SOME STUDIES ON NICKEL ELECTROPLATING BATH

By

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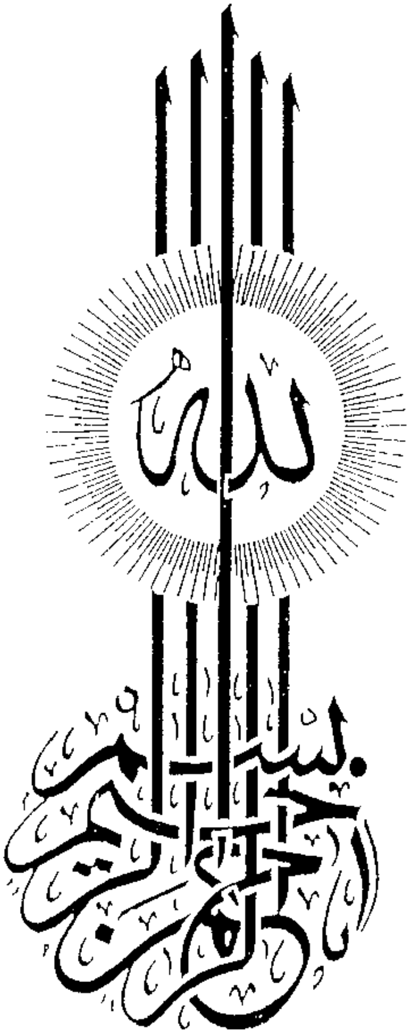
الله

بسم الله الرحمن الرحيم

وقل اعملوا فسيرى الله عملكم ورسوله والمؤمنون

«صدق الله العظيم»



بسم الله الرحمن الرحيم

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NOTE

Beside the work carried out in this thesis, the canditate Emad Aboul Seoud Abd El Maguid has passed Successfull a written examination in the February 1983, in the following courses in a partial fulfillment of the M.Sc degree.

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(2) Advanced Surface chemistry

(3) Statistical thermodynamics

(4) Quantum chemistry

(5) Solvent Extraction

(6) Nuclear chemistry

(7) Inorganic reaction Mechanism

(8) Instrumental analysis

(9) Quantum chemistry and spectroscopic application of group theory.

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Anodic Behaviour of Nickel in Aqueous Media

Electroplating of Cd, Ni and Ni-Cd Alloys from Acetate Bath.

INTRODUCTION

1. Anodic Behaviour and Passivation of Metals

Passivation is an unusual phenomenon observed during the corrosion of certain metals and alloys. It can be defined as a loss of chemical reactivity under certain environmental conditions (1). More specifically, the term is applied to the sometimes observed transformation of active unstable surface to a passive stable surface by the super impostion of a double - layer field which would accelerate the metal dissolution reaction rather than hinder it, i.e. by a shift of the electrode potential in the passive direction. This phenomenon of enforced passivation (2) seems unnatural or at least unexpected. Passivation results as a process of formation of an insoluble oxide, hydroxide or solid salt incontact with the metal.

Protection of the metal will be complete where the film or deposit is absolutely adherent and non-porous.

Passivation theories: There are two commonly expressed points of view regarding the nature of the passive film (3).

a) The adsorption theory: this holds that metals are covered by a chemisorbed film, e.g. of oxygen, which displaces the normally adsorbed water molecules and decrease the reaction rate. The chemisorbed film either shifts the electrode potential in the double layer or infleunces the kinetics of the anodic process, that is, the important effects occur in the small metal solution interface region (4).

The anodic dissolution rate is generally represented by:

$$I = K_1 \ C' \exp \left(\frac{\alpha_1 F}{RT} \right) E$$

where α_1 is the transfer coefficient which is equal to βz. When the valency of the dissolving ion z, is unity, α_1 is equal to the symmetry factor β.

The quantity C' is the number of atoms cm^{-2}. If, with super-imposition of adosrption C' changes with E in such a way that:

$$C' = C'_o \ \exp \left(\frac{-\alpha_2 F}{RT} \right) E$$

The total current becomes.

$$I = K_1 C_o \exp \left[\frac{(\alpha_1 - \alpha_2) F}{RT} \right] E$$

This equation explains the drop of the current with the potential and shows the current independence of potential in the passive region. The basic anodic processes, even in the passive potential region, are the direct dissolution of the metal as one and the competitive adsorption of anions as another.

Uhling (3) showed that one of the factors determining passivation by adsorption is the ratio of the work function to the enthalpy of sublimation. If this ratio is less than unity, conditions favour passivation because the electron would escape more readily than the atom favouring the chemisroption of substance like oxygen. A passive film is composed then of chemisorbed atoms and molecular oxygen (supplemented perhaps by OH^- and H_2O).

The dissolution of nickel and its passivation behaviour in aqueous solutions have received recent attention by a number of investigators. Although there has been considerable activity on studies of the anodic behavior of nickel, there have been few investigations which have determined kinetic parameters of the dissolution reaction. The anodic behaviour of nickel 200 and 270 in 1N H_2SO_4 was studied galvanostatically and potentiostatically by both continuous and pulse polarization techniques. (5) . Results indicate that the passivation parameters can be determined equally well with either continuous or pulse polarization.

Ekilik et al (6) were studied the passivation of Ni in 0.05 M solution of $LiClO_4$ in H_2SO_4 in H_2O , methyl alcohol, ethylene glycol, formamide, acetone, methyl cyanide, DME and mixtures of these solvents with H_2O . To standardize the surface before the tests, the electrode was cathodically polarized (at 0.3 volt) for 30 min. Anodic polarization at the same voltage was then conducted for 20 min in each of the solution. Then the electrode was placed in 0.045 M solution of $LiClO_4$ with the addition of 0.005 M ,of $HCLO_4$ during simultaneous switching off anodic polarization and was polarized by a stabilized cathode current density of 0.1uAcm^{-2} , the change of the potential (E) with time (t) was recorded, the H_2O has a decisive role in the appearance of the holt in the potential on E vs.t curves.

According to osterwald and Co-workers (7), the anodic behavior of Ni in HF solution was studied under potentiostatic and galvanostatic conditions.The polarization curve differs distinctly from the curve in H_2SO_4. Four current density maxima are observed. The last one lying at 2.5 V_H in the vicinity of the corrosion potential and after the last 3 maxima , the electrode is covered by dark surface layers. Slight pitting occurs after the 2nd maximum. Under galvanostatic conditions, positive and negative damped oscillation can be observed before the 1st 3 maxima . This phenomenon indicates that similar mechanisms are responsible for the formation of the maxima . The passivity of Ni can not be explained by the interaction of metal and water alone, but also depends on the nature of the dissolved anion.

b) The oxide-film theory

According to this theory, the passivation is due to the formation of a protective layer on the surface of the metal. The film consists of the products of the reaction of the metals with its environment. Such a film separates the metal from the environment and slows down the rate of the reaction. It is suggested that the passivation follows the formation of a "primary-layer" of low conductivity and porous character which is some times due to precipitation of metal salt on and near the electrode (8). In the pores, the current increases and by polarization an actual passive non-porous layer is formed (9-11).

Bockris, Reddy and Rao (11) have studied the passivation of nickel in acid solution and reported that the primary oxide layer is relatively thick, formed by precipitation, poorly conducting and is transformed into well - conducting non-stoichiometric nickel oxide. This transformation is thought to be the essential step in the passivation process.

Electrochemical behaviour of an active-passive metal

The electrode potential - current density (E-i) curves for an active -passive metal shown an interesting