Activation effect of halides on chromium electrodeposition from chromic acid baths

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The current efficiency of chromium electrodeposition and cathodic polarization curves were determined in halide–chromic acid–sulphuric acid systems. The composition of the cathodic films formed was determined by XPS and AES. The results show that sulphate is an effective catalyst for the deposition of bright chromium and that the current efficiency of the chromium deposition increases remarkably when F^- and Cl^- are added to the bath, and also that F^- and Cl^- participate in the formation of the films. The depth profile curves of the film show that halide is distributed in the inner layer of the film, and SO_4^{2-} in the surface layer. It is deduced that F^- and Cl^- form a bridged complex, $[Cr^{III}-X^--Cr^{III}]^\ddagger$, in which electron transition is easily carried out.

1. Introduction

Metallic deposits of chromium are usually obtained from the electroreduction of solutions of chromic acid containing H_2SO_4. Frequently the current efficiency of the process is no more than 12% in industry, so that work on the deposition mechanism and increasing the current efficiency is of much importance in both theory and practice.

It has been found that halide anions (X^-) have a marked activation effect on both anodic and cathodic reactions in many electro-chemical systems. The activation mechanism, however, has not yet been clarified. It is, in general, believed that X^- forms a transition surface complex with metal ions, which decreases the activation energy of electron transition [1]. But no entirely satisfactory theory has been proposed to account for the formation mechanism of the complex and its structure. Even less research has been reported on the mechanism of the activation of halides on chromium deposition from chromic acid baths. It is generally accepted [1, 2], that a film on the cathode surface layer plays an important role in the electrodeposition of chromium metal from the bath containing halides. However, the composition of the cathodic film remains unclear. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) are two major techniques for surface analysis [3]. We were successful in studying the composition and the structure of the film on silver, copper and tin using XPS and AES [4–6]. This paper reports the determination of the composition of the cathodic film from chromic acid baths containing halides by XPS and AES, and proposes the activation mechanism of

halides on chromium deposition by determining the current efficiency and the cathodic polarization curves.

2. Experimental procedure

2.1. Determination of current efficiency

Steel specimens $2 \times 5\,cm^2$ (containing 0.2% carbon) were polished with a fine-grit paper, degreased and plated in different chromic acid baths (see caption in Fig. 1) at 55 °C and 4.5 V bath voltage using a lead plate as anode.

2.2 Determination of cathodic polarization curves

An electrochemical parameter measurer (DD1 Type, Shengyang No. 8 Radio Plant, China) was used for plotting the curves at a scan rate of $20\,mV\,s^{-1}$. Three compartmental cells were used throughout this work. The working electrodes were mild steel plates $(1 \times 1\,cm^2)$. The working electrodes were polished with a fine-grit paper, degreased with anhydrous ethanol, chromium-plated for 2 min and scanned immediately. The counter electrode was a platinum sheet. The reference electrode was a saturated calomel electrode (all potentials in this paper are quoted against this elec-

2.3. Analysis of cathodic film by XPS and AES

After the mild steel specimens had been polished and degreased, they were electroplated in different chromic acid baths at $20\,A\,dm^{-2}$ and 55 °C for 2 min using a lead plate as anode. The specimens were taken out of the cell very slowly with the current still flowing and the films on the specimens were dried by air blast (cool
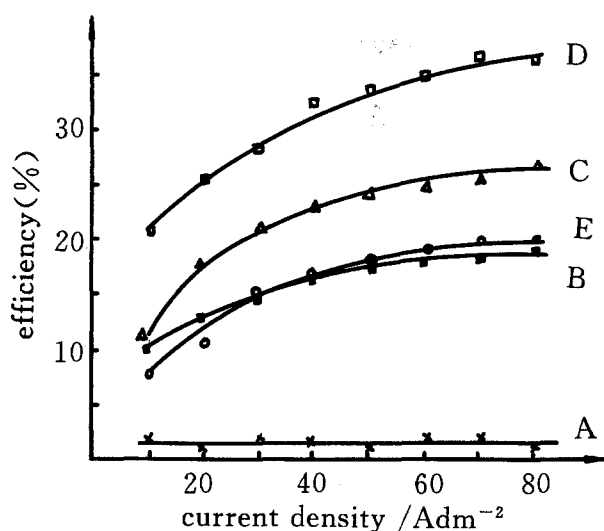
Fig. 1. Variation of the efficiency of chromium deposition with current density. A, CrO_3 2.5 M; B, CrO_3 2.5 M + H_2SO_4 0.025 M; C, B + NaF 0.025 M; D, B + NaCl 0.025 M; E, B + NaBr 0.025 M.

Fig. 2. Potentiostatic polarization curves in various chromic acid baths. (O—O) A, CrO_3 2.5 M; (———) B, CrO_3 2.5 M + H_2SO_4 0.025 M; (– – –) C, B + NaF 0.025 M; (●—●) D, B + NaCl 0.025 M; (*—*) E, B + NaBr 0.025 M.

air) and determined immediately by XPS and AES. A Perkin-Elmer PHI 550 ESCA/SAM electron spectrometer with MgK_α X-ray anode (1253.6 eV) was used. Wide-range and high-resolution spectra were obtained at pass energies of 100 eV and 25 eV, respectively. The pressure in the analyser chamber was maintained at 10^{-7} Pa during the analyses. The voltage and current of the electron beam were 2.5 kV and 25 μA, respectively. An argon ion gun with a voltage of 1 kV and an emission current of 10 mA at 4 × 10^{-3} Pa was employed for depth profiling studies. The binding energy was corrected for charging effects by referencing to the C_{1s} (284.7 ± 0.1 eV) peak. All reagents were AR grade.

3. Results

3.1. Current efficiency

The variations of the efficiency of chromium deposition with current density in chromic acid baths containing different anions are shown in Fig. 1. The current efficiency for chromium deposition without sulphate is almost zero. When sulphate is added to the bath, the current efficiency increases and a bright or semibright deposit is obtained. This shows that sulphate is favourable for deposition of bright chromium. Moreover, the order of the current efficiency of the baths containing F^-, Cl^-, Br^- and SO_4^{2-} is $Cl^- > F^- > Br^- \approx SO_4^{2-}$. This means that F^- and Cl^- play an activation role on the chromium deposition but Br^- has little influence on the efficiency.

3.2. Cathodic polarization curves

Potentiostatic polarization curves in the baths containing various anions are illustrated in Fig. 2. Each curve can be divided approximately into three regions [7]. The initial reaction (region A) is associated with the reduction of Cr(VI) to Cr(III), where the electrolyte solution in the cathode region is violet (Cr(III)), and cathode film formation begins. Region A is followed
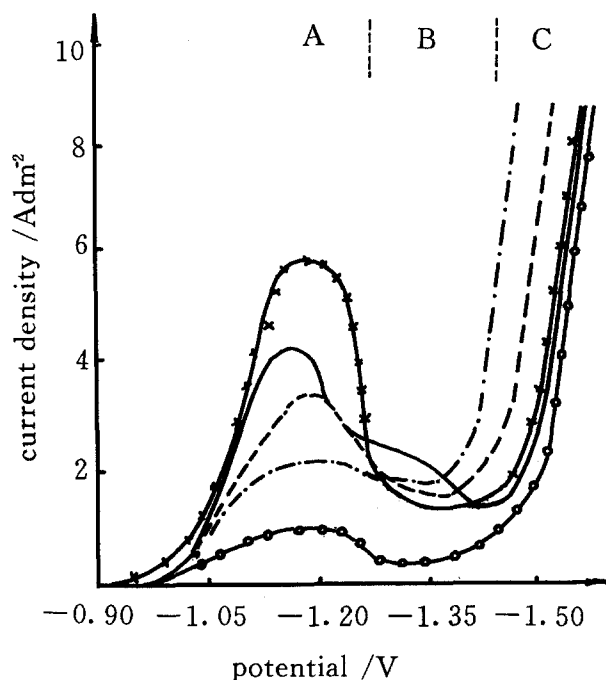
by a passive region (B), where the cathodic film forms completely. The (C) region is attributed to reduction of Cr(III) to Cr(0) and hydrogen evolution. As can be seen from Fig. 2, the passive region in the chromic acid bath alone is wider and the potential of hydrogen evolution more negative than that in the other baths, and only a brown film is obtained on the cathode surface. This shows that metallic chromium was not deposited from the chromic acid bath without sulphate. The passive region (B) was narrowed when sulphate and halides were present, which means that the anions have an activation effect on the dissolution of the cathode film. It can be seen from the region (C) that the chromium deposition potentials of the baths containing F^- and Cl^- are more positive than those of the bath containing sulphate, and the order of the potentials is $F^- > Cl^-$. This shows that F^- and Cl^- have a depolarization effect which facilitates chromium deposition. However, the deposition potential of chromium for the bath containing Br^- is close to that for the bath containing sulphate. This means that Br^- displayed little activation effect, which is probably due to the oxidation of Br^- to form Br_2 by chromic acid.

3.3. Determination of the cathode film by XPS and AES

The composition of the cathode film formed from the chromic acid baths containing different anions was determined by XPS. The results showed that oxygen and chromium were present in all the films, sulphur was present in the films from the baths containing SO_4^{2-} ions, and fluorine and chlorine were present in the film from the baths containing Cl^- and F^-, but no bromine was detected in the film obtained from the bath containing Br^-.
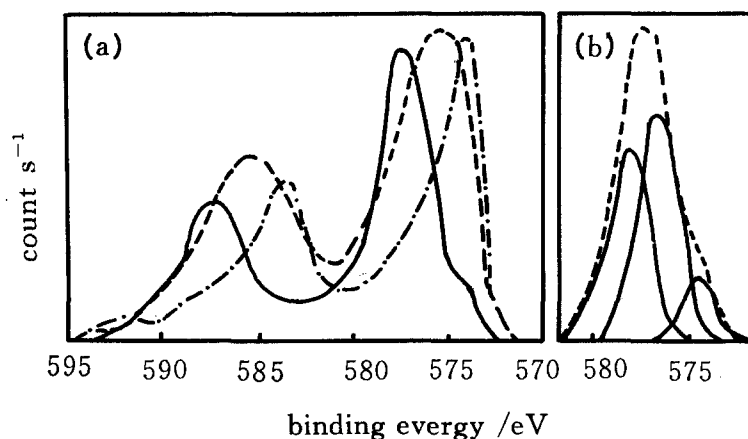
Fig. 3. High resolution XPS spectra of Cr_{2p} (a) Cr_{2p} spectra at various sputtering times: (——) no sputtering, (— — —) sputtering for 3 min, (—·—·) sputtering for 16 min. (b) Resolved spectrum of $Cr_{2p_{3/2}}$ before sputtering.

The valence states of the elements in the film are explained by an example of the film formed from the chromic acid bath containing Cl^- and SO_4^{2-} ions. The result shows that the binding energy of S_{2p} is 168.6 eV, which is identical with that in SO_4^{2-} [8]. The high resolution XPS spectra of Cr_{2p} in the film at different sputtering times are shown in Fig. 3. It can be seen that the distribution of the state of the element varies with the depth of the film. Before sputtering, the full width at half maximum intensity (FWHM) of $Cr_{2p_{3/2}}$ is 2.8 eV, and is wider than those of single $Cr(VI)$ and $Cr(III)$ compounds [8]. This implies that chromium in the film exists in a mixture of valence states. The $Cr_{2p_{3/2}}$ peak was resolved into triple peaks (Fig. 3b) which suggests that three different chromium species are present. The binding energy for the three peaks were 578.4, 576.7 and 574.4 eV, which are close to those of dichromate, $CrCl_3$ and metallic chromium [8], respectively. This suggests that a cathode film containing chromium dichromate is probably present on the cathode. After sputtering for 8 min, the FWHM of $Cr_{2p_{3/2}}$ was 3.6 eV. This shows that chromium in the film exists in mixed valences at this depth. After sputtering for 16 min, the FWHM and the binding energy of $Cr_{2p_{3/2}}$ were 1.7 eV and 574.3 eV, which are close to those of metallic chromium. The binding energy of $Cl_{2p_{3/2}}$ was 199.6 eV, which is similar to that in sodium chloride, but is higher by 0.4 eV, which may be due to the formation of the chromium Cl^- bond to some extent.

The variations in the contents of Cr, O, S and Cl with sputtering time are shown in Fig. 4; Cl^- lies in the inner layer of the film, and SO_4^{2-} in the surface layer.

4. Discussion

To account for the catalytic activity of SO_4^{2-} ion in the chromic acid bath, a number of electrodeposition mechanisms have been proposed [7,9,10]. Based on the experimental results, a probable electrodeposition mechanism is as follows.

4.1. Formation of chromium chromate

Complex chromic acid in a common plating bath (e.g.

CrO_3 2.5 M) is present as trichromic acid, $H_2Cr_3O_{10}$ [9]. The active species in a Cr plating bath is considered to be the trichromate ion, $HCr_3O_{10}^-$. The closest approach to the cathode surface of these negatively charged ions lies just outside the outer plane of the Helmholtz double layer because most of the potential drop between the cathode and bulk solution appears across the electrical double layer. As the thickness of the double layer is about 3 to 6 $\times$ 10^{-8} cm, it is possible to transfer electrons across the double layer by quantum mechanical tunneling. In the first step of this mechanism, the $Cr(VI)$ ion at the end of a $HCr_3O_{10}^-$ ion is reduced to $Cr(III)$ and a chromium (III) dichromate complex is formed:
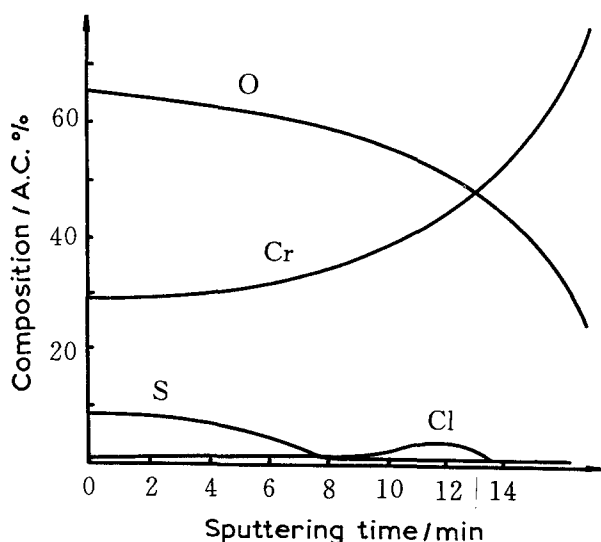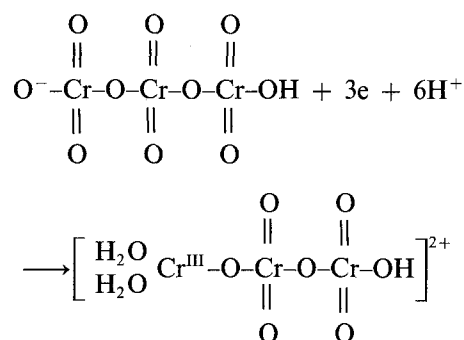

Fig. 4. Depth profiling curves of a cathodic film containing Cl^-.

The chromium (III) dichromate is the material comprising the cathodic film [9]. By binding the Cr(III) in this complex, the formation of a stable aquo complex $[Cr(H_2O)_6]^{3+}$ can be prevented. Since the coordination water at the end of Cr(III) in chromium (III) dichromate are near to the cathode, further reduction of Cr(III) is difficult and the major cathodic reaction is hydrogen evolution. Thus, the current efficiency for the conventional chromic acid plating bath is very low.

4.2. Activation effect of halides

As the hydration of halide anions is incomplete, they can penetrate through the hydration layer and be adsorbed on the metal surface. XPS results show that F^- and Cl^- ions, which are stable in the chromic acid bath may participate in the film formation. This may result from the characteristic adsorption. In fact, so-called characteristic adsorption is that the adsorbed substance forms partially chemical bonds with the metal surface. But the Br^- ion in the bath is probably oxidized to Br_2, which is not adsorbed on chromium metal. Consequently, bromine was not detected in the corresponding film. Haim et al. reviewed a number of electron transition reactions of metal ions in electrolytes containing halides and suggested that the activation mechanism of halides on the electron transition of metals may be related to the bridged transition complex formed from halides and metals [11]. Quantum chemistry results also show that, by the formation of the bridged halide complexes, the activation energy of the electron transition for metal ions can be decreased remarkably [1]. In the course of chromic acid electrodeposition, the probable activation steps of halides are as follows: the adsorbed halides first penetrate through the hydration layer on the chromium surface to reach its surface, and form a bridged transition surface complex with $[Cr^{III}(OH_2)_2Cr_2O_7]^{2+}$:

$$[(Cr_2O_7)(H_2O)_2Cr^{III}-X^--Cr^{III}(OH_2)_2Cr_2O_7]^{\ddagger}$$
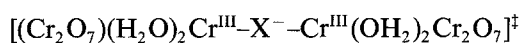
abbreviated as $[Cr^{III}-X-Cr^{III}]^{\ddagger}$. The electrons on the cathode are transferred to Cr^{III} through halides, and the Cr^{III} is reduced to metallic chromium. Probably, because of the formation of $[Cr^{III}-X-Cr^{III}]^{\ddagger}$ and the fact that the 2p electron of Cl transfers partially to Cr^{III}, the binding energy of the Cl_{2p} in the film is higher than that in sodium chloride. By the formation of the transition complex, the activation energy of reduction of Cr(III) to metallic chromium is decreased. The overpotential of chromium deposition is apparently decreased, which facilitates the chromium electrodeposition.

As the relative activation energy of formation of $[Cr^{III}-Cl^--Cr^{III}]^{\ddagger}$ is lower than that of $[Cr^{III}-F^--Cr^{III}]^{\ddagger}$ [11] and the hydration degree for Cl^- anion is weaker than that for F^-, the Cl^- anion is adsorbed easily on the metal surface, and the bridged complex of the Cl^- anion forms easily on the metal surface. Moreover, as the relative energy of the formation of $[Cr^{III}-Cl^--Cr^{III}]^{\ddagger}$ is higher than that of $[Cr^{III}-F^--Cr^{III}]^{\ddagger}$ [11], the former is easily reduced to metallic chromium, that is to say,
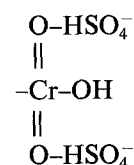
the Cl^- anions have a greater active effect on the reduction of chromic acid. This suggestion may explain that the activity of Cl^- anion is better than F^- anions in common electrochemical reactions.
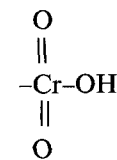
4.3. 'Blocking role' of sulphate

In chromium electrodeposition from chromic acid baths, the non-reduced end of the trichromate ion is also reduced to form a dichromium (III) chromate complex:
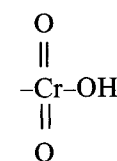
$$\begin{array}{c} O \\ \| \\ [(H_2O)_2Cr^{III}-O-Cr-O-Cr^{III}(OH_2)_2]^{4+} \\ \| \\ O \end{array}$$
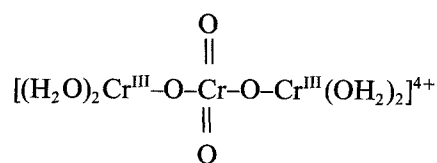
In acid solutions, the complex can be decomposed to trivalent chromium and chromate ions. The Cr^{3+} ions immediately form the aqua complex, $[Cr(H_2O)_5]^{3+}$, which prevents further reduction of Cr(III). The Cr^{3+} ions also form chromic oxide or hydroxide ($Cr_2O_3 \cdot nH_2O$) on the cathode. Therefore, only a brown passive film is obtained from pure chromic acid bath. When sulphate was added quantitatively to the chromic acid bath, a bright chromium was obtained. In the chromic acid solution containing sulphate, one end of the trichromate ion may be protected by sulphate ion, which may prevent the formation of dichromium (III) chromate [9]. In strongly acidic solution (such as chromic acid), the SO_4^{2-} ion can hydrolyse to form HSO_4^- ions, which may form a complex

$$\begin{array}{c} O-HSO_4^- \\ \| \\ -Cr-OH \\ \| \\ O-HSO_4^- \end{array}$$

with

$$\begin{array}{c} O \\ \| \\ -Cr-OH \\ \| \\ O \end{array}$$

through hydrogen bonding. Thus the reduction of

$$\begin{array}{c} O \\ \| \\ -Cr-OH \\ \| \\ O \end{array}$$

would be inhibited, i.e., so called 'blocked'. Three probable cases may be considered for the blocking of HSO_4^-:

(i) neither end of $HCr_3O_{10}^-$ is blocked;
(ii) only one end of $HCr_3O_{10}^-$ is blocked;
(iii) both ends of $HCr_3O_{10}^-$ are blocked.

Hoare proposed that only the $HCr_3O_{10}^-$ blocked at
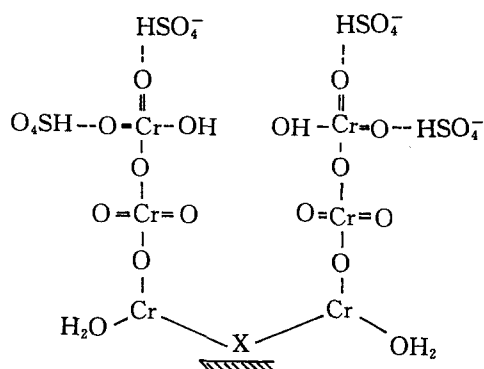
Fig. 5. Structure of transition state.

one end can be reduced to form chromium metal [9]. By controlling the CrO_3/H_2SO_4 ratio, it is possible to make case (ii) preponderant. Apparently, this case is met when the CrO_3/H_2SO_4 ratio is 100/1 in industry. With halides present, the trichromate ion blocked at one end may form a transition state with halide anion, as shown in Fig. 5. The transition state may decrease the activation energy of chromium deposition. The HSO_4^- ions may inhibit the formation of the stable $[Cr(H_2O)_6]^{3+}$ or chromic oxides or hydroxides by the formation of a complex with HSO_4^- ions through hydrogen bonding. This structure may explain the depth profiling curves of the film obtained from the bath containing Cl^- and SO_4^{2-} ions (Fig. 4), that is to say, Cl^- is distributed in the inner layer of the film and SO_4^{2-} ion in the surface layer.

5. Conclusion

The following conclusions are made.

(i) Sulphate is an effective catalyst for the deposition of bright chromium. The current efficiency of chromium deposition increases remarkably when F^- and Cl^- are added to a chromic acid bath.

(ii) Oxygen and chromium are present in all cathodic films. Sulphur is present in films from baths containing SO_4^{2-}. Fluorine and chlorine are present in the films from the baths containing Cl^- and F^-, but no bromine is detected in films obtained from baths containing Br^-.

(iii) The depth profiling curves of the film show that halide is distributed in the inner layer of the film and SO_4^{2-} in the surface layer.

(iv) F^- and Cl^- may form a bridged complex, $[Cr^{III}-X^--Cr^{III}]^{\ddagger}$, in which electron transition is easily carried out.

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