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LEAD-TIN-COPPER ALLOY DEPOSITION FROM FLUOBORATE SOLUTIONS

R VENKATACHALAM, D KANAGARAJ, VL NARASIMHAN and R SUBRAMANIAN

Central Electrochemical Research Institute, Karaikudi - 623 006

ABSTRACT

The electrodeposition of lead-tin-copper alloy from fluoborate solution has been reported. The effects of addition agent, current density, copper content and total metal content of the bath on the alloy composition have been discussed. The structure of the alloy obtained has been compared with that of lead-tin alloy with the help of SEM.

Key words: Pb-Sn-Cu alloy deposition, fluoborate bath

INTRODUCTION

It is recognised in the present days that alloy plating has become a part of bearing manufacturing technology. The electroplates in bearing industry are to be found in three main applications : (i) as bonding layer, e.g. copper and nickel plates on steel which are sometimes used as preliminary step in bonding of bearing alloys such as lead bronze, copper-lead and aluminium-tin (ii) as a protective and decorative plate and (iii) as overlays.

In earlier days white metals were used as a bearing material, but they do not find much use in present days because of their poor load-carrying capacity and unsuitability for use at high temperatures (above 100° C). They are replaced by steel backed copper-lead, lead-bronze and aluminium-tin bearings because such bearings possess good strength and permit operations at high temperatures. However, these bearings have poor resistance, to fatigue, corrosion and seizure, besides high rate of erosion of journal.

With the application of overlays on these bearings, the above mentioned drawbacks are overcome with the advantage of good embeddability and reduced clearance between the journal and bearing surface.

In the modern bearing technology, the recognised overlays are the systems of lead-tin, lead-indium and lead-tin-copper (copper 1-3%, tin 9-12% and the remainder lead). From the view points of cost and plating, lead-indium is not widely used. Though lead-tin possesses good corrosion resistance and is plated with constant composition, it loses to lead-tin-copper system from the point of view of fatigue resistance and hardness. Tables I and II show the fatigue data [1] of various bearing materials and their hardness [2]. Many organic additions such as resorcinol, gelatin, β-napthol, peptone, pyrogallol etc. have been reported in literature for binary alloys deposition [3-8]. Also very little information is found as to the deposition of ternary alloys based on lead-tin in literature.

In the present study, electrodeposition of lead-tin-copper from fluoborate solution has been reported using hydroquinone and animal glue as addition agents.

EXPERIMENTAL

The typical bath used in the present study is:

Lead (as metal)	50 gm/l
Tin (as metal)	5 gm/l
Copper (as metal)	1-4 gm/l (varied depending on the percentage of copper required in the alloy)
Fluoboric acid	40-45 gm/l
Hydroquinone	5 gm/l
Animal glue	0.5 gm/l
Temperature	30° - 35° C
Agitation	Not used
Anodes: Cast 90% Lead - 10% Tin	

Table I: Fatigue data of various bearing materials

Material-nominal composition	Process	Thickness of bearing material (mm)	Fatigue strength kg/mm^2	Average time to fatigue (hrs)
Lead – 10% tin	Plated	0.1	2.53	23
Lead – 10% tin 1% copper	"	"	"	77
Lead – 10% tin 3% copper	"	2	"	113
Lead – 6% copper	"	"	"	26
Tin base babit 3% copper – 7% antimony	Cast	"	"	30

Table II: Hardness data of various bearing materials

Metal composition	Hardness (HV)
Cast lead	4
Lead – 5% tin	8
Lead – 10% tin	10
Lead – 10% tin – 2-3% copper	17-19 (measured at 5 gm load)

In all experiments a p.v.c. tank of one litre capacity, 5.0 mm (dia) stainless steel cathode were used, with two anodes. The anodes are wrapped with terylene cloth and are introduced into the bath just before plating and removed after plating. The cathode is introduced into the bath with current-'on'. Copper is added to the bath as copper fluoborate periodically to maintain the concentration in the bath as it is difficult to use lead-tin-copper ternary alloy anodes, which cause dissolution problems. Effect of copper and glue contents in the bath and of c.d. on the copper content and influence of lead-tin-ratio in the bath on the tin content of alloy deposit, were studied.

RESULTS AND DISCUSSION

From the unagitated solution it is possible to get uniformly smooth, fine grained and soft deposit free from nodules in the current density ranges (4-9 $A.dm^{-2}$) studied. The colour of the deposit gives an idea about the copper content in the deposit. If the deposit is slightly reddish in colour, copper content is around 3-4% in the deposit.

Fig. 1 shows the effect of copper content in the bath on the percentage of copper in the deposit at three current densities. It is evident that the copper content in the alloy deposit is increased as the current density decreases. At 4 A/dm^{-2} a higher percentage of copper in the deposit is obtained whereas a lesser percentage is obtained at 8 A/dm^{-2}, i.e. as the current density increases, the noble metal in the bath is less in the alloy deposit as in the case of the deposition of Bi-Cu, Ag-Cd and Sb-Sn systems [9] which shows that the alloy behaves as a regular codeposition system. Also the copper content in the deposit increases linearly as the copper content in the bath, irrespective of the current density.

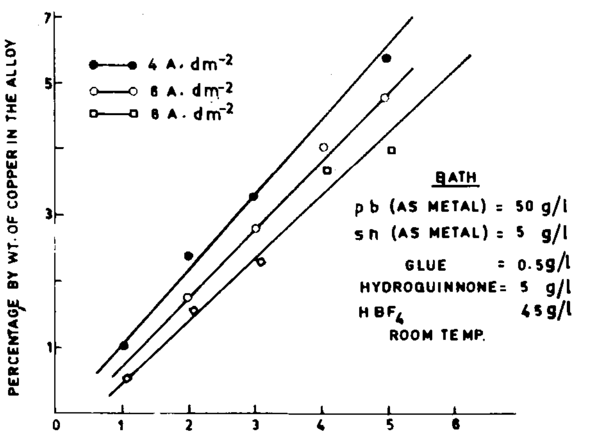

Fig. 1 : Effect of copper content in the bath on the percentage of copper in the deposit

Fig. 2 gives the effect of current density on the percentage of copper in the deposit for different total metal contents, with copper content constantly kept at 4 g/l. The copper content in the alloy decreases with the increase in current density in all cases as well as with increase in total metal content. This is the case with all regular codeposition system, which is diffusion controlled.

Fig. 3 shows the effect of glue content on the percentage of copper in the deposit for different amounts of copper in the bath. It is clear that up to a concentration of 3 g/l copper in the solution, the copper in the deposit increases linearly and thereafter tends to level off. Lesser the glue content in the solution, higher is the percentage of copper in the deposit, which indicates the inhibition of copper deposition in the presence of glue. This may probably be due to the increasing degree of polarisation of the noble metal in the presence of glue. However, in the case of lead-tin-antimony codeposition, a reverse effect has been reported [10].

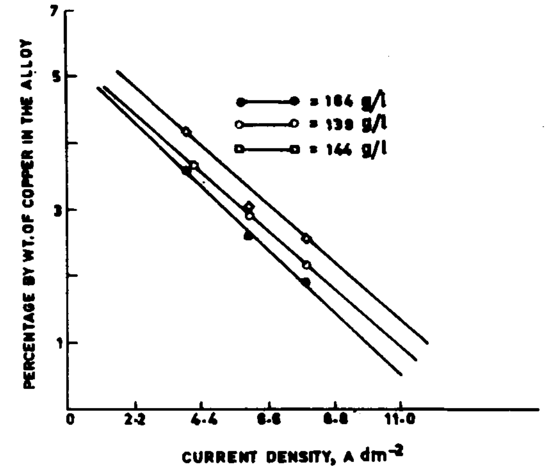

Fig. 2 : Effect of current density on the percentage of copper in the deposit at difficult total metal content. Copper fixed at 4 g/l

Fig. 4 shows the effect of lead-tin ratio in the bath on the percentage of tin in the alloy keeping total metal content at 114 g/l with constant copper content (4 g/l). In the current density ranges studied, as the lead-tin ratios increase the tin in the deposit decreases. However, the tin content in the deposit increases with an increase in current density. A similiar trend has been reported in the lead-tin binary system. It is also found that with higher ratios of lead and tin in the bath, the alloy deposit tends to deposit lead and tin in the same ratio as in the bath.

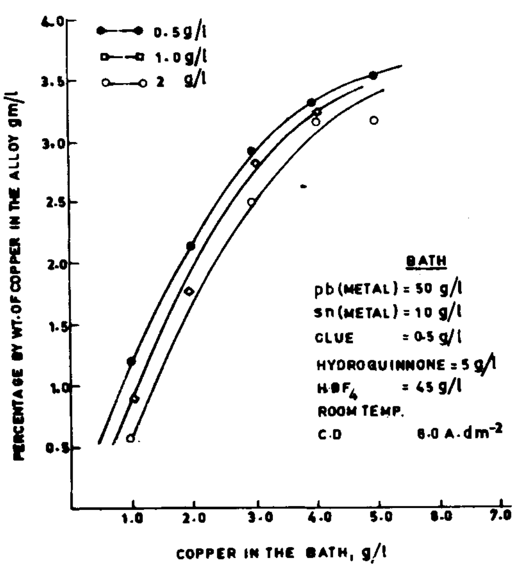

Fig. 3 : Effect of glue content on the percentage of copper in the deposit.

This shows the metal depletion in the bath is not rapid and it can be adjusted periodically by adding copper fluoborate to the bath.

Scanning electron micrographs have been taken at a magnification of 3000 X for (a) Pb-Sn alloy (b) Pb-Sn-Cu alloy (less than 2% of copper by wt.) and (c) Pb-Sn-Cu alloy (higher than 3% of copper by wt.) plated from fluoborate solution with a glue concentration of 0.5 g/l at 5 A/dm^{-2} In the lead-tin alloy deposit, the crystallites are bigger and with the codeposition of copper in the alloy, lesser with be size of the crystallites, which increases the hardness of alloy. It has also been reported that the presence of copper in the bearing alloys adds to the hardness of the alloy [14].

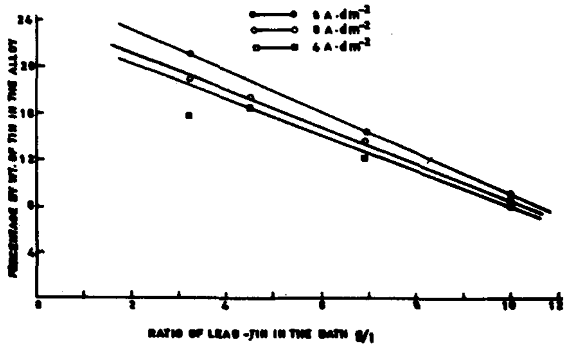

Fig. 4 : Effect of lead-tin ratio on the percentage of tin in the deposit. Total metal content 114 g/l

The codeposition of lead-tin is quite possible because their standard electrode potentials are very closer (for lead – 126 mV, for tin – 136 mV with respect to normal hydrogen electrode). But the codeposition of copper ions with lead and tin seems to be unexpected from the point of view of its nobler potential (+ 334 mV), and a difference of 460-470 mV. Codeposition can also be done by the use of organic addition agents, particularly at low concentrations which usually increases considerably the polarization associated with deposition and their effect is specific.

The codeposition of lead and copper from their sulphates or benzene sulphonates has been studied [11]. using an addition agent. Also the codepositon of tin and copper from sulphate solutions in the presence of gelatin, β-naphthol and diphenylamine has been reported [12]. In the presence of an addition agent, the codepositon occurs at very low current densities. The mechanism by which an addition agent works is different from complexation. These addition agents are effective only in solutions containing simpler ions. The composition of the deposit is affected by the addition agent. If resorcinol is added to lead-tin bath, tin in the deposit would rise above 6% as compared to 1.6% with glue alone. The addition agents have practically no effect on the anode polarization.

To put it in a simple way, the addition agent retards the deposition of nobler metal without affecting the depositon potentials of less nobler metals thereby enabling codeposition. Also as the current density increases the noble metal in the bath will be found less in the deposit (as in the case of Bi-Cu, Ag-Cd and Sb-Sn).

In our experiments, it has been established that the addition of glue inhibits the codeposition of copper, a nobler metal. It has been shown that with the proper control of concentration of addition agents and total metal content, a ternary alloy deposit of lead and tin with copper content controlled at 2-3% can be deposited. The depletion of copper in the bath with time of deposition has also been investigated. It is now possible to replenish the copper in the bath by the addition of copper fluoborate-stock solution at a controlled rate by incorporating an ampere-hour meter in the circuit. A simple volumetric procedure for estimation of the metals in the bath has also been reported to maintain the bath composition at the optimum level of metal contents [13].

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