EXPERIMENTAL DETAILS
CHAPTER - III

EXPERIMENTAL DETAILS

3.1 CHEMICALS USED

The following analar grade chemicals were used.

1. NickelSulfamate
2. SodiumTungstate
3. AmmoniumChloride
4. TriammoniumCitrate
5. DMSO
6. Sodium hypophosphite
7. Sodium (meta) borate.

3.2 INSTRUMENTS

The ammeters and voltmeters used in this work were properly calibrated. The D.C. regulated power supply used as current source for plating trials had A.C. ripples of less than 0.1 mV. For weight measurements, single pan digital electronic balance was used. The Hull cell and other cells used were fabricated as per the specifications. High purity (99.95%) soluble nickel anodes were used. The anode to cathode area ratio was maintained as 1:1 in the studies.

3.3 PRACTICAL ELECTRODEPOSITION

Since practical electrodeposition is highly diverse in nature, no single universal experimental procedure is found satisfactory to cover all aspects of electrodeposition of metals and alloys. However, it is very essential to select relevant methods to correlate laboratory experiments with actual industrial operations. Though absolute reproducibility is rather impossible to achieve due to several factors, reproducibility with minimum errors is of considerable importance. Precautions are necessary for maintaining the size and shape of
the cathode, nature of the cathode surface, proper design and plating procedures.

Surface preparation prior to deposition is an important factor and can be achieved by mechanical chemical and electrochemical methods. Table-1 presents the pretreatment conditions for alloy deposition on copper panel.

Table -1

<table>
<thead>
<tr>
<th>PRETREATMENT CONDITIONS FOR COPPER PANELS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Degreasing with trichloroethylene.</td>
</tr>
<tr>
<td>2) Alkaline electro cleaning in a solution consisting of</td>
</tr>
<tr>
<td>Sodium hydroxide - 35 g/1</td>
</tr>
<tr>
<td>Sodium carbonate - 25 g/1</td>
</tr>
<tr>
<td>at a current density of 2 A/dm² for 1 minute.</td>
</tr>
<tr>
<td>3) Washing with running water.</td>
</tr>
<tr>
<td>4) Mild acid dip in 5% (v/v) sulphuric acid for 15 seconds.</td>
</tr>
<tr>
<td>5) Washing with running water.</td>
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<tr>
<td>6) Distilled water dip.</td>
</tr>
</tbody>
</table>

Table No: 1 presents the pretreatment conditions for alloy deposition on copper panels measuring 1cm x 5cm. The copper specimens were mechanically polished to mirror finish. They were then treated as follows. Degreasing with trichloroethylene
Electrocleaned cathodically for 1 minute in the following solution.

- Sodium carbonate : 20 gpl.
- Trisodium orthophosphate : 9 gpl.
- NaOH : 7 gpl.
- Temp : 80°
- Anode : Stainless steel
- Current density : 4 A/dm²
- Swilled in running water
- Dipped in 5% V/V sulphuric acid for 15 seconds
- Rinsed with distilled water

3.4 BATH PREPARATION AND PURIFICATION

For any electroplating, proper method of preparing baths and preconditioning the solutions to remove metallic and other impurities are essential to get good deposits of required physical and chemical properties. The plating bath of the following composition was prepared and used in the investigation for electrodeposition.

Ni-W

- Nickelsulphamate : 0.15 M
- Sodiumtungstate : 0.15 M
- Ammoniumchloride : 0.2 M
- Triammoniumcitrate : 0.3 M
- Dimethylsulphoxide : 0.06 M
- Temperature : 70°C
- pH : 8
- Current density : 3 A/dm²
- Vigorous constant stirring

58
Ni-W-P

- Nickelsulphamate : 0.15M
- Sodiumtungstate : 0.15 M
- Triammoniumcitrate : 0.3 M
- Ammoniumchloride : 0.2 M
- Dimethylsulfoxide : 0.06 M
- Sodiumhypophosphite : 0.05 M
- Current density : 3A/dm²
- Temperature : 70 °C
- pH : 8
- Vigorous constant stirring

Ni-W-B

- Nickelsulphamate : 0.15 M
- Sodiumtungstate : 0.15 M
- Triammoniumcitrate : 0.3 M
- Ammoniumchloride : 0.2 M
- Dimethylsulfoxide : 0.06 M
- Sodium (meta)borate : 0.05 M
- Current density : 3 A/dm²
- Temperature : 70 °C
- pH : 8
- Vigorous agitation
3.5 HULL CELL EXPERIMENTS

Fig: 3.1 Standard Hull Cell
A useful method of testing a plating bath is to employ a specially designed cell like Hull Cell Fig 3.1, so that one can observe the nature of the deposit over a range of current densities as determined by the cell current for the Hull Cell test (1). The cathode surface is inclined at an angle to the anode so that different points on the cathode correspond to different current densities. Polished stainless steel cathodes of 100x75x0.25 mm size and cell current of 1.0 A were used for duration of 10 minutes. The following formula enables calculation of the current density at a desired point on the Hull Cell cathode.

\[
\text{Cell current in } A/\text{dm}^2 \text{ at any point on the incline cathode} = C(5.1-5.24 \log L)
\]

Where, 
\( C = \) total current passing through the cell
\( L = \) distance in cm of the point from the nearer end of the cathode.

This equation is applied to the range of 0.64-8.25 cm. The bath composition was decided by this study and the nature of deposition was also noted for different additives.

3.6 CURRENT EFFICIENCY MEASUREMENTS (2)

Copper specimens of size 1cm x 5cm were mechanically polished and degreased with trichloroethylene. One side of the specimen was masked with lacquer. The specimens were alkaline cleaned cathodically in the alkaline cleaning solution for 3-5 minutes. They were then inserted into a 100ml beaker containing the electrolyte. Pure Nickel anode was used. Deposition was carried out at constant current densities in the range of 5A to 8A/dm² (for 30 minutes) & at const. pH in the range 5 - 8 & at constant tungsten concentration with range 0.05 M to 0.2 M & at constant in the range of 50°-80°C for 30 minutes. A copper coulometer was used to follow the charge flown in the circuit. After deposition the cathode was remarked, washed well with distilled water, dried and weighed. The cathodic current efficiency was calculated as follows.
M x 100
CCE of Ni-W alloy = Where \( M \) = mass of the
alloy deposit (g).

\( e_{\text{Ni-W} \times Q} \)

\( Q \) = quantity of electricity passed in columns (A x secs).

The electrochemical equivalent of Ni-W alloy was calculated as

\[
e_{\text{Ni-W}} = \frac{e_{\text{Ni}} x e_{\text{W}}}{(e_{\text{Ni}} x f_{\text{Ni}}) + (e_{\text{W}} x f_{\text{W}})}
\]

Where \( e_{\text{Ni}} \) & \( e_{\text{W}} \) are the electrochemical equivalents of Ni & W, respectively, \( f_{\text{Ni}} \) & \( f_{\text{W}} \) are their respective fractions in the deposit.

3.7 THROWING POWER MEASUREMENTS (3, 4, 5)

![Haring - Blum Cell Diagram](image)

Fig 3.2 Haring - Blum Cell for the determination of Throwing Power

A convenient way of determining the throwing power is by employing a Blum and Haring Cell Fig 3.2. The assembly consisted of a rectangular cell containing two sheet metal cathodes of 9 x 5 x 0.1 cm size at the ends of the cell and one perforated anode of the same size. The anode was placed
between the cathodes so that its distance from one of the cathodes was one fifth of its distance from the other. If the polarization were negligible as compared with the potential drop in the electrolyte, and if the cathode current efficiency was 100 percent, the metal distribution will be determined by the inter-electrode distances. The mass of the metal deposited on the nearer cathode \((C_n)\) would be five times as much as that deposited on the farther cathode \((C_f)\). Under such conditions the electrolyte would behave in accordance with Ohm's law and the metal distribution would be proportional to current distribution. In this hypothetical case, the current distribution is referred to as primary distribution. However, when contact resistance at the interface between the electrolyte and the cathode is high compared with the resistance of the electrolyte due to polarization, the resulting current distribution would be known as secondary distribution. The Field formula for the throwing power is as follows:

\[
\text{Throwing power (\%) } = \frac{K-C}{K+C-2} \times 100
\]

where \(C(=C_n/C_f)\) is the metal distribution ratio and \(K\) is the ratio of the distances respectively of the farther and nearer the cathodes from the anodes. Thus \(K\) is current distribution ratio and normally it is maintained at the value of 5. It gives values which are more realistic and range from +100 percent to -100 percent. Throwing power was calculated for different solutions using the field formula.

3.8 Adhesion

The adhesion of an electrodeposited coating is an important measure of its serviceability. The principal causes for poor adhesion are (1) the presence of foreign material between the coating and the basis metal, (2) the presence of a weak layer of metal either upon the surface plated or on the initial deposit, and (3) the incidence of stress in the deposited metal. Adhesion testing methods \((6, 7)\) can be broadly classified into (i) quantitative test and (ii) qualitative test.
The quantitative tests such as Oliard test, Cobalt nodule test and Peel test require a thick deposit, which is time consuming. Hence, it is not suitable for testing of thin coatings actually used in service conditions. The qualitative tests are simple and have some significance for the practical plater, but are of little value for precise specifications. Operations which can be included in this category are bending, twisting, buffing, abrading, chiseling, and filling cupping and thermal cycling.

One of the simplest methods, known as the bend test (8) was followed have to evaluate the adhesion of Zinc, coatings on mild steel. Copper specimens (5x5x0.1 cm) were plated with the respective metals and were then bent at 180°, repeating the bending up to the point of fracture of the copper base.

3.9 POROSITY

Porosity of electrodeposited coatings can be defined as the degree of uncovered microscopic regions of the base metal (9, 10). In general, the degree of porosity of the deposit decreases with increases in thickness. Porosity is however important in the case of deposits which are nobler than the base metal since in such coatings, the rate of attack at the pores is likely to be accelerated. Traditional and reliable tests for porosity are based on the application of a reagent which will react with the base metal through the pores in the coating and will not attack the deposit.

For determining the porosity of nickel tungsten alloy deposits on steel substrates, the Ferroxyl test was used (11). The electrodeposits were degreased, electro cleaned and dried. The Ferroxyl test solution was prepared by dissolving sodium chloride and white gelatin in distilled water at 45°C to obtain a concentration of 0.86 M (50 g/l) sodium chloride. Filter paper strips of 10 x 10 mm size each were impregnated with the above solution and dried. Before placing a strip on the plated surface it was moistened with a few drops of sodium chloride solution (50 g /l). In the case of nickel-tungsten alloy deposits, ten minutes were allowed. The papers were then removed and
placed at once in a K₃Fe(CN)₆ solution 0.03 M (10g/l). The porosity of each deposit was evaluated on the basis of the number of green spots formed.

3.10 MICROHARDNESS

Hardness of the electrodeposits Ni-W Ni-W-P, Ni-W-B was measured using a LECO Microhardness tester Model M400 by the static indentation method (12). A diamond pyramid indenter was pressed on to the deposit under a load of 50g for 15 seconds and the indentation diagonal was measured after the load was removed. Each electrodeposit used for this measurement was of 25 μm thickness. The microhardness of the deposit in kg/mm² was determined in each case by using the following formula.

\[
\text{Hardness, VHN (kg/mm}^2) = \frac{1854xP}{d^2}
\]

Where, \(P\) = load applied in grams and
\(d\) = diagonal of the indentation obtained in μm.

3.11 ABRASION INDEX

The abrasion resistance was determined using a Taber Abraser Model 503 as per ASTM D-4060). The specimen 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 1000g for 1000 cycles. The specimen was then reweighed and the weight loss (in mg) observed was expressed as the abrasion index.

3.12 CRACK DENSITY

The presence of cracks in the nickel - tungsten alloy deposits was observed using a PMT-3 Soviet make microscope at a magnification of x250. The number of cracks cutting the cross wire of the eyepiece were counted and the cracks present per cm was calculated.
3.13 Characterization of Tungsten and its alloy Electrodeposits

3.13.1 Physicochemical characterization

Practical electrodeposition is highly diverse in nature and no single universal experimental procedure is found satisfactory to cover all aspects of electrodeposition of metals and alloys. However, it is very essential to select relevant methods to correlate laboratory experiments with actual industrial operations\(^1,2\). Though absolute reproducibility is rather impossible to achieve due to several factors, reproducibility with minimum error is of considerable importance. It is therefore desirable to perform experiments in triplicate. The precautionary measures regarding the size and the shape of the cathode surface, design and plating procedures are necessary to obtain reproducible results.

Surface preparation prior to deposition is an important factor and can be achieved by mechanical, chemical and electrochemical methods.

The characteristics of the deposits from a plating solution are 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.

3.13.2 Potentiodynamic polarization studies

For polarization studies Tungsten - Nickel deposit was obtained on the copper electrode of area 1 cm\(^2\) from the bath at their optimum concentrations. A rectangular platinum foil was used as the counter electrode. Saturated calomel electrode was used as the reference electrode. A 5% NaCl solution was used as the test solution. Polarization studies were done from 0 mv to -900mv with respect to their rest potential at a scan rate of 10 mV/sec.

The E Vs log I plots were made from which the corrosion current and corrosion potential were calculated.
3.13.3 Impedance Measurements

The EIS experiments were carried out at the DC deposition potential with superimposed AC voltage of amplitude 10 mV in the frequency range of 100 mHz to 100 KHz using EG&G impedance analyzer, Model 6310 software model M270. The coated alloy plate and platinum foil were used as the working and counter electrodes respectively. The SCE was used as the reference electrode. The 5% NaCl solution was used as the electrolyte medium. The real part (Z') and the imaginary part (Z'') of the cell impedance were measured at various frequencies. From the Impedance diagrams the charge transfer values and double layer capacitance values were calculated.

For Ni-W-P and Ni-W-B the potentiodynamic linear polarization (PLP) and electrochemical impedance studies were performed using a potentiostat (Autolab PG STATE 30) for corrosion analysis. The photograph of the system is shown in Fig 3.3. A saturated calomel electrode (Hg/Hg2Cl2 ) and Pt were used as reference and auxiliary electrodes respectively.

3.13.4 Atomic Absorption Spectroscopic (AAS) analysis

AAS 800 (Perkin Elmer, 249.7 nm and slit 0.7 nm) was used to analyze boron. The photograph of the system is shown in Fig 3.4. The composition of the alloy was determined by EDX (Energy Dispersive X-ray analysis).

3.13.5 Cyclic Voltammetry

Cyclic Voltammetric studies were carried out with BASI00WB Electrochemical analyzer. For the CV studies, a platinum foil was used as the working electrode and large area of Pt foil used as the counter electrode. Saturated calomel electrode was used as the reference electrode for both Nickel and its alloy baths.

Cyclic Voltammetric studies were done at different scan rates. The sensitivity of the system was adjusted by 1 mA /V. The range of scanning potentials were +800to-800 mV and +600to-600mV for NiW and NiWP and NiWB baths respectively.
Fig. 3.3 Autolab PG STATE 30 for electrochemical impedance studies
Fig. 3.4 Atomic Absorption Spectrophotometer 800 (Perkin Elmer, 249.7 nm and slit 0.7 nm)
3.14 Pulse Plating

Pulse Plating can be defined as a method of electroplating by means of an “on-off” direct current (or potential) in place of continuous direct current used in conventional plating (13, 14). In conventional direct current plating only one electrical parameter is variable, the current (or potential). On the other hand in pulse plating an interrupted current is used (the current may or may not drop to zero between pulses), three parameters are independently variable. There are three parameters, which can be varied independently in pulse plating are,

(a) The peak current (density) $I_p$ during “current-on” pulse.
(b) The length of time of the “current-on” pulse ($t_{on}$) and
(c) The ”current-off” period ($t_{off}$).

This determines the physical characteristics of the deposits obtained from the given electrolyte (15).

Hence by a judicious choice of the above parameters one can create a variety of mass transport situations as well as a 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 absorbed on the cathode have a chance to desorbs, thus facilitate deposition of very pure metals. The metallic ions deposited after each relaxation period are on new nucleation sites and this leads to more amorphous, fine grained and pore-free deposit. The resulting grain refinement, in turn, improves physical properties (higher hardness, higher density, lower porosity, lower wear rates etc). Hence pulse plating has become an accepted method of improving the quality of electrodeposited finishes. It would be possible to get electrodeposits of predetermined
properties and quality by a judicious choice of the pulse conditions. Pulse plating has many advantages over conventional plating as described below.

(i) **Decreased porosity**: this is mainly due to grain refinement. The grain size is generally finer after pulse plating as compared to that after direct current.

(ii) **Improved adhesion**: the peak voltage of each pulse can be several times greater than the direct current voltage and this may help to break down any passive films on the cathode substrate and facilitate even deposit of the plating layer.

(iii) **Improved deposit distribution**: in DC plating, greater deposition or “burning” will occur in the high current density areas of the work piece. This effect is greatly reduced and improved by means of a pulsed current.

(iv) **Greater macro throwing power**: this is obtained in recesses, plated-through holes and other complex shapes.

(v) **Improved covering power**: the coating thickness required to achieve a given characteristic (e.g. colour, freedom from porosity) can be reduced by a factor of 1/3 to 1/2. This effect is due to the micro throwing power.

(vi) **Anode dissolution**: In conventional D.C. plating, an oxide film is sometimes formed on the anode, thus inhibiting dissolution of the anode materials, and this will cause a change in the bath composition. The problem is usually overcome by the use of an addition, e.g. chlorides in nickel baths. In pulse plating, oxide film formation is reduced at the anode, thus eliminating a need for an anode breakdown additive.

(vii) **Improved physical properties**: Increased density decreased surface resistivity, decreased volume resistivity, greater ductility, and control of hardness, greater water and corrosion resistance are the properties
Reduction of stress in the electrodeposit: The nucleation and growth of the deposit during D.C plating tends to build lattice imperfections, impurities, voids nodules, etc. into the deposit. This result in the formation of stresses that can be reduced by using additives such as saccharin, which may lead to further problems. In pulse plating, the codeposition of impurities and imperfections are greatly reduced and, hence the internal stresses in the deposit will be considerably, lowered. Thus, it is possible to produce crack-free chromium by this method.

### 3.15 pulse plating parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cycle time</td>
<td>( = \frac{\text{Time on} + \text{Time off}}{\text{Time on } \times 100} )</td>
</tr>
<tr>
<td>2. Duty cycles (%)</td>
<td>( = \frac{\text{Duty cycle}}{\text{Time on} + \text{Time off}} )</td>
</tr>
<tr>
<td>3. Peak current</td>
<td>( = \frac{\text{Average Current}}{\text{Duty cycle}} ) or ( = \frac{(\text{Time on} + \text{Time off}) \times \text{Average Current}}{\text{Time on}} )</td>
</tr>
<tr>
<td>4. Time forward ((T_F))</td>
<td>( = \frac{\text{Ampere -Time}}{\text{Average current}} )</td>
</tr>
<tr>
<td>5. The total time</td>
<td>( = T_F + T_R )</td>
</tr>
<tr>
<td>6. Factor (X)</td>
<td>( = \frac{\text{Time forward ((T_F))}}{\text{Time reverse ((T_R))}} )</td>
</tr>
<tr>
<td>7. Select (T_R)</td>
<td></td>
</tr>
<tr>
<td>8. (T_F) is calculated as follows</td>
<td></td>
</tr>
</tbody>
</table>
9. Select a forward pulse ON and OFF times

\[ T_F = TR \times X \]

Forward Time
\[ \frac{\text{ON Time + OFF Time}}{\text{ON time + OFF time}} = \text{A whole number (1, 2, 3, etc.,)} \]

10. Peak forward current = \( \frac{\text{ON time + OFF time}}{\text{Pulse ON Time}} \times \text{Ave. current} \)

11. Select reverse ON and OFF Times

Reverse Time
\[ \frac{\text{ON Time + OFF Time}}{\text{ON Time + OFF Time}} = \text{A whole number (1, 2, 3, etc.,)} \]

12. Peak reverse current = \( \frac{\text{ON time + OFF time}}{\text{Pulse ON Time}} \times \text{Average current} \)

13. Forward average amperes

\[ \frac{\text{ON Time}}{\text{ON Time + OFF Time}} \times \frac{\text{Forward Time}}{\text{Forward Time + reverse Time}} \times \text{Average ampere} \]

14. Reverse average amperes

\[ \frac{\text{ON Time}}{\text{ON Time + OFF Time}} \times \frac{\text{Reverse Time}}{\text{Reverse Time + Forward Time}} \times \text{Average ampere} \]

15. Forward ampere time = \( \text{Average forward meter current} \times (T_F + T_R) \)

16. Reverse ampere time = \( \text{Average reverse meter current} \times (T_F + T_R) \)

The experimental set up for the pulse plating is shown in Fig 3.5
Fig. 3.5 Pulse plating cell set up
3.16 Structural and Morphological Evaluation

3.16.1 Scanning Electron Microscope

Scanning Electron microscopical analysis is used to provide structural information in much finer detail than optical microscopy, due to the superior resolution. They also have enhanced depth of field and hence surface coatings are examined directly in the microscope. The surface appearance and topography of Ni-W, Ni-W-P, and Ni-W-B alloy plating were studied using Scanning Electron microscope, JEOL unit.

3.16.2 X-ray Diffraction (XRD)

The arrangement of atoms determines the structure of electrodeposits. Most electroplated metals are crystalline and the atoms are arranged in a regular three dimensional pattern. The smallest arrangement is called a unit cell. Unit cells are the building blocks of larger, three dimensional structures called crystals or grains. All unit cells within each grain are oriented the same way.

X-ray and electron diffraction analysis is widely used to ascertain the spacing of atoms in a crystal and the orientation of unit cells. The crystal structure of the Ni-W alloy deposit grains was examined through X-ray diffraction. The samples were scanned between 20°-80° (2θ) at a scan rate of 1 degree per minute using Cu Kα (λ=1.5405 Å) radiation. The peaks due to the different phases were identified and the lattice parameters also calculated. The particle size of the deposit is computed from,

\[ D_{hkl} = \frac{k\lambda}{\beta \cos \Theta} \]

Where k is Scherrer constant with the value of 1, X-ray wave length is \( \lambda \) (1.5405 nm for Cu target), \( \Theta \) Bragg angle, and \( \beta \) peak half-width in radiation unit.

3.16.3 Differential Thermal Analysis (DTA)

DTA measurements for Ni-W system were performed using Diamond TG/DTA (Perkin Elmer) system. The results were compared with XRD analysis.
References