CONCLUSIONS

CHAPTER V

CONCLUSIONS

Tin being the most widely used metal with lot of applications and the very little work undertaken with eco-friendly nature of the process, chemicals have prompted the present study as stated earlier. The important conclusions arrived at are listed below:

1. The plating bath parameters such as bath constituents, current density, pH, temperature and concentration of various additives were optimized with the help of Hull cell studies. In order to develop suitable tartrate based bath for tin and its alloy plating baths of the following compositions were optimized and suggested.

Bath I for pure tin deposit	Bath II for Sn-Ni alloy deposit	Bath III for Sn-Co alloy deposit
Stannous chloride – 0.1M	Stannous chloride – 0.1M	Stannous chloride – 0.1M
Sulphuric acid - 1.0M	Nickel chloride - 1.0M	Cobalt chloride - 1.0M
Sodium potassium	Sodium potassium	Sodium potassium
tartrate - 0.2M	tartrate - 0.2M	tartrate - 0.2M
	Hydrochloric acid - 1.0M	Hydrochloric acid - 1.0M
Current density - 0.5-1 Adm^{-2}	Current density - 2-4 Adm^{-2}	Current density - 2-4 Adm^{-2}
Temperature - 30°C	Temperature - 70°C	Temperature - 70°C
pH - 1	pH - 0.5	pH - 0.5
Anode - Tin slab	Anode - Nickel slab	Anode - Stainless steel
Cathode - Mild steel	Cathode - Mild steel	Cathode - Mild steel

2. To improve the quality of the deposits and to achieve better throwing power, plating rate and current efficiency different additives were tried. Optimum concentrations of different additives for tin and its alloy baths summarized from Hull cell studies are given below.

S.No	Additives	Bath I for pure tin g/l	Bath II for Sn-Ni alloy g/l	Bath III for Sn-Co alloy g/l
1	Peptone	0.4	0.4	0.2
2	Gelatin and β-naphthol	1 + 0.04	1 + 0.04	1 + 0.04
3	Thiourea	10	20	15

Among these three additives, 1 g/l gelatin and 0.04 g/l β-naphthol produced bright and smooth deposit in tin tartrate bath. Whereas thiourea produced a mirror bright deposit in Sn- Ni alloy bath in the absence of which a gun metal coloured deposit was obtained. In Sn-Co alloy bath thiourea produced only a semi bright deposit in the absence of which a grey coloured deposit was obtained.

3. The influence of operating parameters such as current density, temperature, pH and additives have been studied and found to have considerable effect on the rate of deposition, current efficiency and alloy composition. A current density of 0.5 - 1 Adm^{-2} at 30°C operations was more beneficial to get higher cathodic current efficiency and to get smooth uniform bright deposit for tin electrodepositon, while 2 Adm^{-2} at 70°C was more beneficial for Sn-Ni and Sn-Co alloy baths. It was found that the additives used did not drastically change the current efficiencies. Though the additives did not have any significant influence in changing the alloy composition, but still they had a major role in controlling the quality of the deposit particularly in improving the appearance.

4. In an attempt to increase the cathode efficiency and nickel/cobalt content of the alloy, pulse plating had been tried under various pulse duty cycles and frequencies. It was found that plating under low duty cycles and high frequency had improved both. On comparing the alloy composition of the deposits obtained by DCP and PCP, the nickel content of the deposit increased from 24% to 28% in the absence of thiourea and from 29% to 34% in the presence of thiourea. In the case of tin-cobalt alloy, the cobalt content of the deposit increased from 14% to 17% in the absence of thiourea and from 17% to 19% in the presence of thiourea when DCP is compared with PCP.

5. Throwing power of the baths was found to be influenced by parameters such as current densities, pH and temperature. The influence of the additives with regard to throwing power was seemed to be minimal.

6. Of the different additives used, gelatin and β-naphthol is recommended to be the best additive for tin plating bath and thiourea for its alloy plating baths.

7. The specific conductivity of the bath was measured in the absence and presence of sodium potassium tartrate. It increased with increase in temperature in all the three baths. But addition of tartrate decreased the specific conductivity of the bath indicating the formation of a complex with tartrate. The decrease in specific conductivity values in presence of tartrate with Sn^{2+}, Ni^{2+}, and Co^{2+} ions individually, indicated that the extent of complexation is maximum with Sn^{2+} and minimum with Co^{2+} ion.

8. In UV studies no change in the wavelength of absorbance but reduction in the absorbance value in the absence and in the presence of tartrate in pure tin bath and wavelength shift incase of nickel/cobalt chloride indicated the formation of

complex. Whereas it did not alter either the wavelength or the absorbance in the case of alloy baths.

9. The electrochemical spectrum was recorded on Pt electrode under varied scan rates, concentration of the electroactive species and pH of the medium for the plating baths in the absence of the additives. The linearity between the peak currents and square root of scan rates indicated the reduction process to be under diffusion controlled. In the case of the deposition of tin and its alloys, the role of pH as revealed from CV studies was in confirmative with the conditions encountered in the practical plating on steel substrate. The electrode kinetic parameters such as the diffusion coefficient, the heterogeneous rate constant and the charge transfer coefficient values had been calculated. Cyclic voltammetric studies are helpful in understanding the mechanism of the deposition/dissolution process. The electrochemical spectrum in the presence of additives had not been altered significantly compared to that of plain bath suggesting that there was no change in the basic deposition/dissolution mechanism of tin and its alloys from the plating baths. Gelatin and 2-naphthol was noted to be the best for tin bath whereas thiourea for alloy baths, giving maximum cathodic peak currents, due to the decrease in energy barrier for the deposition process evident from the positive shift of the deposition potentials.

10. The impedance measurements made by superimposing the AC voltage over the respective deposition potentials of the electrode processes indicated, through the R_t values, the same order of performance among the additives as observed in CV studies or the actual plating processes.

11. Having standardized and studied the characteristics of the plating bath, it was then proceeded to understand the properties of the deposits obtained in the presence and in the absence of additives by means of DCP and PCP methods.

i) The adhesion of the deposits was very good uniformly with pure tin as well as its alloys – measured through the conventional bend test.

ii) The deposits were pore free even at 6 μm thickness for tin and tin-cobalt alloy deposits and at 7 μm thickness for tin-nickel alloy deposit. Porosity of pulse plated coatings was less when compared to that of DC plated tin and its alloy coatings.

iii) The additives of the plating bath control the quality of the deposit which is related to the hardness. Hence, the micro hardness studies assume importance in the present investigation. The enhanced micro hardness should be the result of grain refinement of the deposition process controlled by the additives present in the plating bath. As with corrosion resistance, the hardness improvement is again related to the surface morphology of the deposit. Hardness of the pulse plated deposits was very high. The order of hardness among the deposits being, Sn-Ni (710,762) > Sn-Co (215, 258) >Sn (23.3, 25.1) both in the as-plated and heat treated conditions.

iv) The wear resistance of the deposits was found and they withstood for 100 cycles when a load of 500g was applied.

v) The corrosion behaviour of the deposits in 3.5% NaCl was monitored through polarization, impedance measurement and salt spray tests. Corrosion resistance increased with the thickness of the deposits as well as with increase in the nickel or cobalt content of the alloy.

In the case of pure tin or its alloys there was an improvement in the corrosion resistance for the deposits obtained from plating baths containing the additives. The control of the corrosion process in the presence of the additives had been identified by Tafel polarization measurements. The reduced double layer capacity values measured through impedance method had confirmed the better corrosion inhibition offered by the deposits obtained from the baths carrying the additives. The improved corrosion resistance may be attributed to the fine grained structure, evident from surface morphology examination techniques. The weight percentage of nickel and cobalt present in the deposit was analyzed through EDAX analysis. Deposits obtained by PCP showed improved corrosion resistance compared to the deposits from DCP.

vi) Deposits obtained from baths without tartrate exhibited a coarse grain structure whereas the surface morphology was completely changed in its presence. The coarse grain structure was reduced to fine grained and free from surface defects. The studies indicated the role of the additives and pulse current in the plating in obtaining deposits having compact and grain refined structures which were responsible for improved corrosion resistance.

vii) The X-ray diffraction studies in the as-plated conditions indicated that the crystallographic structure of the tin deposits to be body-centered tetragonal structure with lattice parameters a = b = 5.8194 and c= 3.1753 A°. The more intense (101) and (211) orientations were responsible for the brightness of the deposits in the presence of tartrate and also in the presence of additives. The deposits from Sn-Ni alloy baths with and without tartrate had hexagonal structure. The deposits were mixtures of the equilibrium compounds Ni_3Sn, Ni_3Sn_2, Ni_3Sn_4 and the metastable form of NiSn. But the deposit from thiourea

added bath showed only two well defined peaks corresponding to the NiSn phase. The deposits from tartrate free Sn-Co alloy bath existed as a mixture of CoSn, $CoSn_2$, Co_3Sn_2 and Sn whereas the deposit from tartrate containing bath consisted of only CoSn and $CoSn_2$. But the deposit from thiourea added bath showed only two well defined peaks (200, 111) corresponding to the CoSn phase. The calculated lattice parameters for the tin-cobalt deposits suggested hexagonal structure.

In the present investigation an earnest attempt had been made to follow the plating process for tin, tin-nickel and tin-cobalt alloy from tartrate bath. The plating parameters had been optimized and the deposits quality in terms of corrosion resistance and mechanical strength had been assessed. With the judicious choice of additives, the throwing power, cathode current efficiency and plating rate had been optimized to make the process commercially exploitable.

Among the mechanical and corrosion properties of tin, tin-nickel and tin-cobalt deposits obtained from this tartrate bath, the order of performance is

Tin-nickel > tin-cobalt > tin deposits

Tin-nickel alloy deposit was found to be the best among the three deposits. It was due to the presence of NiSn phase. Similarly, CoSn phase is responsible for the bath performance of tin-cobalt alloy deposit when compared to the tin deposit which is a very soft metal but having good corrosion resistance compared to steel. The tin-cobalt deposit though may not be attractive for mechanical applications but still is useful for solar energy devices.

SCOPE OF THE FUTURE WORK

Any furtherness of knowledge in the thrust area of plating field on the development of tin and tin-alloys from tartrate bath will be significant. Studies with other additives as brightener and development of ternary alloys of tin constitute the future scope of the work. The synergistic effect of additives with some other brightener can be evaluated. Studies with periodic reverse current plating can be done which is expected to give better performance than pulse plating. The crystallographic structure on surface morphology of the tin and its alloy deposits can be analyzed elaborately using thermal study, DSC, TEM, AFM and XPS analysis.