

CHAPTER 2

EXPERIMENTAL

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" EXPERIMENTAL "

2.1 EXPERIMENTAL SET UP :

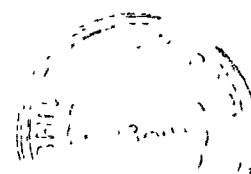
The experimental set up used for single metal and alloy deposition is illustrated in Diag.1. It is self explanatory. It consists of an electrolytic cell (a pyrex glass beaker of 250 ml capacity) containing bath solution. It was provided with a stirring arrangement, a precision type ammeter, electrodes with holders, a copper coulometer, an adjustable resistance and a D.C. power supply unit all connected in series but for a voltmeter (or potentiometer) as shown in the diagram.1.

2.2 EXPERIMENTAL PROCEDURE FOR THE DEPOSITION OF SILVER DEPOSIT.

The standard stock solutions of the required compounds were prepared in double distilled water. The chemical bath as detailed under the respective tables was prepared by adding together the calculated amounts of the required constituents and then making up the total volume with double distilled water accurately to 200 ml.

2.3 COPPER COULOMETER AND PREPARATION OF OTTAL'S SOLUTION.

A copper coulometer was found to be more convenient and relatively more accurate than others to measure the quantity of electricity passing through the circuit, during electrolysis. The coulometer solution was prepared as per Ottal's recommendations (19).



Thus, it was prepared by adding 150 gm of recrystallised copper sulfate, 50 gms of sulphuric acid (sp. gr. 1.84) and 80ml. of ethyl alcohol in a litre of double distilled water. During electrolysis, the coulometer cell containing the Ottal's solution and provided with two copper plates of the same size to serve as anode and cathode, were connected in series with the experimental cell. The copper cathode in the coulometer was weighed accurately before and after deposition. It was washed with distilled water and alcohol, before weighing. The amount of copper deposited in the coulometer during electrolysis gave the measure of current from which cathode efficiency for metal deposition was calculated.

2.4 ANODE AND CATHODE MATERIALS :

Anodes used in the work were of pure metals such as nickel sheet (5 cms x 2.5 cms) or platinum electrodes (5 cms x 2.5 cms) etc. depending on the nature of the deposit.

Copper plates of desired size were used as substrate for deposition. Copper is preferred as cathode to any other base metal, because it is easier to clean and much smoother surface can be obtained for deposition than any other metal. For qualitative and quantitative work cathode of copper or of platinum of the same dimensions were employed.

Even a trace of grease on the cathode spoils the deposition. The cathode should be as clean and greaseless as possible. Hence its cleaning is very important in deposition. The cleaning was carried out as follows :

A thin rectangular copper plate cut according to the desired size was first rendered free from grease by dipping it in a hot and strong 20 % alcoholic caustic soda solution for a while, and then washed with water. It was next immersed in a moderately strong nitric acid solution, containing very little concentrated sulphuric acid and copper nitrate. This removes the surface scales. The copper nitrate checks the violent action of the acid on the plate. It was then washed with sodium carbonate and again dipped in a slightly acidic solution to remove the alkali adhering to the plate. This is done because acids are easier to wash off from copper plate than alkalies which adhere to the plate and have pronounced chemical action on the metal. Then the copper plate was thoroughly washed with tap water, distilled water and finally with alcohol or acetone, and then dried well. It was then accurately weighed and used as cathode.

2.5 WORKING PROCEDURE OF ALLOY DEPOSITION :

The experimental set up of the apparatus described in 2.1 is first arranged and then 200 ml of the chemical bath prepared according to 2.2, were taken in the electrolytic cell

Provided with stirring arrangement, The cell was kept at the desired constant temperature ($\pm 2^{\circ}\text{C}$) in a thermostat. To avoid deposition by immersion, the current was first switched on and then well cleaned rectangular cathodic plate (5.0 cm x 2.5 cm) was placed between two parallel anodes and the electrolysis carried out under a definite set of experimental conditions specified under the corresponding tables.

In almost all the experiments, duplicate runs were taken from the same bath solution which was discarded after the work and the metals were recovered from the waste.

After electrolysis, the cathode which was previously weighed, was withdrawn from the cell and washed thoroughly under tap water, which was followed by distilled water and alcohol wash. It was then dried, cooled in the vacuum desiccator and finally weighed accurately. The difference in weight before and after deposition gave the amount of alloy deposited, during electrolysis.

The ammeter roughly measured the current in amperes passing through the cell and the voltmeter (or potentiometer) recorded the voltage. Copper coulometer gave the quantity of electricity accurately passing through the circuit during electrolysis.

In order to establish the optimum conditions for the production of smooth, fine grained, bright, uniform, adherent and comparatively harder deposit, the effect of the following parameters was studied in details in each of the systems.

- 1) Concentration of the electrolyte,
- 2) Current density,
- 3) Temperature,
- 4) Duration of electrolysis,
- 5) Electrode distance,
- 6) Addition agents.

2.6 ANALYSIS OF DEPOSITS :

The accurately weighed deposit was carefully dissolved from the cathode in the minimum amount of conc. HCl/ HNO₃ and then diluted with double distilled water accurately to a known volume, from which qualitative and quantitative analysis was done.

First of all the presence of metal ions in the test solution of the pertinent deposit was detected by applying the spot test technique (20) and the usual tests in qualitative analysis.

After ascertaining the presence of particular ion/ions in the test solution the qualitative analysis of the metal was carried out by either chemical (21) or physical method. Various physical methods were employed for analysis of alloy deposit as well as for bath solutions by different workers in the past. For example colorimetric and spectrophotometric methods were used for analysis by Claubaugh W.S. (22) and Bayley (23) Spectrographic analysis was followed by Gordon H.E.Z. and Roberts E.R.⁽²⁴⁾ While polarographic methods were used by Kolthoff I.M. and Lingane J.J., Singh V.B. and Tikoo, P.R. (25).

However, on comparison of various methods of analysis, we found spectrophotometric and chemical methods suitable for our work.

Employing these methods, the estimations of single metal content or two metal contents (binary system) at a time were carried out.

Principles and relevant procedures for quantitative estimation of Ni^{+2} , Zn^{+2} , Cr^{+3} , Sn^{+2} etc. individually or in presence of each other have been adopted from standard text book (12).

Calculations :

From the knowledge of the weights of the alloy deposit and the codeposited metals, the metal content % in the alloy deposit was calculated, similarly knowing the weight of the copper deposited in the coulometer, cathode current efficiency % for each metal was determined on the basis of Faraday's laws (26). The following formula was used.

$$\frac{100 \times \text{Eq. Wt. of copper} \times \text{wt. of metal deposited.}}{\text{Wt. of copper deposited in the coulometer} \times \text{Eq. Wt. of metal.}}$$

The results ^{of} metal content and CCE % for each parameter are shown under respective tables and graphically under corresponding figures.

2.7 MICROPHOTOGRAPHS

The nature especially the grain size and the structure of the deposits was visually examined with a microscope having high magnification. Microphotographs of the deposits were taken wherever necessary, using uniform magnification (x 40) in all the photographs.