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FUSED SALT PLATING OF LEAD-CADMIUM ALLOY ON MILD STEEL

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The electrolytic deposition of lead - cadmium alloy was carried out on mild steel substrate, using fused salt bath, such as sodium nitrite, containing lead nitrate and cadmium nitrate. The influence of electrolyte composition, current density and time to get satisfactory deposit has been investigated. The physical and corrosion resistant properties of the coating were studied and reported in this paper.

Key words: Lead-cadmium alloy, fused salt plating

INTRODUCTION

The electrodeposition of lead-cadmium alloy has not been widely reported in literature. Interest in the electrolytic deposition of metals from fused salts has been generated for a number of reasons. Metallic coatings from fused salt baths have certain unique properties, e.g. freedom from stress, high purity and ductility.

Fused salt plating is a process by which a large number of common engineering metals may be deposited on various substrates at a temperature lower than the hot dipping temperature and with advantage of simultaneous deposition and diffusion. Electrolytic deposition of heavy metals like Cd, Pb, Sn and Th from fused salt has already been reported [1-5]. High deposition rate and high throwing power are possible to achieve in the fused salt medium due to the higher conductivity of the carrier salt. The use of overlay electrodeposits for bearing applications is generally limited to the soft metal such as lead and tin, which can satisfactorily meet a number of apparently conflicting requirements including load bearing fatigue and corrosion resistance. There is considerable interest in the development of new alloys to meet the requirements listed above. One such alloy is Pb-Cd and this study has been concerned with the development of suitable fused salt composition for Pb-Cd alloy deposition. These alloy coatings may be used for preventing bimetallic corrosion. The deposition of Pb-Cd alloy on mild steel from fused salt bath and its physical and corrosion resistance properties are presented here.

EXPERIMENTAL

(i) Preparation of mild steel plates

Mild steel specimens of size 2.5 cm × 2.5 cm with a long stem were used for all the experiments. They were pickled in hydrochloric acid containing inhibitor and then polished with 120 emery wheel. The specimens were thoroughly degreased with acetone before electrodeposition.

(ii) Cell set up

A furnace with a provision to open from the top was constructed for this purpose with thermostat control. The cell consisted of a graphite crucible and a mild steel cathode placed in between two stainless steel anodes. Tungsten wires were used as current leads (Fig 1).

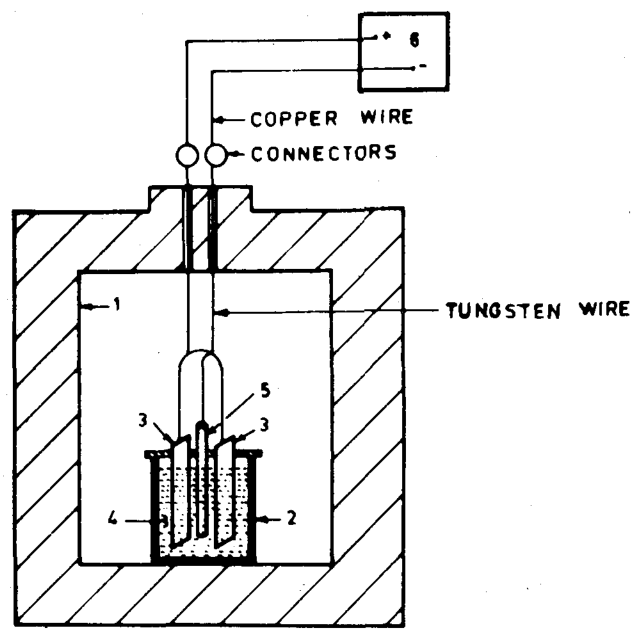

Fig 1: Fused salt-plating set-up
1. Furnace *2. Graphite crucible*
3. S.S. anode *4. Fused-salt-mixture*
5. M.S. cathode *6. Rectifier*

(iii) Thickness measurements

The thickness of the electrodeposits mild steel plates was determined with a pencil type magnetic thickness meter at 3 or 4 places on the specimen and the average value was taken.

(iv) Weight of the deposit

Lead deposited specimens were initially weighed and then stripped in 20% nitric acid, containing 100 g/l ammonium nitrate at 60°C, till the deposit is completely removed, as indicated by the appearance of greenish black deposits. Similarly Pb-Cd plated specimens were stripped for Cd by using a mixture of CrO_3 (200 g/l) and H_2SO_4 (27 ml/l) followed by stripping for Pb as already mentioned.

(v) Electrochemical studies in NaCl

Potential vs time study was conducted for mild steel, Pb plated mild steel and Pb-Cd plated mild steel (1 sq.cm) in 3% NaCl with reference to saturated calomel electrode (SCE). Potentiodynamic anodic and cathodic polarisations were conducted at a scan rate of 1mV/sec in 3%NaCl solution. These data were also supplemented by corrosion rate values, determined on 1 sq cm area specimen from the difference in weight before and after immersion of these specimens in 3% NaCl solution for a duration of 2 hours. Humidity tests were also conducted on these specimens at 100% R.H. at 48°C.

RESULTS AND DISCUSSION

Table I shows the conditions for the lead and lead-cadmium plating on mild steel substrate from $NaNO_3$ - $NaNO_2$ (1:1) eutectic salt mixture containing lead nitrate. Satisfactory coating upto 25 μm thickness could be obtained by using a current density of 38A/dm^2 at a temperature of 400°C, for a plating duration of 45 minutes. Diffusion of Pb into the mild steel matrix has also been established from metallographic studies [5].

The influence of adding cadmium nitrate in the bath of eutectic $NaNO_3$: $NaNO_2$ (1:1) mixture, containing 10% $Pb(NO_3)_2$ in the salt melt is given in Table I. Experiments were conducted at a current density of 38 A/dm^2 by varying the concentration of cadmium nitrate from 3% to 25% in the melt. The appearance of the plated surface was lustrous greyish black. However, the coating thickness revealed a decreasing trend with increase in the concentration of cadmium nitrate in the melt. Therefore, an attempt was made to change the composition of the supporting salt-melt for better Pb-Cd deposit on mild steel substrate.

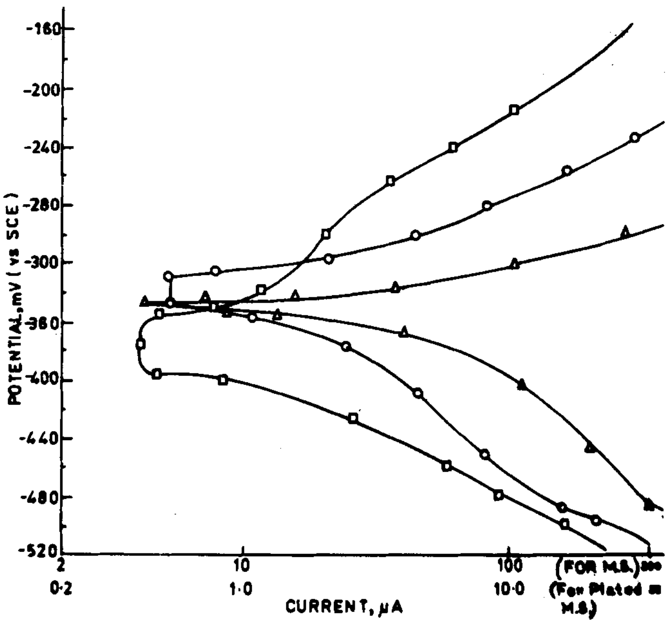

Fig.2:Potentiodynamic anodic and cathodic polarization for M.S., Pb-plated M.S. and Pb-Cd plated M.S. Electrolyte = 3% NaCl solution.
-O-O-M.S
-□-□-Pb-plated M.S.
-Δ-Δ-Pb-Cd plated M.S.

Table I: Bath composition and operating condition for lead and lead-cadmium alloy deposits
Temperature = 400°C

Sl. No.	Lead nitrate (%)	Cadmium nitrate (%)	Current density (A/dm^2)	Time (min)	Thickness (ml)	Nature of deposits
1.	5	—	38	60	25-27	Uniform lustrous grey deposits, edges cracked
2.	5	—	28	60	7-10	Grey deposits
3.	5	—	38	45	7-10	Uniform lustrous deposits without cracked edges
4.	5	—	38	15	2-4	Uniform grey deposits
5.	10	—	38	45	25-27	Thick uniform and lustrous deposition
6.	10	3	38	45	9-10	Grey black uniform deposits
7.	10	7	38	45	4-7	Grey black uniform deposits
8.	10	17	38	45	4-7	Grey black uniform deposits
9.	10	25	38	45	4-7	Grey black uniform deposits

Table II reveals the influence of flux composition on the nature and thickness of the deposit. It is seen that in all the concentrations of cadmium nitrate (3%-25%), satisfactory deposits were only obtained in the case of salt melt containing sodium nitrite as flux, while sodium nitrate alone resulted in unsatisfactory deposits. Thickness of the deposit increased from 4.1 μm to 13 μm by increasing cadmium nitrate concentration from 3% to 25%.

Table III shows the corrosion resistance properties of mild steel, Pb plated mild steel, and Pb-Cd plated mild steel in 3% NaCl solution and in humidity chamber. Fig. 2 shows the anodic and cathodic polarization curves for mild steel, Pb plated mild steel and Pb-Cd plated mild steel in 3% NaCl solution. Tafel extrapolation technique has been used to find the i_{corr} and E_{corr} values. The values of i_{corr} and E_{corr} of mild steel, Pb plated mild

Table II: Effect of flux composition on the deposition of Pb - Cd alloy

Sl. No.	Concentration of cadmium nitrate (%)	Composition of the flux (Salt mixture)	Thickness of the deposit (μm)	Appearance of the deposit
1.	3	Sodium nitrite	4.1 - 5	Uniform grey black
2.	10	-do-	4.1 - 6.8	-do-
3.	15	-do-	13 - 14	-do-
4.	20	-do-	13 - 14	-do-
5.	25	-do-	13 - 14	-do-
6.	20	Sodium nitrate	4.1 - 5	Nonuniform deposit
7.	25	-do-	4.1 - 5	-do-

Table III: Corrosion resistant properties of the coatings

Sl. No.	Material	i_{corr} (μA/cm²) (3% NaCl)	E_{corr} (mV) (3% NaCl)	Weight loss corrosion rate (3% NaCl) (g/cm²)	O.C.P. (mV) (3% NaCl)		72 hours exposure studies in humidity chamber (48°C)
					Initial	After 24 hrs	
1.	Mild steel	20	- 330	29×10^{-4}	- 500	- 650	Pitted and rusted within 24 hours
2.	Pb-plated mild steel	0.6	- 368	4×10^{-4}	- 300	- 450	Rusting observed after 72 hours
3.	Pb-Cd plated mild steel	7	- 352	10×10^{-4}	- 300	- 350	Rusting observed after 72 hours

Table IV: Analysis of Pb-Cd deposit as plated on mild steel

Sl. No.	Thickness of Pb-Cd deposit (μm)	Weight of Pb in the Pb-Cd alloy deposit (g/m²)	Weight of Cd in Pb-Cd alloy deposit (g/m²)	Percentage of Cd in Pb-Cd alloy deposit (%)
1.	2	50.215	3.871	7.16
2.	4	91.7209	7.742	7.78
3.	10	346.88	38.709	10.04

steel and Pb-Cd plated mild steel are respectively 20μA/sq.cm, 0.6 μA/sq.cm, 7μA/sq. cm. and - 330 mV, - 368 mV and - 352 mV. It is already seen that Pb plated mild steel, shows lowest i_{corr} value, followed by that of Pb-Cd plated mild steel, and mild steel. The corrosion current of Pb-Cd plated mild steel specimen is one third of bare mild steel; Pb plated mild steel reveals ten times higher resistance than Pb-Cd plated mild steel. The weight loss values of these specimens are also in conformity with the values of i_{corr} obtained from potentiodynamic studies. Exposure test for a period of 72 hours at 48°C in humidity chamber revealed that at 100% R.H. pitting and rusting initiate within 24 hours for mild steel, while the Pb plated and Pb-Cd plated specimens resist upto 72 hours. O.C.P. values of Pb plated and Pb-Cd plated specimens were more positive than mild steel specimens. Moreover, the potential time studies for mild steel, Pb plated mild steel, and Pb-Cd plated mild steel in 3% NaCl solution revealed that the plated specimens were more positive than the bare mild steel specimen after 24 hours of immersion.

Table IV shows the analysis of Pb-Cd deposit plated on mild steel substrate, for coating thickness from 2 μm to 10 μm. It is seen that percentage cadmium shows an increasing trend, as the coating thickness increases from 4 μm to 10 μm. Otherwise, the weight of Pb and Cd in the Pb-Cd coating increases with increase in coating thickness.

CONCLUSION

It was possible to deposit lead and lead-cadmium alloy on mild steel substrate to a thickness of 10 to 25 μm from fused salt bath composition, based on an eutectic mixture (1:1) of sodium nitrate and sodium nitrite and sodium nitrite alone respectively. The results show that lead plating is more corrosion resistant than lead cadmium alloy plating on mild steel for the same thickness (10 μm).

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REFERENCES

1. Yu K Delimarskii and B F Markov, *Electrochemistry of fused salts,* Sigma Press, New York (1961) p 1

2. S V Kirpachev and S Rampal, *Zh Fiz Khimi,* **11** (1961) 144

3. R Piontelli and G S Sternheim, *J Chem Phys,* **23**, (1955) 1

4. K Matiasovsky, S Lubyava and V Denck, *Electrodeposition and surface treatment,* **1** (1972) p 7

5. D Mukherjee, C Rajagopal, R Argode and S Guruviah. *Proc Symp Corros and its Control in Power and Chem Industries,* M S University, Baroda, Dec. (1982)