

**IMMERSION COPPER COATING OF STEEL***K N SRINIVASAN, N V SHANMUGAM, M SELVAM and S JOHN*

Central Electrochemical Research Institute, Karaikudi-623 006, INDIA

[Received: 1987 October; Accepted: 1988 February]

When steel articles are dipped in acidic copper sulphate solution, copper deposits on them by galvanic displacement and these deposits are porous and nonadherent. In this paper, a suitable complexing agent for such a solution to get bright, adherent deposits of copper on steel is reported. The effect of immersion time on deposit thickness and potential-time behaviour of the steel electrode with and without the incorporation of complexing agent were studied. The effect of temperature on potential-time behaviour was also reported.

**Key words:** Immersion coatings, copper, steel substrate

**INTRODUCTION**

**M**etal deposition by chemical displacement has been widely used for the production of thin coatings [8]. This involves an exchange reaction between a metallic substrate and metal ions in solution. In practice, the range of conditions under which the reaction proceeds in such a way as to result in the formation of an adherent, bright and reasonably continuous coating on the more active base metal are:

- (a) The electrolyte must dissolve the base metal without the formation of insoluble salts, oxides or other products which might hinder contact with the surrounding ions.
- (b) Attack of the base metal by the electrolyte should not be too vigorous, otherwise there will be no suitable substrate or lattice on which the depositing metal can develop a continuous structure.
- (c) The noble metal ion must deposit at a rate such that its lattice structure is filled in as orderly a fashion as possible.
- (d) The driving force (EMF) must be sufficiently low to meet the requirements of (b) and (c).

The immersion deposit of copper formed on steel from simple acidic copper solutions are nonadherent and spongy. Direct copper plating of steel from acid sulphate solution using allyl thiourea as the inhibitor has been studied [9]. The displacement of copper on steel from sulphate solutions was also reported [10]. Bright adherent copper deposit on steel was obtained using copper sulphate, ethylene diamine tetra acetic acid and wetting agent [11].

Applications of copper coating are as a lubricant during wire drawing, as a conductor of heat, as a protective coating and also as an undercoat. In this paper, the development of a sulphate based solution for immersion copper coating on steel with suitable complexing agent has been reported and the rate of deposition and change of potential of steel with time are also included.

**EXPERIMENTAL**

Mild steel panels (100 x 25 mm) were mechanically finished to a mirror finish. The samples were degreased with trichloroethylene,

electrocleaned in alkali and washed with water. Later, they were pickled in 10% v/v hydrochloric acid at a temperature of 313K for one minute.

Initial experiments were carried out by the incorporation of various complexing agents such as ethylene diamine tetra acetic acid (EDTA), glycine, diethanolamine (DEA), tartaric acid, in copper sulphate and sulphuric acid electrolyte. Of them, tartaric acid was found to be very effective in producing smooth, adherent and bright coatings on steel substrates. Hence, further experiments were carried out using copper sulphate (100 g/l), sulphuric acid (35 g/l) and tartaric acid (80 g/l) in distilled/deionised water.

The prepared panels were weighed, and immersed in the copper solution for 1 to 8 minutes, washed well, dried and reweighed. The weight loss due to pickling was taken into account in determining the amount of copper deposited by chemical displacement. Experiments were conducted with and without the incorporation of complexing agent. The adhesion of the coating was tested by tape test.

The potential of mild steel electrode was measured with time using saturated calomel electrode (SCE) as the reference. The influence of temperature (maintained by a constant temperature water bath) on potential-time behaviour was also measured.

**RESULTS AND DISCUSSION****Influence of immersion time on rate of deposition**

Fig. 1 shows the relationship between weight of copper deposited and time. The deposition rate is almost constant in the solution having no complexing agent but the deposit is nonadherent and porous. Complexing agent increases the rate of copper deposition resulting in a smooth, adherent and bright copper deposit.

**Influence of time on the potential of the steel electrode**

Fig. 2 shows the variation in the potential of mild steel electrode with time at different concentrations of tartaric acid. The chief

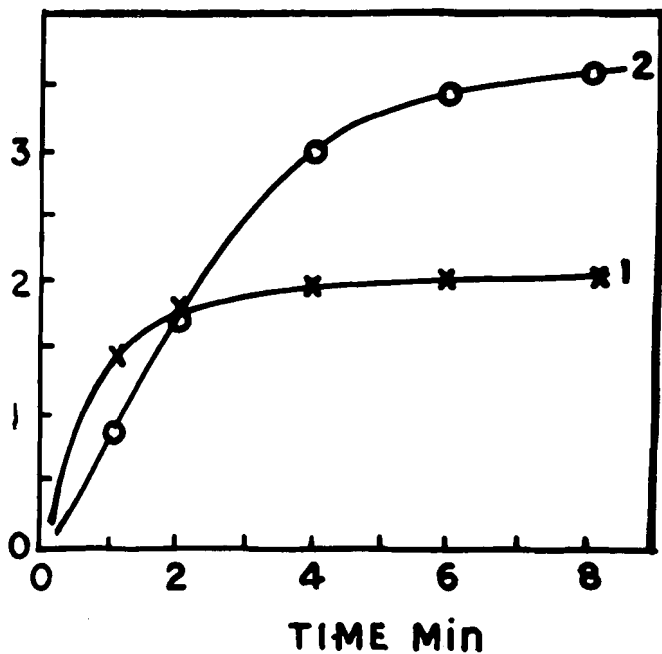


Fig.1: Relationship between weight of immersion copper deposit and time: Temperature = 303K (1)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 100 g/l,  $\text{H}_2\text{SO}_4$  35 g/l (2)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 100 g/l,  $\text{H}_2\text{SO}_4$  35 g/l, tartaric acid 80 g/l.

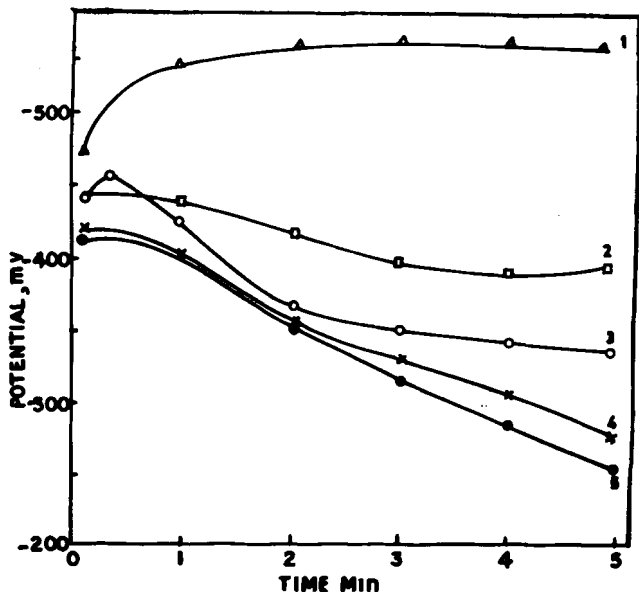
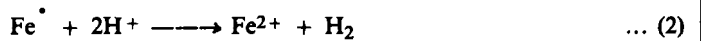
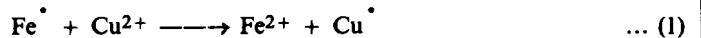


Fig.2: Influence of tartaric acid concentration on the electrode potential- time behaviour of mild steel electrode: Temperature = 303K, electrolyte  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  100 g/l,  $\text{H}_2\text{SO}_4$  35 g/l, (1) without tartaric acid; (2) tartaric acid 100 g/l; (3) tartaric acid 20 g/l; (4) tartaric acid 40 g/l; (5) tartaric acid 80 g/l; temperature for all the solutions 303K

reactions taking place during immersion deposition of copper on iron are:



The poor adhesion of the deposit is due to reaction (2). The complexing agent essentially suppresses the evolution of hydrogen on steel, resulting in the formation of adherent deposit of copper on steel. Further, it can be seen from the figure that the potential of the steel electrode in complex- free solution is constantly negative with time. That is, large part of the surface is exposed to the solution and remains negative. Addition of tartaric acid to the copper sulphate solution makes the potential of the steel electrode less negative resulting in the decreasing of anodic sites, the large decrease being at a concentration of 80 g/l tartaric acid. Addition of sulphuric acid does not affect the potential-time behaviour of the steel electrode but helps in getting adherent deposit on steel.

**Influence of temperature on potential-time behaviour**

Fig. 3 shows that at high temperature the potential is more negative thereby increasing the rate of reaction (1) above. Only at room

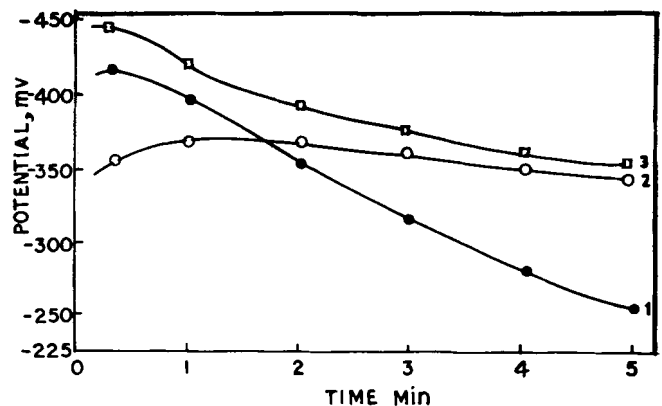


Fig.3: Influence of temperature on the electrode potential-time behaviour of mild steel electrode in the solution containing  $\text{CuSO}_4$  100 g/l,  $\text{H}_2\text{SO}_4$  35 g/l, tartaric acid 80 g/l (1) 303K (2) 308K (3) 313K

temperature, the potential is more positive and thereby increasing the area of cathodic sites.

The pH of the solution was varied from 0.5 to 10 and it was found that adherent deposit was obtained only at a pH range of 0.5 to 1.

**Adhesion of the deposit**

Tape test performed on thin coatings indicated that the coating is strongly adherent. The deposit formed in the immersion solution was built up in the regular copper plating solution for a period of 15 minutes and bent test was carried out to examine the

adherence of the coating. No peeling of the deposit was observed.

### CONCLUSION

Based on the study, the following conditions are suggested to obtain bright and adherent immersion copper deposit on steel substrates.

Copper sulphate - 100 g/l, tartaric acid - 80 g/l, sulphuric acid - 35 g/l, pH - 0.5 to 1, temperature - 298 - 308K, time - 1 to 3 min.

### REFERENCES

1. S Wernic and R Pinner, *The surface treatment and finishing of aluminium and its alloys*, Vol. II, Robert Draper Ltd, Teddington, (1972) p 888
2. F A Lowenheim, *Modern Electroplating*, III Ed, John Wiley & Sons Inc. New York, (1974)
3. R M Burns and W W Bradley, *Protective coatings for metals*, III Ed, Reinhold Pub. Co. New York, (1967) p 164
4. F A Lowenheim, *Electroplating*, Mc Graw Hill Book Co, New York, (1978) p 389
5. H Silman, G Isserlis and A F Averill, *Protective and decorative coatings for metals*, Finishing Pub. Ltd, Teddington, (1978) p 301
6. F H Reid and W Goldie, *Gold Plating Technology*, Electrochemical Pub. Ltd, Ayr, Scotland, (1973) p 73
7. C R Draper, *Printed circuits and electronic assemblies*, Robert Draper Ltd, Teddington, (1969) p 190
8. J Fischer and D E Weimer, *Precious metal plating*, Robert Draper Ltd, Teddington, (1964) p 93
9. R Sharmaitis, L Yampolskaya and Y Matulis, *Proc. 10th Lithuanian Conf. of electrochemists*, 1968, Isreal Program for Scientific Translations, Jerusalem, (1970) p 108
10. L Domnikov, *Metal Finish*, 63-2 (1965) 64
11. *Ann Electroplating*, 5-12 (1952) 415