Chapter 5
SUMMARY

The present investigation focuses on.

Development of High Speed Deposition (HSD) process by adopting fast solution spray system of the electrolyte to reduce the diffusion layer thickness that causes higher limiting current density and ensure speedy deposition with optimized power consumption. Also the studies aim at the development of suitable acid copper bath formulation, which can yield deposits of improved mechanical properties such as tensile strength, elongation, hardness and low wear resistance. Towards the end, incorporation of Zirconium additive has been tried. Incidentally this incorporation has also helped to scavenge dissolved oxygen in the deposit besides offering reduced electrical resistivity.

The summarised results of the studies are presented below:

1. Modified acid copper baths were prepared with varying the copper sulphate concentrations of 200, 250 & 300 gpl and maintaining the acid concentration at 100 gpl. Similarly alkaline cyanide bath and pyrophosphate bath were prepared. All these baths were properly purified and tried.

2. Hull cell studies were carried out with the above bath formulations at different temperature of 303K & 313K. Further some of the operating parameters were optimized. The addition of zirconium was tried in 300 gpl of copper sulphate (bath 3) and optimization was done. Hull cell studies were also carried out in cyanide and pyrophosphate baths of modified formulations for comparison of the deposit nature.

3. Flow characteristics were studied on orifices of 2, 3 and 4mm diameter on 25 and 32mm diameter PVC pipes. Hybrid type
studies on nozzle and orifices were also carried out in the same pipes. Reynolds numbers of corresponding orifices and nozzles namely Q, H & T were calculated to have an idea of the turbulence of flow.

4. Using the High Speed Deposition (HSD) facility, 100 µm thick copper foils were prepared from the above baths. The deposits were prepared at different current densities using Q, H & T nozzles from all the baths. Nearly 70 numbers of deposits were electroformed under different conditions. These foils were used to measure the tensile strength, elongation, hardness and other properties.

5. The effect of cell voltage on different composition of acid baths, concentration of zirconium and nozzles were studied. Various charts have been prepared with the data collected to have an instant idea of the influence of different parameters on the working plating condition. It is noted at a lower current density, higher turbulence (Q nozzle of Re-15600) consumed a lower voltage (bath1-3) while at higher current density with medium turbulence (H nozzle of Re-12880) is able to achieve this. Similar is the result with zirconium containing bath also (bath 4-6).

6. The deposits were made into specimens as per ASTM standard and tests were conducted for their tensile strength and elongation. The strength of deposits from bath 1 of 200gpl of CuSO₄ is at the order of 340 to 390MPa with an elongation of 9.8 to 16.7 percent. The deposits from bath 2 of copper sulphate concentration of 250 gpl gives the strength values of 340 to 460MPa with an elongation of 9.6 to 18.5 percent. In higher metal concentration of bath 3 with 300 gpl of CuSO₄, the deposit exhibits the strength of 360 to 490MPa and an elongation of 15.6 to 22.2 percent. This improved strength has been obtained because of higher metal concentration and turbulence.
7. The mechanical properties were further improved with the addition of Zirconium in acid copper bath of copper sulphate 300 gpl (in bath 3). At lower concentration of Zirconium of 0.25 gpl in acid copper bath (bath 4), the strength is at the range of 360 to 385MPa with an elongation of 15.6 to 21.3 percent. By increasing the concentration of zirconium to 0.5 gpl in acid copper bath (bath 5), the strength is further improved to a value of 410 to 430MPa & ductility 10.8 to 14.6 percent. The further enhancement of zirconium concentration to 1.00 gpl in acid copper bath (bath 6), the strength reached a maximum value of 480 to 500MPa with an elongation range of 9.8 to 11.8 percent. This maximum value of strength is obtained with Q nozzle at a current density of 12.5A/dm².

8. The hardness tests have been carried out with the deposits prepared at 7.5A/dm² using Q nozzle from all the baths. The plain copper deposits prepared from bath 1 to bath 3, produce a hardness value of 66.80 to 81.25 Vickers. The addition of zirconium (bath 4–bath 6) improves the hardness from 86.10 to 118.65 Vickers. The maximum value has been observed for the deposit prepared from bath 6 with higher zirconium content. It is observed that zirconium could effect some structural changes resulting in improved hardness.

9. Wear property was also studied, as the electroforms have to withstand wear and tear strain in some applications. The wear index of the plain copper deposit prepared from bath 3, showed a value of 85 with a load of 1000 gm. With the addition of zirconium, the wear index is reduced to 70 for 1.00 gpl of zirconium (bath 6). Wear may be controlled by texture of the deposit. Generally the deposit from acid copper baths exhibit [111] texture and in some cases [100] and [110] are also reported. The texture [111] is having good wear resistance normally. From XRD studies, the
deposit for plain copper is found to be in [111] texture orientation and with zirconium it is in [101] orientation. These texture combinations may be responsible for the lower wear index.

10. While trying to improve mechanical properties of electroformed copper, one may not like to lose this special property of good electrical conductivity of the metal. Hence measurements were also been made for this. The deposit from 200 gpl of CuSO₄ (bath 1) gave a resistivity values in the order of 1.520 to 2.283 micro ohm-cm. The resistivity values of deposits prepared form 250 gpl of CuSO₄ (bath 2) showed a marginal increase in resistivity values of 1.760 to 2.269 micro ohm-cm. The deposit produced from 300 gpl of CuSO₄ (bath 3) gave the resistivity values of 1.405 to 2.312 micro ohm-cm. It has been observed that medium type of agitation (H nozzle) is suitable to obtain a low resistivity deposits from plain baths at a low current density.

The incorporation of zirconium in copper decreases the resistivity values of the deposits. In lower concentration of zirconium of 0.25 gpl (bath 4), the values were in the range of 1.415 to 2.748 micro ohm-cm. The resistivity values of the deposits prepared from the bath containing medium concentration of zirconium of 0.50 gpl (bath 5), were 1.451 to 2.000 micro ohm-cm. At higher concentration of zirconium of 1.00 gpl in bath 6, the obtained resistivity values were in the range of 1.420 to 1.788 micro ohm-cm. It is observed the increasing concentration of zirconium reduces the resistivity values prepared at higher turbulence condition (Q nozzle).

11. The addition of Zirconium has acted as an oxygen scavenger in the copper deposit. With the usage of ETP (electrolytic tough pitch) copper anode (contains 135 ppm of oxygen) all the deposits were prepared. The importance of zirconium along with copper shows a marked reduction of dissolved oxygen content nearly to 50 ppm.
even without purging of nitrogen gas in the electrolyte. Also low current density and lower temperature were able to produce deposits with lower oxygen content (16 ppm). It is observed that the dissolved oxygen is likely to be tied up with Zirconium to form ZrO₂ and that reduces the level of free oxygen in copper-zirconium deposits.

12. Internal stress is having effect on the thickness of heavy deposits in few engineering applications. The present study revealed that, the acid copper bath with higher copper sulfate concentration gave a stress value of 5.433MPa; but with the addition of zirconium, the stress has been further increased to 6.904MPa (in tensile mode). The reason was the incorporation of foreign material (zirconium) in the copper deposit. In the case of pyrophosphate bath, the stress values were -3.038 MPa for plain bath & -3.065 MPa for Zirconium bath. In pyrophosphate bath this type of peculiar phenomenon has been observed. It was found that, initially the stress was in tensile mode for a brief period and then it became compressive in nature.

13. The C.V. studies have indicated the addition of zirconium to the plating solution has not basically altered. The deposition mechanism of copper except that it has hindered the hydrogen evaluation process.

14. The XRD studies were carried out on the prepared deposits. During the studies, XRD curves for plain copper deposits have not shown any peak for value less than 2.1° A and found to the texture of [111] orientation. The deposits with zirconium indicated the peaks corresponding to d values of 2.466 and 2.486 for the temperature of 303 K and 313 K. The zirconium deposit was found to be a texture of [101] pattern. The above studies confirmed, the presence of Zirconium in copper deposit.
15. The structure of the deposit depends on the relative rates of the formation of nuclei and the growth of the existing ones; if the conditions are favorable, the formation of fresh nuclei and then fine-grained deposits are formed. From the SEM images it is predicted that, increase in current density causes a reduction of the metal ion concentration near the cathode films with a consequent increase in concentration over potential and decrease in grain size. By incorporating zirconium in copper deposit, the growth has been changed into elongated grains and grain shape has distorted macroscopically and anchoring of grains has been noticed. The addition of zirconium changes the structure of plain copper deposit from medium fine grained to smooth fine-grained orientation with elongated grains. This is another reason for obtaining the improved strength, hardness and wear resistance of copper zirconium deposits. In pyrophosphate deposits, the growth is in three-dimensional orientation with nodular structure. The fine grained deposit with voids has been observed in cyanide deposits and it is the main reason for very high tensile strength with brittleness.

The present investigation has established the possibility of producing the copper-zirconium deposition by aqueous deposition route that can find place in some of the industrial applications listed below:

- Water-cooled cooling grids in Neutral beam ion injector in Nuclear fusion studies.
- Targets for neutron irradiation units.
- Fusion Reactor first wall.
- Hypervapotron elements - A heat transfer unit at higher densities in the order of 10MW/m² in nuclear fusion reactor.
- Coating for Semiconductor components.
- Water cooled gas turbine blades.
- Component for some missile.
Papers presented in Seminars/ Conferences.


**********