Corrosion-resistance of cadmium electrodeposits from tetravalent titanium containing fluoborate bath

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Investigations by way of the neutral salt spray test and electrochemical techniques were carried out on corrosion of cadmium-deposited cold rolled steel specimens. When once corrosion had set in, the corrosion of specimens was more, irrespective of unchromated or chromated as against those from a titanium free bath. The corrosion current densities were found to be $16-30~\mu A.cm^{-2}$ by the electrochemical techniques.

Key words: Corrosion evaluation, cadmium deposits, salt spray tests

INTRODUCTION

There are areas of use such as aerospace and defence where electroplated cadmium is unlikely to be replaced. This paper reports the results of investigations by the neutral salt spray test and electrochemical techniques, carried out on corrosion of cadmium-deposited cold rolled steel specimens from a 0.5 g.dm⁻³ titanium containing fluoborate bath.

EXPERIMENTAL

Matt-white, smooth electrodeposits of cadmium were produced on cold rolled steel specimens (8.0 \times 5.5 \times 0.02 cm) by electrodeposition after subjecting them to the usual degreasing and electrocleaning treatments. Deposits were produced in average thicknesses of 5.8 and 12 μ m, from a 2-litre solution composed of cadmium fluoborate (222.0 g.dm⁻³), ammonium fluoborate (5.5 g.dm⁻³), boric acid (20.0 g.dm⁻³), tetravalent titanium (0.5 g.dm⁻³) and dextrin (2.0 g.dm⁻³) with fluoboric acid addition to a pH of 2.3, as prepared for earlier work [1]. Plating was carried out at current densities of 200 A.m-2 and 300 A.m-2 at room temperature (298 K). Titanium was introduced into the bath in the form of a solution obtained from appropriate quantities of potassium titanium oxalate and EDTA. Pure cadmium anodes were used. The anode-to-cathode distance was maintained at 11.0 cm. Specimens intended to be chromated to an olive green finish were plated for such extended durations that the deposit thicknesses were higher by 2.0 μ m. A solution composed of chromium trioxide (30.0 g.dm⁻³), hydrochloric acid (sp.gr. 1.18, 5.0 ml.dm⁻³), nitric acid (sp.gr. 1.42, 5.0 ml.dm⁻³) and phosphoric acid (sp.gr. 1.75, 10.0 ml.dm⁻³), and of pH 0.5, was used for the 120 seconds treatment.

All the specimens were subjected to the salt spray test with a 5% solution of analytical grade sodium chloride at

ambient temperature (298 K), under conditions reported earlier [1]. Corrosion rates were also determined by the potentiostatic and galvanostatic polarisation techniques, making use of the Wenking instruments and 5% solutions of analytical grade sodium chloride. SEM micrographs of unchromated and chromated specimens were also taken.

RESULTS AND DISCUSSION

From Table I it appears that there is no extraordinary difference between deposits from titanium-containing and titanium-free baths except when the plating current density is 200 A.m⁻² giving rise to delayed first red rust formation. The presence of titanium is however advantageous [2] for plating on high strength steel because of the reduction in hydrogen pick-up during deposition of cadmium. While chromating does bring about a substantial delay in the first red rust formation, the overall corrosion performance of chromated specimens seems to be not so good as when deposition is carried out from a titanium-free solution [1].

Potentiostatic and galvanostatic experiments for determination of corrosion current densities gave values of 16-30 μ A.cm⁻² but showed no consistently appreciable difference between unchromated and chromated specimens with deposits of the same thickness. However there was generally a reduction in the corrosion current density with an increase in deposit thickness as expected.

SEM micrographs of unchromated and chromated specimens (Fig. 1) show the presence of some new material, probably of titanium being present in the deposit, as indicated by its reaction-product on chromating (Fig. 1b). It is probable that titanium is included in the deposits in a very small quantity.

TABLE-I: Elapsed times for first red rust and 50% red rust formation on cadmium plated cold rolled steel

Unchromated Deposited thickness (μm)						Chromated Deposited thickness (μm)					
First	50%	First	50%	First	50%	First	50%	First	50%	First	50%
200	600	480	648	528	>888	480	696	504	>888	696	> 888
360	624	504	792	576	>888	504	792	576	> 888	724	>888
	Tir (h First	5 Time (h) First 50% 200 600	Deposited to	Deposited thickness 5 8 Time (h) Time (h) First 50% First 50% 200 600 480 648	Deposited thickness (μm 5 8 Time (h) (h) Time (h) First 50% First 50% First 50% First 50% First	Deposited thickness (μm) 5 8 12 Time (h) (h) (h) First 50% First 50% 200 600 480 648 528 >888	Deposited thickness (μm) 5 8 12 5 Time (h) (h) (h) (h) (h) Time (h) (h) Time (h) (h) First 50% First 50% First 50% First 50% First 50% First 50% First 50% First 50%	Deposited thickness (μm) Deposited thickness (μm) 5 8 12 5 Time (h) Time (h) Time (h) Time (h) First 50% First 50% First 50% First 50% 200 600 480 648 528 >888 480 696	Deposited thickness (μm) Deposited 5 8 12 5 Time (h) (h) (h) (h) Time (h) (h) Time (h) First 50%	Deposited thickness (μm) Deposited thickness 5 8 12 5 8 Time (h) Time (h) Time (h) Time (h) Time (h) Time (h) First 50% First 50% First 50% First 50% First 50% First 50% 200 600 480 648 528 >888 480 696 504 >888	Deposited thickness (μm) Deposited thickness (μm) 5 8 12 5 8 Time (h) (h) (h) (h) Time (h) (h) (h) Time (h) (h) Time (h) (h) Time (h) (h) First 50% Fi





Fig. 1: SEM micrographs (1000 X) of unchromated (a) and chromated deposits (b) (12 μ m)

CONCLUSION

Presence of 0.5 g.dm⁻³ titanium in a fluoborate cadmium bath, though desirable for a low hydrogen pick-up by steel

substrates during deposition, appears to bring down the corrosion resistance of the deposits to some extent.

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