Efficient Trivalent Bath For the Recovery of Chromium

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An electroplating bath for the deposition of chromium from its trivalent solution in dilute sulfuric acid is proposed. A simple two-compartment cell with a cylindrical silver anode and a rotating copper disc cathode has been employed. The effect of factors such as concentration of Cr(III) and H+ ions, role of additive and current density on the deposition rate has been studied. At an average current density of 125 A/dm^2, a cathode efficiency of around 45 percent is achieved from a bath containing 7 g/L Cr(III) and 1 g/L Na_2SO_4 maintained at a pH of 1.4. The deposits are in semibright nodular form. The practical utility of the proposed bath has been demonstrated by recovering pure chromium from chromium-laden effluent from a tannery.

Chromium electrodeposition provides a tarnish-resistant durable surface finish. Most chromium systems used for this purpose have been based on hexavalent electrolytes that contain fluoride and sulfate ions as catalysts and operate at a low cathode efficiency (12-25%). Because of strict environmental regulations on the discharge of hexavalent chromium, processes based on trivalent chromium are becoming popular.[1-6] The deposits from trivalent baths generally tend to be softer, porous and somewhat darker in color. Although temperature and current density requirements are lower, strict electrolyte controls are imperative. Some attempts have been made to obtain deposits comparable to those from hexavalent baths,[7-11] but certain drawbacks, such as the requirement of higher Cr(III) concentration, excess evolution of gas, and expensive electrode systems have discouraged the use of these systems for commercial applications. Keeping in mind the environmental advantage of a Cr(III) bath for the electrodeposition, we have tried to develop a system that gives improved deposits with higher cathode efficiency. The proposed bath operates at dilute Cr(III) concentrations with lower energy requirements. During electrodeposition there is no evolution of toxic gas, and no special complex additive is required. The bath has been used to recover metal from a purified chromium-laden effluent from a tannery.

Experimental Procedure

Bath Preparation & Operation

The electrodeposition cell consists of a rectangular Pyrex glass trough (250 mL), in which a G-4 porous disk 1.2 mm-thick sintered glass crucible (25 mL) is fixed to one of its sides. The crucible constitutes the anodic compartment of the cell and is filled with dilute H_2SO_4. The anode used is a silver cylinder with a surface area of 20 cm^2. The remaining part of the trough is used as a cathodic compartment. The catholyte is a mixture of chromium(III) and sodium sulfate solution in dilute sulfuric acid adjusted to the pH of the anolyte. The cathode is a rotating (75–125 RPM) circular copper disc of surface area 5 cm^2. The bath was operated at 25 ± 30 °C. There was no significant change in the deposition characteristics up to 600 °C.

Results & Discussion

Cathode Efficiency & Chromium/Na_2SO_4 Concentration

The effect of Cr(III) concentration on the cathode efficiency was investigated from 1.5 to 15 g/L for a period of 30 min at a current density of 125 A/dm^2, keeping the pH at 1.4. The results are shown in Fig. 1. It is seen that the Cr(III) concentration has no effect on the cathode efficiency above 3 g/L. Also, an increase of about 8 percent in the cathode

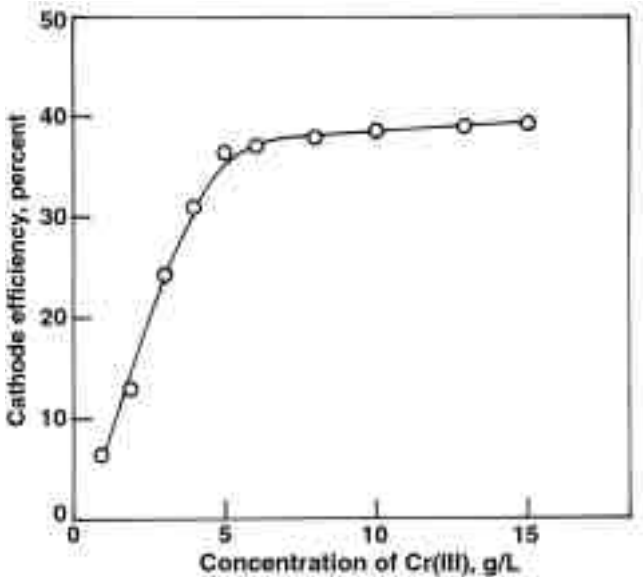

Fig. 1—Cathode efficiency as a function of Cr(III) concentration.

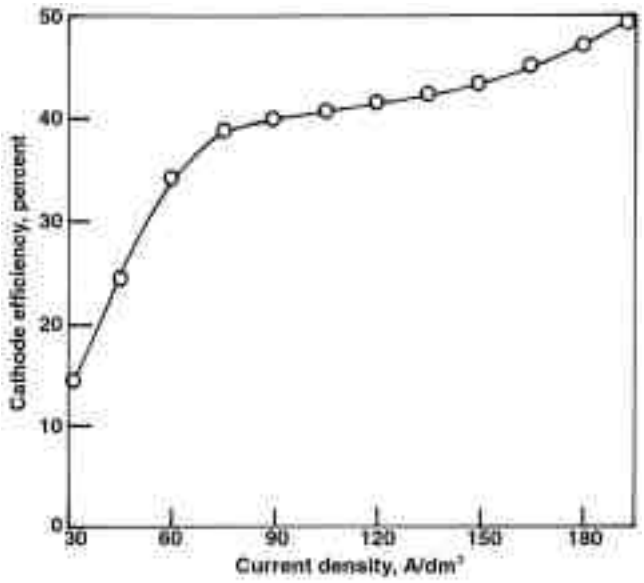

Fig. 2—Cathode efficiency as a function of current density.

efficiency is realized by the addition of Na_2SO_4, which should be at least one-seventh of the Cr(III) concentration (by weight). In all subsequent experiments, a Cr(III) concentration of 7 g/L containing 1 g/L Na_2SO_4 was used.

Cathode Efficiency & pH

Experiments studying the effect of electrolyte pH on cathode efficiency revealed that a pH range of 1.2 to 1.5 allows a faster deposition rate with improved deposit quality. Below this range, the deposition rate slows down, whereas above it, slow dissolution of cathode occurs. A pH of 1.4 was maintained in all other studies.

Cathode Efficiency & Current Density

The effect of current density on cathode efficiency is shown in Fig. 2. The cathode efficiency increased with increasing current density. An average current density of 90 to 150 A/dm^2 was maintained, however. At current densities above this range, blackening of deposits and excess evolution of gas at the anode were observed.

Grayish, semibright nodular deposits are obtained by operating the bath at 7 g/L Cr(III) and 1 g/L Na_2SO_4, adjusted to pH 1.4. At a current density of 125 A/dm^2, the cathode efficiency is about 45 percent. The copper and silver electrodes do not dissolve with the passage of time. A SEM photograph of the electrodeposited chromium is shown in Fig. 3. An impurity-free surface is produced.

The utility of the proposed bath for the recovery of pure metal from spent chromium-laden effluent was tested. Prior to electrodeposition, the spent tannery effluent was purified by a method described elsewhere.[12] It involved precipitation by MgO and a subsequent purification of the solution by solvent extraction, using bis (2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301). The deposit is similar to that obtained from a pure Cr(III) solution.

Conclusions

The suggested electrolyte is simple and operates with high cathode efficiency at a reasonably low Cr(III) concentration. Also, high temperature operation is not involved. There is no apparent evolution of toxic gas, which makes it safer to operate. In light of environmental and energy considerations, the proposed bath may be very useful for the recovery of the metal from Cr(III)-bearing solutions. The bath can be conveniently scaled up.

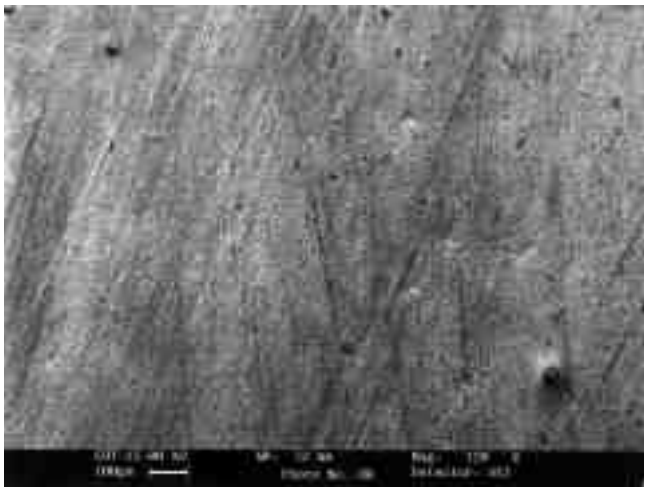

Fig. 3—SEM photograph of the electrodeposited chromium.

Acknowledgment

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