen overvoltage increased with increasing atomic number, while the anode potential became more positive with the increasing of the atomic number.

The electrochemical behaviour of an Al-5 % Mg alloy [11109-06-1] was studied by Bonore and Co-workers.(6) They concluded that: the choice of experimental conditions allows one to differentiation the electrochemical behaviour of an alloy susceptible to, or free from localized corrosion and with increasing temperature the difference become less marked. This can be explained on the basis of the decreasing protective power of the oxide and the consequent active role in the anodic process of the less oriented grains, where the thermal treatment to which stabilization is due, was not efficient. These grains at the lowest temperature did not act as corrosion cells because of the high electrical resistance of the oxide.

Rao and Co-workers(7) showed that the satisfactory protection of Al [7429-90-5] from cavitation damage was provided by inhibitors such as $K_2Cr_2O_7$, Na_2MoO_4, $Na_2WO_4.2H_2O$ and $NaNO_2$, application of impressed current cathodic protection and the combination of cathodic protection and inhibitors.

Yoshimura and Co-workers(8) studied the effects of the addition of oxidizing agent such as $KMnO_4$, NH_4NO_3, $K_2Cr_2O_7$, $K_2S_2O_8$, H_2O_2, and $K_3Fe(CN)_6$ on the a.c. anodization of Al in alkaline solutions. In the case of NaOH solutions the addition of $KMnO_4$ gave the thickest film followed by those of NH_4NO_3, $K_2Cr_2O_7$, $K_2S_2O_8$, $K_3Fe(CN)_6$ and H_2O_2, in that order. The optimum conditions were as followed: pH 11-12, c.d. 0.8-1 A/dm^2, electrolysis time 0.5 hr.

Kato(9) found that the rates of initial corrosion of Al in normal hydrochloric acid and normal sodium hydroxide, were largely dependent on the treatment given to the aluminium sample before immersion. When an oxide film was present on the surface of a specimen, the rate of corrosion was large in sodium hydroxide and small in hydrochloric acid at the begining, then it gradually decreases in sodium hydroxide and increased in hydrochloric acid respectively with the elapse of time until a definit value was reached. This indicates that some active part is formed in sodium hydroxide solution on the surface of aluminium. In hydrochloric acid, the rate of growth of oxide film and the rate of dissolution or breakage maintain equilibrium and the deviation from this equilibrium affects the rate of corrosion. Dissolved oxygen accelerates the rate of corrosion at first, but its effect diminishes with time in hydrochloric acid, while in sodium hydroxide, dissolved oxygen has nothing to do with the corrosion.

Several studies on the aluminium corrosion in alkaline solutions have been carried out by different authors. Thus, Kabanov and Zak(10) studied the spontaneous rate solution of 1.62 and 0.82 mm aluminium wires of (99.995 % purity), annealed in water at 250^{o} in 15 seconds. Three minutes experiments in a stream of nitrogen, 5.3 N solution of lithium hydroxide and in (0.5 - 2.5 N) of potassium hydroxide, increased rapidly with cathodic polarisation with current density from one to 10 amp./cm^2. Whereas in a mixed solution of Me_4NBr and MeNOH, corresponding to a 0.52 N alkali, the rate of solution of aluminium wire in polarisation with up to 9 amp./cm^2 was not over 10^{-4} - 10^{-5} amp./cm^2, in 0.5 KOH it attained the equivalance of several amp./cm^2. The presence of chloride ions has no effect on the rate of solution of aluminium in potassium hydroxide, at high cathodic polarisations. K_2CrO_4, 0.002 gm equivalent/liter added to 2.5 N KOH, reduces the rate of solution considerably (from 0.06 amp./cm^2 at a cathodic current density of 4 amp./cm^2). In 5 N HCl, even at high cathodic polarisation (10-12 amp./cm^2) there is no effect on the rate of solution of aluminium. The rate of stirring with nitrogen stream has no effect on the rate of solution under high cathodic polarisation. The strong acceleration of the rate of solution by cathodic polarisation cannot be explained by a reduction of surface oxide as the hydrogen overvoltage on aluminium in lithium hydroxide is somewhat lower than in Me NBr, whereas its rate of solution is very considerably greater.

Makram(11) claimed that the rate of corrosion of aluminium in one —0.2 N NaOH is proportional to the alkali concentration, whereas at lower concentrations this proportionality is not valied.

Sundararajan and Ramachar(12) found that the corrosion rate of aluminium increases linearly with the concentration of NaOH but the linearity is not present at high concentration. The plot of corrosion rate against time gives a curve of the same shape as an adsorption isotherm, this indicates that the products of dissolution inhibit the attack on certain areas of the surface after a given time.

According to Dionis'ev and Antropov(13) the corrosion rate of aluminium in 0.03-5.0 N NaOH was directly proportional to the square root of the alkali concentration.

The same authors(14) found that the corrosion of aluminium in alkaline solutions take place with mixed cathode-anode control. Inhibition of the corrosion rate of aluminium can be carried out by inhibition of both the anodic and cathodic processes with equal effectiveness for protection of aluminium for disintegration in alkaline media. The slow step in the cathodic evolution of hydrogen during the corrosion of aluminium in alkaline media is the particular reaction of addition of an electron to a water molecule with the formation of hdyrogen atoms.

Sundararajan and Ramachar(15) studied the inhibition of corrosion of aluminium in acid solutions by polarisation. They concluded that the corrosion process is essentially under cathodic control. The present protection at current densities of 0.1-, 0.15, 0.32 and 0.40 amp./dm^2 is 40·45, 80, 86 and 100 respectively. Without current, the inhibition efficiency is 7C, 80 and 94 % for 1, 2 and 5 gm thiourea/litre respectively. A combination of 0.1 amp./dm^2 and 1-5 gm thiourea/litre gives close to 100 %.

The inhibition of corrosion of Al (99.8 %) and Al-Mg (2 %) alloy in decinormal solutions of trichloroacetic acid by different inhibitors, was studied by Talati and Patel.(16) The effeciency of the inhibitors increases in the order: gum tragacenth, agaragar, acacia, permanganate, gelatin, K-thiocyanate, $NaNO_2$, thiourea, Na-arsenate, aniline, $K_2Cr_2O_7$, Na_2CrO_4 and K_2CrO_4. The inhibition achieved with potassium chromate 100 %.

Delong and Searson (17) showed that the surface of articles of Mg of Mg alloys base is passivated as a pretreatment step for the electrophoretic application of coatings in a process in which the surface is treated with an aqueous solution containing an alkali hydroxide, an acidic fluoride, an alkali, or NH_4 chromate until a clear coherent coating is formed. The treated surface is then washed with H_2O. Preferably the articles are chemically polished before the passivating treatment with the acidic solution containing AcOH and $NaNO_3$. The passivating solution