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Passivation model of nickel in sulphuric acid

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Passivation of Nickel in acid solutions has been examined by various groups of investigators by making use of different instrumental techniques. Typically impedance measurements, ellipsometry, galvanostatic/potentiostatic studies and X-ray diffraction (XRD) methods have been made use of. These studies have demonstrated that passivation is primarily due to the formation of a chemisorbed film of non-stoichiometric nickel oxide layer. Another school of investigators has indicated the possibility that nickel is not passivated by the oxide film, but it is because of "pseudo" passivation triggered by the crystallisation resulting in the coating of the nickel salts that corrosion got arrested. As the ingress of acid through the salt coating is retarded, the pseudo passivation conditions obtain. It was thought useful to resolve the issue as to what is the real mode of passivation. The present study is aimed at the same. In fact, this study was highly relevant to our attempts at preparation of nickel sulphate solution by dissolving pure nickel briquettes with sulphuric acid for use in nickel catalysts.

By making use of XRD technique (fingerprinting the components present in the passive layer) and wet chemical methods, the presence of nickel sulphide on the metal has been substantiated in this present study (in sulphuric acid at 100°C. This demonstrated the role of the sulphide as the passivating film under open circuit conditions.

With lower acid concentrations as the nickel dissolution proceeded, higher concentrations of nickel sulphate levels were registered. However, when the conditions of supersaturation with respect to the nickel sulphate salt sets in, nickel hexa aquo sulphate, retersite (syn), started to coat the nickel metal and triggered the retardation of nickel dissolution. However, when this coating step was eliminated by skipping the supersaturation conditions (viz. by dilution with water or by tribomechanics), corrosion avidly occurred with profuse hydrogen evolution with the smell of hydrogen sulphide. This revealed that retersite coating caused pseudo-passivation at elevated nickel sulphate levels A plausible mechanism has been postulated to embrace the above findings.

At lower nickel sulphate levels, sulphide dermosorption was the exclusive passivation mode, whereas at elevated nickel sulphate concentrations both sulphide dermosorption

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and sulphate coating collectively passivated the metallic nickel.

Studies on Corrosion and Electrochemical Behaviour Medium Strength Aircraft Aluminium Alloys

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Corrosion and electrochemical behaviour or aircraft aluminium alloys pertaining to Al-Li series have been evaluated and compared with a conventional aircraft alloy 2014. Light weight, high strength and high stiffness of lithium containing alloys have received much attention in aircraft industry as a candidate material for structural applications. Any material useful for aircraft application should undergo a thorough evaluation of the corrosion behaviour in comparison with presently used alloys. In the present study, the corrosion and electrochemical behaviour of Al-Li alloys 8090, 2091 and 1441 were evaluated and compared with a conventional alloy 2014. All the studies were carried out in NaCl solution of different concentrations and pH levels to understand the nature and mechanism of corrosion. A novel technique where an current input of exponentially decaying nature was applied to the system and the potential response was measured to determine the corrosion and electrochemical parameters. This technique has various advantages over other techniques. Potentiodynamic polarization experiment and metallographic observation of exposed samples were also carried out. The results showed considerable pitting tendency for lithium containing alloys compared to 2014 even though the general corrosion rate appears to be same as that of the conventional alloy.

Assumption that the area alone may not be responsible for the change in capacitance. The dielectric constant could have same effect. This has to be looked into.
Local pH in the pit in presence of Al-Li is quite high and hence passivation is higher.

Corrosion Behaviour of Magnesium Based AZ-91 + 10% SiCp Composite

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Metal matrix composites are slowly making inroads into several engineering applications such as IC engine pistons, mooring masts, automobile bumbers etc. Before these can become everyday materials use, there is need to characterise them and evaluate their performance in actual service. No matter what application is envisaged for these materials their corrosion behaviour

seems to control the extent of application. It was therefore decided to examine the corrosion behaviour of a light weight magnesium alloy (AZ-91) composite made with 10% addition to particulate SiCp. The MMC was made in dynamic Argon atmosphere by stir cast technique and made into cylindrical ingots by squeeze casting in a cylindrical die. Specimen coupons cut out from these squeeze cast ingots were surface finished and ground to 600 grit emery and then used in corrosion experiment. Continuous immersion in salt solution was used to evaluate the corrosion rate variation with time. Corroded samples were examined in Scanning Electron Microscope to determine the mechanism of corrosion and supported by potentiometric and galvanometric polarization studies. Corrosion in MMC was compared with the base alloy. These specimen coupons were also examined for intergranular behaviour. On an overall estimate AZ-91+10% SiCp Composites seem to behave as good as base material without exhibiting any significant reduction in its resistance to corrosion.

Simulation and Modelling to predict the effect of Pitting Corrosion

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Corrosion is inevitable and in practice the way in which it attacks the metallic materials of construction limits the useful life of the component and the total device. It is therefore necessary to keep track of the signs of corrosion and determine the extent to which corrosion deteriorates the properties of the material. In an application like aircraft, the effect of corrosion seriously limits the life of the aircraft. Since the material of construction is aluminium alloy, a project has been initiated to study the effect of corrosion on the life of the aircraft. As a beginning, the effect of pitting corrosion on the residual properties of the aluminium alloy 2024 was taken up. Coupons exposed to conditions of localized pitting were used to determine the pitting pattern. The pitting parameters were then fitted into a model to determine the effect on the residual tensile strength. It is possible to define an equivalent elastic modulus for the corroded samples and use the same in predicting the extent of impact on the properties of the aluminium sheet. Assuming a Weibul distribution and a uniform growth rate for the pits, no matter when they initiate during the exposure, a model has been developed that will predict the extent of pitting damage to the material of construction,viz.2024 aluminium alloy. It is hoped that this study will be the forerunner for many other similar studies that will eventually be able to predict the residual life of an aircraft that has been subjected to pitting type of localised corrosion.

Deep Sea Corrosion of Materials

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The scientific exploration and exploitation of ocean depths is now proceeding at an accelerated pace. Fundamental to the development of such materials is a requirement of the knowledge of how they will behave in deep sea. In deep water the deterioration is due to a cumulative effect of various environmental conditions like hydrostatic pressure, temperature, pH, dissolved oxygen, salinity, sea current etc. The information available on materials is limited in 2000 m depth. In-situ measurements of the effect of deep sea environment on some metals, alloys and carbon fibre reinforced composites were carried out in the deep ocean at depths 500, 1200, 3500, 4800 and 5100 m for two periods of 95 and 167 days. Materials studied include pure and commercial aluminium, several high strength aluminium alloys, steels, maraging steel, stainless steels, austempered ductile iron (ADI), copper alloys and carbon fibre reinforced composite. Corrosion rate calculated in terms of mm per year and have been correlated to the prevailing environmental parameters. Results indicate that the corrosion of aluminium based alloys is lower than that of pure and commercial aluminium at all depth levels. Pure aluminium is prone to get affected mainly by pitting type corrosion, which is most severe at the deepest level studied, possibly due to the high hydrostatic pressure and the stagnant sea water conditions. Copper base alloys in general show much less corrosion. Titanium, Titanium alloy (Ti-6Al-4V) and stainless steel (SS 304 & SS 316) did not show corrosion and the glossy appearance was retained even after exposure. ADI is most unsuitable for deep sea application. Carbon fibre reinforced composite (CFC) did not show any change in weight and electron micrographs revealed no change in the surface of the exposed specimens.

Current Density Distribution during Electrodeposition of Seal Disc

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In the area of electroplating, it is advantageous to find out the current

density distribution over the cathode/ sample surface in order to arrive at optimum conditions to get uniform electrodeposit over it, especially when irregular cathode surfaces are involved. Several numerical methods are available in literature for the determination of current density distribution in such field problems. This paper deals with the application of a numerical method adopted for the calculation of current density distribution over the sample surface when an annular region of a circular seal disc is electrodeposit. The method is based on the solution of Laplace's equation and relaxation under finite difference approximation. Such calculations are very useful in planning a plating process for electrodeposition on complex surface.

Preliminary Study of the Anomalous Electrodeposition of Nickel-Cobalt Alloy from a Sulfate-Chloride Bath

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The electrodeposition of nickel-cobalt alloy is anomalous type as cobalt is deposited more readily than nickel. The anomalous codeposition can be either enhanced or suppressed by changing the deposition conditions. In this work, nickel-cobalt codeposition from a sulfate-chloride bath has been investigated. The effect of plating variables on the composition of the deposit was studied. The microhardness of the deposits with different cobalt contents were measured and compared with that of a pure nickel deposit obtained from a bath of similar composition, pH and temperature in the absence of cobalt. The microstructure of the deposits with different cobalt contents were studied.

Electrochemical and Scanning Tunnelling Microscopic Studies on the Stability of the Octadecanethiol Self Assembled Monolayer onto some Pre-treated Noble Metal Surfaces

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Long chain alkanethiols chemisorb strongly and form highly ordered and stable self assembled monolayers on metal surfaces such as gold, silver and copper. The various factors that governn the formation, structure and properties of self assembled monolayers need to be understood in order to utilise them to study various interfacial phenomena such as

wetting, adhesion etc. We have studied the role of surface pretreatment on the structural stability and defect formation of octadecanethiol monolayer covered gold, silver and copper surfaces using cyclic voltammetry and scanning tunnelling microscopy. Absorption of alkanethiol on surfaces subjected to various pretreatments like mechanical polishing, electropolishing besides chemical etching was carried out. It is found that a surface which is polished with 0.05 micron alumina has a greater number of defect sites thereby allowing access to redox species compared to a surface treated with coarse emery. The surfaces which are chemically etched are found to have the best blocking ability. Scanning tunnelling microscopic studies reveals that for a given area an alumina polished surface has more number of grains (and consequent grain boundaries) compared to a surface roughened with coarse emery. Interestingly it is found that the defect density increases gradually as the number of grains in a given area increases. The behaviour of all the three metals studied has a remarkable similarity in this respect.

Electro Synthesis of Succinic Acid

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Succinic acid is manufactured either by electrochemical reduction or catalytic hydrogenation of maleic anhydride/maleic acid/fumaric acid. In the industrially practiced electrochemical method for succinic acid production, mostly lead sheets are used as the electrode materials in an undivided cell using aqueous sulphuric acid as the supporting electrolyte. While using lead as the electrode materials, the product is found to be contaminated with lead impurity and moreover the lead sheet used as the anode is very much corroded. As a result of the anode corrosion, the anode sheet has to be frequently replaced which makes the cell operation a difficult one. To overcome these difficulties number of other electrode materials such lead alloys, copper, silver, carbon and copper alloys are evaluated for their performance. In this paper the results obtained in the studies carried out using copper cathode and dimensionally stable anode in an undivided cell are presented.

3-D Nimonic Blades Machining by ECM

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Electrochemical machining (ECM) is a chipless machining process employing

electrolytic dissolution as a method of a removal of material. This method is extensively used to produce components out of difficult-to-machine and/or complex shapes. Required shapes are generated out of a 'work-piece' by making it anode and dissolving at very high current densities i.e.50-500 $A.cm^{-2}$. Electrochemical face machining process was developed for correcting the profile of nimonic twisted blades forged to near shape. The correction that was necessary was removal of an envelope of 0.5mm to 1.00 mm. For such a small envelope one cannot employ dynamic ECM alone, because to reach the steady state machining, by dynamic ECM, one needs a larger thickness. Due to this constraint a combination of static and dynamic ECM was used. A suitable fixture/ pressurized cell for this was designed and fabricated. The fixture was machined and out of aluminium and the necessary flow cavities were formed by moulding PVC, thus ensuring good flow velocity across the face of the blades. EC machined rotor blades do not require further machining/finishing operations. This paper deals with the machining of 3D Nimonic rotor blades to accurate profile dimensions and their production.

Titanium (III) Reduction of Dimethyl Glyoxime: Electrochemical and Kinetic Studies

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Titanium (III) species have been electrolytically generated and characterised. Titanium (III) mediated electroreduction of dimethyl glyoxime (DMG) was carried out and the reduction product was isolated and characterised in aqueous sulphuric acid medium. The kinetic investigations of titanium (III) reduction of dimethyl glyoxime was carried out under stoichiometric conditions at 306K. It has been found that the reaction follows overall second order kinetics, first order each in [Ti(III)] & [DMG] and fractional order in sulphuric acid. The progress of the reaction was monitored spectrophotometrically under varying concentrations of Ti(III), DMG, H_2SO_4, ionic strength and solvent composition. Effect of temperature was also studied and activation parameters were computed from

Arrhenius and Eyring plots. Mechanism constant with observed results was proposed and discussed.

Conductometric Studies on Solvation Behaviour of Tartaric Acid in Various Solvent Mixtures at 288-313K

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The study deals with experimental investigation on the ion-solvation behavior of Tartaric Acid in water-MeOH and water-EtOH at 288 to 313K by conductometrically. The conductance data were analysed by Krauss - Bray and Shedlovsky conductivity model. Ionisation and association constant were computed in all the cases. Walden product is also calculated. The Stoke's molecular radius was calculated by primitive model and Evan's semi-emperical relationship. Thermodynamic parameters have been estimated in all the cases. All these data were used to investigate the nature of ion-solvent and Solute-solvent interaction in the system under prevailing conditions.

Corrosion Failures in Aircraft Industries

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Failures do occur due to variety of reasons, among these, corrosion stands out to be a serious and costly damage particularly to flying machines such as aircraft. Causation of corrosion formation is many and mostly relates to the factors such as, material, stress, environment and process-related deficiencies.

To highlight the serious nature of failures from corrosion, the author discusses here three case-studies.