Characteristics and properties of electrodeposited chromium from aqueous solutions*

M. McCormick, S. J. Dobson

Department of Electronic and Electrical Engineering, Sheffield University, Mappin Street, Sheffield S1 3JD, UK

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The characteristics and properties of chromium deposited from sulphate-catalysed chromic acid solutions of varying composition over both a current density and temperature range have been examined. An attempt to interpret the mechanical test results on the basis of inherent crack incidence and crack length within the deposit has also been presented.

Comparisons between laboratory and commercial platings have established the viability of extrapolating the laboratory results, enabling test gun tube performance to be related to the various coating structures produced in the 120mm barrel by the varying current density conditions experienced. These current density variations have been predicted using the boundary element numerical method which demonstrates the inherent problems associated with gun tube geometry.

1. Introduction

Although the deposit mechanisms of hard chromium plating are incompletely understood, the production of sound, high-quality coatings from catalysed chromic acid solutions has been thoroughly researched [1, 2] and is consistently practised. Most engineering coatings are produced from baths catalysed by the sulphate acid radical with an accepted optimum ratio of chromic to sulphuric acid of 100 : 1. Alternative catalysts have been investigated but not adopted [3]; however, additives are commonly added to the standard electrolyte to enhance some aspect of either the process performance or deposit characteristics. The role of the catalyst is still incompletely understood and a review by Hoare [4] presents several differing schools of thought as well as a proposed mechanistic role for the sulphate radical. However, at present, no completely satisfactory explanation exists for the cathodic process during electrodeposition. This is not altogether surprising considering the number of chromic complexes [5–7] present, the species involved and the competing reactions.

Galvanostatic and potentiostatic polarization curves have been usefully employed in elucidating some of the effects concomitant with the addition of catalysts [4, 7–9].

Further investigations using linear sweep and cyclic voltammetry on a 250g l\textsuperscript{-1} CrO\textsubscript{3}, sulphate-catalysed electrolyte using chromium, nickel, copper and vitreous carbon cathodes have also recently been reported by Lin-Cai and Pletcher [10, 11]. Their results confirm the basic reactions occurring at successively more negative potentials in chromium electrolytes and explain other features such as the effect of the sulphate ion concentration on the limiting current of the Cr(VI) to Cr(III) reduction, the effect of the substrate on the potential at which the initial passivating film is dissolved and, finally, the conditions necessary for the nucleation of the metallic phase.

Until recently [12] perhaps the most useful addition to the standard electrolyte was considered to be a complex fluoride which improves both process efficiency and deposit hardness [13]. The major disadvantage of fluoride additions is that non-plated areas are etched, and for appli-

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cations such as the plating of gun tubes they are consequently unsuitable. Although high efficiency, non-etching solutions are now available [12, 14], these have not been considered and this paper concentrates on chromium coatings from basic sulphate-catalysed solutions.

The typical performance of aqueous sulphate-catalysed hexavalent chromium electrolytes is illustrated in Fig. 1, where linear sweep current-potential curves are shown for four substrates used in a standard 100:1 ratio CrO$_3$/H$_2$SO$_4$ (450:4.5 g l$^{-1}$) electrolyte. Each curve shows the distinctive regions associated with chromium electrolytes as the potential at the working electrode is made more cathodic. The initial reaction (A) is that associated with the Cr(VI) to Cr(III) reduction and is followed by a passive region and a second peak (B) due to hydrogen evolution. As reported by Saiddington and Hoey [15] this peak is followed by a second passive region before the onset of chromium plating together with renewed Cr(VI) to Cr reduction and hydrogen evolution (C).

As can be seen from Fig. 2, the potential at

![Fig. 1. Linear potential sweep curves on copper, steel, chromium and vitreous carbon for a standard solution.](image)

![Fig. 2. Cyclic voltammograms for a 450 g l$^{-1}$ CrO$_3$ + 4.5 g l$^{-1}$ H$_2$SO$_4$ solution (a) copper and (b) vitreous carbon. Potential sweep rate, 20 mV s$^{-1}$.](image)