

EXPERIMENTAL DETAILS

CHAPTER III

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3.1 MATERIALS, CHEMICALS AND INSTRUMENTS USED

1. Stainless steel and mild steel specimens of area 5 x 1 x 0.1 cm were used for the deposition of tin and its alloys.
2. Analar grade chemicals were used in the preparation and analysis of tin and its alloys.
3. The experimental solutions for studies on electro deposition were prepared by dissolving analar grade chemicals in double distilled water and those for electrochemical investigations were prepared in Millique water.
4. Instruments used:
 - Properly calibrated ammeter and Voltmeter
 - DC regulated power supply (Aplab) as the current source for all the deposition studies.
 - Single pan balance (Dhone, Calcutta) for weight gain determination.
 - Hull cells and Harring and Blum cell.
 - High purity (99.55%) soluble and insoluble anodes were used. The anode – cathode area ratio was maintained as 1:1 throughout the studies.

3.1.1 Practical electro deposition

Since practical electro deposition is highly diverse in nature no single universal experimental procedure is found satisfactory to cover all aspects of electro deposition of a metal or alloy. Though absolute reproducibility is rather impossible to achieve due to several factors, to obtain reproducibility with minimum errors, experiments in

triplicate were performed taking precautions for maintaining the size and shape of the cathode, nature of the cathode surface, design and plating procedure.

3.1.2 Pretreatment of substrate surface

The surface should be free of all “foreign” matters like heavy scale of oxide films, heat scale, workshop soils and oils, grease, dirt and any other material so that the electro deposit alone adheres to the substrate of the component. This was achieved in practice in three stages: removal of heavy grease or oils, descaling and cleaning.

- ❖ Steel specimens were first pickled in concentrated HCl.
- ❖ Polished on a 120 emery wheel followed by cloth mop polishing.
- ❖ Degreasing with trichloroethylene.
- ❖ Alkaline electro cleaning using the following bath solution.
 - Sodium hydroxide 35 g/l
 - Sodium carbonate 25 g/l
 - Trisodium orthophosphate 10 g/l
 - Current density 3 A/dm²
 - Temperature 70°C
 - Time cathodic 2 mts and anodic 1mt
 - Anode stainless steel
- ❖ Acid dip in 5% H₂SO₄
- ❖ Washing with running water
- ❖ Rinsed with distilled water

3.2 BATH PREPARATION AND PURIFICATION

For any electroplating, proper method of preparing baths and preconditioning the solutions to remove metallic and other impurities is an essential part to get good deposits of required physical and chemical properties.

In the present investigation the plating baths of the following composition were prepared and used for electro deposition.

1. Electro deposition of tin

Stannous chloride	0.1 M
Sodium potassium tartrate	0.2 M
Sulphuric acid	1.0 M
pH	1
Temperature	30°C
Current density	0.5 Adm ⁻²
Anode	Tin slab

2. Electrodeposition of tin-nickel alloy

Stannous chloride	0.1 M
Nickel chloride	1.0 M
Sodium potassium tartrate	0.2 M
Hydrochloric acid	1.0 M
pH	0.5
Temperature	70°C
Current density	2 Adm ⁻²
Anode	Nickel slab

3. Electro deposition of tin-cobalt alloy

Stannous chloride	0.1 M
Cobalt chloride	1.0 M
Sodium potassium tartrate	0.2 M
Hydrochloric acid	1.0 M

pH	0.5
Temperature	70°C
Current density	2 A dm ⁻²
Anode	Stainless steel

3.3 CHARACTERIZATION OF PLATING BATH

3.3.1 Hull cell studies

Hull cell is widely used for the development, evaluation and control of a plating bath. It provides a simple and rapid method of visually testing the quality of electroplated deposit over a wide current density range [1]. The function of the cell is to provide by geometric configuration of a deposit on a flat surface which reproducibly records the character of the deposit formed at all current densities within the operating range. 267 ml of solution in a depth of 48mm of the cell was used. Anode of 60 x 65 x 1.0 mm in size and polished and cleaned cathode of 100 x 75 x 1.0 mm in size inclined at an angle of 38° were used. Cell current of 1 A was used. The current density at a point was calculated by using the formula

$$I = C (5.10 - 5.24 \log L)$$

Where,

I = current density in A/dm² at any point on the inclined cathode

C = the cell current used for the test

L = distance in centimeters of the point on the cathode at which current density is desired from the higher current density end of the cathode.

The formula was applicable over a distance of 0.64 to 8.25 cm on the panel. The results were expressed using standard codes to indicate the nature of deposits. The effects of the following additives were carried out using the optimized bath compositions with Hull cell at a cell current of 1A: peptone, gelatin and β-naphthol and thiourea.

3.3.2 Rate of deposition and cathode current efficiency (CCE) measurements [2]

Rate of deposition is the weight of thickness of deposit obtained in unit time. It is expressed in $\mu\text{m/h}$. Current efficiency is defined as the percentage of the total current usefully employed for the cathode deposition of the metal. This is calculated from the relationship

$$\text{CCE} = \text{Experimental weight/Theoretical weight} \times 100$$

For the measurement of rate of deposition and cathode current efficiency, the experimental set up used consisted of a regulated power supply unit (Aplab LD 3205 multi output power supply), a coulometer (IEC) and an ammeter (Zenith model ZE 1501 digital multimeter) connected in series to the plating cell. In the cell, the electrolyte under investigation was taken along with two electrodes, the positive anode and the negative cathode ($5 \times 1 \times 0.1 \text{ cm}$) immersed in it. The backside of the cathode was covered with lacquer. Electrodes were suitably connected to complete the circuit. Previously cleaned and weighed mild steel cathodes were used. Electro deposition was carried out at specific current densities for specific time durations and the deposits were dried and weighed. From the increase in mass (m) and the coulombs passed (Q), the rate of deposition and cathode current efficiency were determined using the equations given below.

$$\text{Rate of deposition} = \frac{m \times 10,000}{a d t}$$

Where,

m = Amount of metal deposited (g)

a = area of the deposit (cm^2)

d = density of the metal (g/cc)

t = time duration in hour

For a single metal deposition,

$$\text{Cathode current efficiency \%} = \frac{\text{Actual gain}}{\text{Theoretical gain}} \times 100 = \frac{m \times 100}{e Q}$$

Where, 'e' is the electrochemical equivalent of the metal.

For alloy deposition,

$$\text{CCE \%} = \frac{m \times 100}{e_{\text{alloy}} Q} = \left(\frac{p_1 m}{e_1 Q} + \frac{p_2 m}{e_2 Q} \right) \times 100$$

Where,

p_1 and p_2 are the % by weight of each metal of deposit

e_1 and e_2 are the electrochemical equivalents of Sn and Ni or Co

m = Mass of the alloy deposit (g)

Q = Quantity of electricity passed in coulombs (Ax Sec)

Otherwise, the electrochemical equivalent of the alloy (e_{alloy}) is calculated as

$$e_{\text{alloy}} = \frac{e_1 \times e_2}{(e_1 \times f_2) + (e_2 \times f_1)}$$

Where, e_1 and e_2 are the electrochemical equivalents of metals respectively, f_1 and f_2 are their respective fractions in the deposit.

Experiments were carried out both in tin and its alloy bath solutions with optimum concentration of the addition agents and without addition agents.

3.3.3 Throwing power [3, 4]

The degree of uniformity of metal distribution or evenness of deposit thickness obtained on a cathode of triangular shape is called the throwing power. Haring-Blum cell was used for determining the throwing power of plating baths, the cell consisted of a box of PVC of dimensions 15 x 5 cm. The solution was used to a depth of 5cm.

Cathodes of 5.2 x 8 cm x 0.25 cm were fitted at both ends of the box and connected by a rod. A perforated anode was placed between the cathodes in the distance ratio of 1:5. The cathodes were weighed initially and finally after deposition for a known time. From this the throwing power was arrived at by using the formula

$$\text{Percentage of Throwing Power} = \frac{L - M}{L + M - 2} \times 100$$

Where L is the linear distance ratio and M is the metal ratio. These are defined as

$$\text{Linear ratio (L)} = \frac{\text{Distance of a far cathode}}{\text{Distance of near cathode}}$$

$$\text{Metal ratio (M)} = \frac{\text{Weight of deposit on near cathode}}{\text{Weight of deposit on far cathode}}$$

3.3.4 Pulse plating

In conventional direct current plating only one electrical parameter, the current, is the variable. On the other hand in pulse plating, an interrupted current is used [5, 6]. In the present study the current supplied to the plating bath is not a constant direct current (DC) but is a series of short pulses. Three parameters, the peak current density (I_p), the length of time the current on (t_{ON}) and the current off period (t_{OFF}) are independently varied to determine the physical characteristics of the deposits obtained from the given electrolyte. Hence, by judicious choice of the above parameters one can create a variety of mass transport situations as well as wide range of nucleation conditions and adsorption and desorption phenomena during both “current-on” and “current-off” time. In pulse plating, the metal is deposited only during flow of current

pulse: no deposition occurs during “off” time. This intermittent current flow allows polarization conditions to subside and hence permits the use of higher current density without affecting the quality of deposit. During the off time or no deposition period, gas bubbles and impurities adsorbed on the cathode have a chance to desorb, thus facilitate deposition of very pure metals. It would be possible to get electrodeposit of predetermined properties and quality by a judicious choice of the pulse conditions. Electrodeposits were obtained by varying the duty cycle and the frequency at the optimum current densities in the absence and presence of the additives.

Pulse plating parameters

$$1. \text{ Cycle time} = \text{Time on} + \text{Time off}$$

$$2. \text{ Duty cycles (\%)} = \frac{\text{Time on}}{\text{Time on} + \text{Time off}} \times 100$$

$$3. \text{ Peak current} = \text{Average current} / \text{Duty cycle}$$

$$4. \text{ Frequency} = 1 / \text{Duty cycle}$$

3.3.5 Conductivity measurements

The conductivity of the different solutions was determined by means of a digital conductivity meter. The cell was calibrated with 0.01 M KCl over the range of 15-30°C for which detailed conductivity data was available [7], and the cell constant of 1cm^{-1} did not vary outside the accuracy of the bridge. The conductivity of the tin and tin alloy bath solutions with and without sodium potassium tartrate was determined.

3.3.6 UV Studies

Tin and its alloy solutions were identified using ultraviolet-visible spectroscopy using a Shimadzu-UV-Visible-2401 spectrophotometer. In the experiments performed the spectra were recorded after filling a standard quartz cuvette (cell path length of 1.0 cm) with the particular electrolyte, and the absorbance was recorded at a fast scan over the wavelength range of 200-800 nm. The quartz cuvette was rinsed and dried after each scan before filling it with next solution. UV spectroscopy analysis was repeated for all the constituents. Finally, the UV spectra of the tin and tin alloy baths in the presence and absence of sodium potassium tartrate were measured.

3.3.7 Electrochemical behaviour of the baths

a) Cyclic voltammetry

Cyclic voltammetric studies were carried out with BAS 100 WB Electrochemical analyzer. A three electrode cell assembly was used. A platinum foil was used as the working electrode, a large area of platinum foil was used as counter electrode and saturated calomel electrode was used as the reference electrode for both tin and its alloy baths.

The sensitivity of the system was adjusted by 1mA/V. The range of scanning potential was from +50 to -750mV for tin bath and from +200 to -850 mV for all alloy baths. The experiment was carried out under varied scan rates, concentration of the electroactive species and pH of the medium for the plating baths in the absence of additives and also for additives at their optimum concentrations.

b) Impedance measurements

To understand the grading among the additives in terms of facilitating the cathodic process, impedance measurements were carried out by superimposing AC

voltage over the respective deposition potentials of the electrode processes using the same cell set up as mentioned above in CV studies.

3.4 CHARACTERIZATION OF TIN AND ITS ALLOY DEPOSITS

3.4.1 Physico-chemical characterization

Surface preparation prior to deposition is an important factor and was achieved by mechanical, chemical and electrochemical methods. The characteristics of the deposits from a plating solution were influenced by plating conditions, nature of the substrate, composition of the solution and its purity. The obtained deposits under different conditions were studied by Scanning Electron Microscope (SEM), Energy Dispersive X-ray analysis (EDAX), and X-ray Diffraction studies (XRD) technique.

3.4.1.1 Adhesion

There must be adequate bonding between the coating and the substrate and can be tested by methods like bend test, burnishing test, file test, grinding test, peel test, scratch test, heat cycle test and tape test. If no peeling, flaking and / or blister formation is seen after the test, the adhesion is satisfactory. For achieving proper deposit adhesion a suitable pretreatment of the substrate is necessary.

One of the simplest methods, known as the bend test [8] was followed to evaluate the adhesion of tin and its alloy coatings on mild steel. Mild steel specimens were plated with the respective metals and were then bent at 180°, repeating the bending up to the point of fracture of the steel base.

3.4.1.2 Porosity

Electrodeposits contain pores and cracks to a varying extent. They constitute the opening in the deposit, enabling access of corrosive medium and moisture to the substrate. Porosity is of more importance for coating which is more cathodic than the

basis metal. Porosity tests were designed to detect all discontinuities such as pores and cracks in the deposits. The methods described to test the porosity are electrographic tests, Hot water test, Ferroxy test [2] and Gas porosity test.

Porosity of the electrodeposited tin and its alloys coated over steel, from the three baths, were detected by the ferroxy test. Special test papers were prepared by impregnation in a solution containing 50 g/L NaCl and 50 g/L gelatin and drying. They were rewetted in 50 g/L NaCl solution again just before the test, then pressed against the electrodeposited panel and left for 10 min. The papers were immersed in 10 g/L solution of potassium ferricyanide. Blue marks developed in the region where steel was exposed through discontinuities in the coating, were counted by examining the surface in a microscope at 10X magnification. The porosity of the coating was expressed in number of pores per cm^2 .

3.4.1.3 Micro hardness

The method used was the penetration method. A diamond indenter, pyramidal in shape, called a Vickers indenter, was employed. The test consisted of pressing the indenter with a known load against the deposit for 30 to 60 seconds, releasing it and measuring the diagonal (average of diagonals) using a microscope.

With the load L in Kgs and the diagonals in millimeters the micro hardness was calculated as follows:

$$H_v = 1.854 L / d^2 \quad \text{Kg/mm}^2 \text{ or gms / micrometer}$$

$$H_v = \text{Vickers number}$$

In the present investigation micro hardness was measured using VHN. Hardness of the electrodeposited tin and its alloy surface obtained from baths with and without various additives was measured using a LECO Micro hardness Tester Model M400 by the static indentation method [9] and each electrodeposit was of 30-35 μm thickness.

3.4.1.4 Wear resistance

The wear resistance was determined using a Taber Abraser Model 503 as per AASTMD – 4060. The electrodeposited specimen (10 x 10 cm) was weighed initially and mounted on the turn table of the instrument. It was then subjected to abrasion by using Cs-10 abrading wheels for a load of 500g for 100 cycles. The specimen was then reweighed and the weight loss (in mg) observed was expressed as the abrasion (index) resistance.

3.4.2 Corrosion characteristics of tin deposits

One of the important properties of electrodeposited coatings is their corrosion resistance ability. Porosity of the electrodeposits is closely related to corrosion. The structure of the electrodeposits would vary with the deposition conditions. Evaluation for better corrosion resistance may be carried out by non-electrochemical and electrochemical techniques.

3.4.2.1 Potentiodynamic polarization method

The polarization measurements were made to evaluate the corrosion current, corrosion potential and the Tafel slopes. Experiments were carried out in a conventional three-electrode cell assembly. The working electrode was mild steel specimen of 1 cm² exposed area, with the rest being covered with lacquer. A large platinum foil and saturated calomel electrode were employed as auxiliary and reference electrode respectively. 3.5% sodium chloride was used as test solution.

The working electrode was polished and degreased with trichloroethylene. The reference, working and counter electrode were assembled in position and the electrical contacts were given. A time interval of 10-20 minutes was given to each experiment to attain the steady state open circuit potential. Then the electrode potential was fixed at open circuit potential. To the open circuit potential (OCP) the steady state polarization

was carried out from +200 mV to -200 mV to the OCP at a scan rate of 10 mV/sec. E_{corr} and i_{corr} values were obtained from the plot of E vs log i curves by Tafel extrapolation method.

3.4.2.2 Impedance measurements

For the measurements of impedance, the cell used was the same as that used for potentiodynamic polarization. An A.C. potential of 10 mV was superimposed on the steady open circuit potential in the frequency range of 10 mHz to 100 KHz using EG & G impedance analyzer, Model 6310 Software Model M270. The real part (Z') and the imaginary part (Z'') were measured at various frequencies. A plot of Z' vs Z'' was made. From the plot the charge transfer resistance and double layer capacitance values were calculated.

3.4.2.3 Salt spray test

The electrodeposited specimens (5 x 5 x 0.1) were subjected to salt spray after the edges and the top un-deposited portion were sealed with masking adhesive tape. They were degreased with trichloroethylene and subjected to 3.5% NaCl neutral salt spray exposure. The test was conducted at the rate of 8 hours spraying per day and 16 hours rest successively. The hours of spraying, as well as total hours spent in the cabinet until the onset of failure of the sample, as indicated by red rust formation, were recorded. The corrosion resistance of the panels was evaluated according to ASTM standards [10].

3.4.3 Surface characteristics of tin deposits

3.4.3.1 Scanning Electron Microscope (SEM)

In order to understand the nature of the deposits obtained, the deposits obtained from different electrolytes were studied visually and by using a Scanning Electron Microscope. SEM photographs were taken by using the Model JEOL instrument. The

deposits obtained from various baths with and without tartrate and addition agents at optimized plating conditions by means of DCP and PCP methods had been examined for their morphology.

3.4.3.2 X-ray Diffraction studies (XRD)

The crystal structure of tin and its alloy deposit grains were examined through X-ray diffraction. The deposits produced with and without sodium potassium tartrate and additives by means of DCP and PCP methods were studied. The samples were scanned between $30^\circ - 100^\circ$ (2θ) at a scan rate of 1 degree per minute using Cu K_α ($\lambda = 1.5405 \text{ \AA}$) radiation. The peaks due to the different phases were identified and the corresponding lattice parameters were also calculated.

References

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