

A NONCYANIDE COPPER PLATING ELECTROLYTE FOR DIRECT PLATING ON MILD STEEL

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Copper electrodeposits are employed for a number of applications such as decorative copper-nickel-chromium plating, production of printed circuit boards and selective case hardening. In general, copper is deposited on steel components exclusively from cyanide based electrolytes. In view of the toxicity of such electrolytes, work is being pursued all over the world for development of suitable noncyanide solutions. In this paper, the authors report the use of an electrolyte containing copper-NTA complex for production of adherent copper deposits on steel.

Key words: Copper plating, noncyanide solution, NTA containing copper bath

INTRODUCTION

Copper, because of its colour, is one of the most decorative of the metals which can be polished to high brilliance or can take up an attractive satin finish. In view of the ease with which it can be deposited, it is used as a preplate before deposition of nickel, gold or silver. In decorative copper-nickel-chromium plating, copper deposition helps in improving the appearance and under certain conditions, corrosion resistance also. Because of high electrical conductivity, copper deposits have acquired importance for electrical contacts and in printed circuit board production. Another application is in connection with selective case hardening of steel. During times of shortage of nickel, attention had been focussed on its partial replacement with electrodeposited copper depending on the service requirement and conditions of the base metal. Immersion deposition of copper on steel surfaces poses greater problems in regard to adhesion and other mechanical properties. Now and then efforts have been taken to develop a suitable electrolytic composition to overcome this difficulty. Though cyanide based solutions do not give rise to any immersion deposition, there is a need to replace them by nontoxic ones. Nitrilo-tri-acetic acid as complexing agent [1,2] has been employed as a constituent of electroless copper plating baths to increase the solution stability but has not been experimented for using electrodeposition of copper. In this paper, we report the results of investigation carried out with copper NTA complex based electrolyte for production of adherent copper deposits on mild steel.

EXPERIMENTAL

Initially the formation of immersion copper deposit on mild steel was studied by immersing the mild steel panels ($2.5 \times 7.5 \times 0.025$ cm) in different solutions containing varying quantities of copper sulphate and NTA sodium salt. Each of the solutions was also examined visually for any precipitation of copper.

Hull cell experiments were then carried out with solutions containing varying quantities of copper sulphate in order to optimise the conditions for production of good deposits that could serve as preplates for further build-up of copper. A cell current of 1A was used for a duration of 10 minutes. A regulated power supply was used as the d.c. source, and a calibrated ammeter along with the cell constituted the electrical circuit. Hull cell

panels of mild steel were used. Sodium hydroxide was employed for adjusting the pH of the solution to the desired level. The temperature was maintained at ± 1 K. Electrolytic copper was used as the anode material.

For current efficiency experiments, the electrodeposition assembly consisted of electrolytically pure soluble copper anodes and a steel cathode of equal size ($5 \times 4 \times 0.025$ cm) immersed in a 800 ml solution in a 1 litre wide mouthed glass vessel. The solution was normally agitated and when necessary heated by using a heater cum magnetic stirrer. For current efficiency determination, each specimen was weighed before and after plating and the weight of the deposits found from the difference.

RESULTS AND DISCUSSION

Galvanic displacement and stability

Immersion deposits of copper on mild steel by galvanic displacement can be avoided by complexing the copper ions. Copper complexes not only help prevent immersion deposition, but also give rise to electrodeposits with good adhesion.

Table I brings out the effects of copper sulphate in alkaline NTA solutions. An increase of copper sulphate above 0.16M produces immersion deposits and stability of the bath decreases. When the pH is below 10.5 at 303K, immersion deposits are again found to occur. An increase of temperature at pH 10.5 has no effect on stability. At all temperatures, immersion deposition was not observed for a solution of pH < 10.5 (Table II) but when the pH was lowered from 10.5, the solution became less stable.

Nature of the deposits

The results of Hull cell experiments for optimisation of the conditions for production of good deposits that could serve as preplates for further build up of copper are presented in Figs. 1 and 2.

Effect of copper sulphate

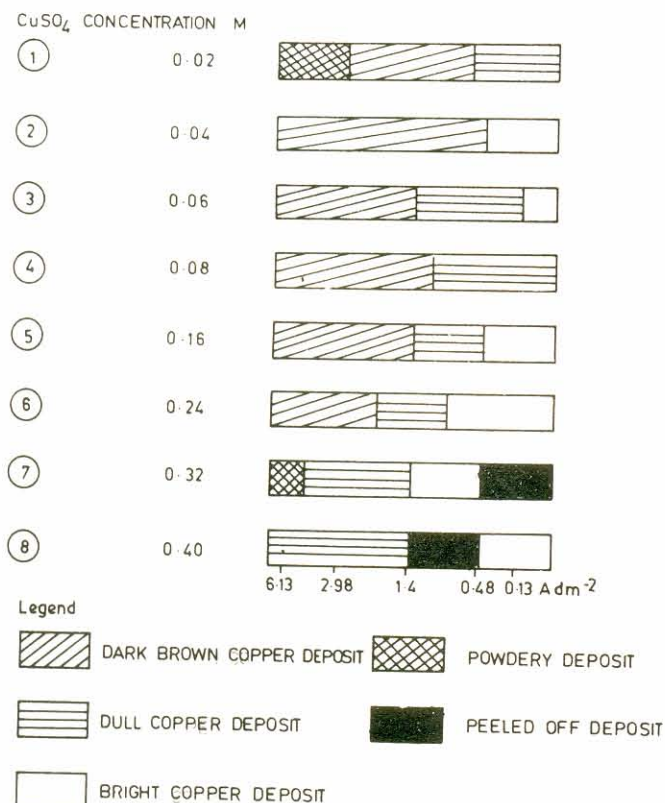
At 0.02 M copper sulphate concentrations, the copper layer became powdery towards the high current density end whereas dark brown and dull pattern were observed over middle and low current density areas respectively. The whole pattern gradually improved with an increase in copper concentration upto 0.24M but a further increase in concentration resulted in the formation of exfoliated deposits.

TABLE-I: Effect of copper sulphate on galvanic displacement on mild steel and on bath stability at pH 10.5 and 303K

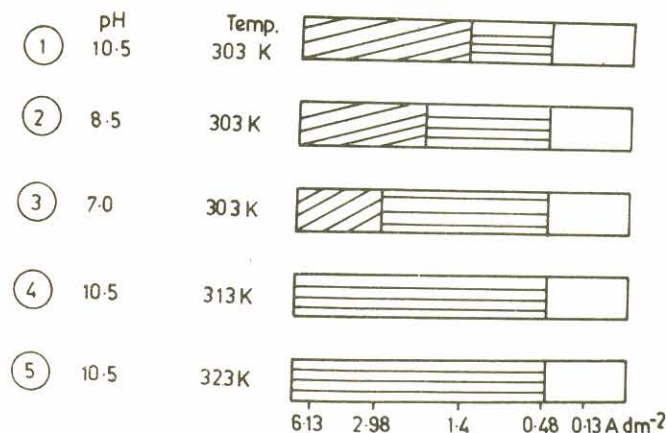
Concentrations of ingredients other than CuSO ₄ (M)		Concentrations of CuSO ₄ · 5H ₂ O (M)	Observation on immersion deposition	Stability
NaOH	1.5	0.04	Nil	Good
NTA	0.5	0.08	Nil	Good
		0.16	Nil	Good
		0.24	Occurrence of deposit	Not good
		0.32	" "	" "
		0.40	" "	" "

TABLE-II: Effect of pH and temperature on galvanic displacement of copper on mild steel and bath stability

Bath ingredients M		pH	Temperature K	Observation on immersion deposition	Stability
NaOH	1.5	7.0	303	Occurrence of deposit	Good
NTA	0.5	8.5	303	"	"
CuSO ₄	0.16	10.5	303	Nil	"
		10.5	313	"	"
		10.4	323	"	"

**Fig. 1: Effect of copper sulphate on the nature of the deposit obtained from NaOH 1.5M, NTA 0.5M at pH 10.5, temperature 303K and 1 ampere cell current**

Both blistering and exfoliation of the deposits occurred at higher concentrations (Fig. 1).

**Fig. 2: Effect of pH and temperature on the nature of the deposit obtained from NaOH 1.5M, NTA 0.5M and CuSO₄ 0.16M at 1A cell current**

Effect of pH and temperature

A decrease of pH from 10.5 improved the nature of the deposit and widened the current density range for formation of dull copper. At pH 7.0, a uniform looking dull copper layer was observed over most of the Hull cell plate area but at the low current density region a bright deposit was obtained. The behaviour at 323K was similar to that at 313K while an increase of temperature favoured the production of a better deposit (Fig. 2). The improvement in the nature of the deposit may be due to the increase in the mobility of the ions and hence the conductivity of the solution. Thus it appears that NTA based alkaline copper baths may be operated at 303–323K and at pH 10.5.

Current efficiency and rate of build-up

Studies were carried out with the optimised electrolyte composition at different current densities. The current efficiency went on increasing with an increase in current density and attained a maximum value at 1.0 A/dm² and decreased further to attain a steady value. The rate of build-up gradually increased with current density (Table III). An increase of current density led to widely different results. Semibright and dull deposits were obtained in place of bright ones when the electrolyte was operated from 0.5 to 1.0 A/dm². The formation of powdery deposits was observed at edges of cathodes at 1.5 and 2 A/dm². The formation of powdery copper is due to forced reduction and insufficient time for the adatom to move round the surface, nucleate and grow at active sites.

TABLE-III: Current efficiency, rate of build up and nature of deposit in NTA based bath

Current density (A/dm ²)	Current efficiency (%)	Rate of build up (μmhr ⁻¹)	Nature of deposit
0.50	25	1.7	Uniform, bright
0.75	82	8.2	Uniform, semibright
1.00	91	12.1	Uniform, dull
1.50	71	14.2	Uniform at the centre and powdery at the edges
2.0	68	18.1	Uniform at the centre and powdery at the edges
2.5	67	22.4	Powdery deposit

CONCLUSION

REFERENCES

Direct copper plating on steel with good adhesion can be successfully carried out with the following composition

NaOH 1.5M; NTA 0.5M; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.16M

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