

Hard chromium electrodeposition from a trivalent chromium bath containing water-soluble polymer

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Abstract: The effect of polyvinylpyrrolidones (PVPs) with different molecular weights as polymeric additives to a sulfate trivalent chromium bath was ascertained. Introduction of PVPs to the plating bath was stated to result in improvement in the surface appearance of chromium deposits and stabilization of current efficiency value in long-term electrolysis. The rate of metal deposition is practically independent of the deposition time. Thus, using PVP additive allows one to obtain high-quality Cr-coatings with a thickness of several tens of micrometers. It is found by means of turbidimetric analysis that the polymer additive has an accelerating effect on the aggregation of particles of the chromium(III) hydroxide sol formed in the near-electrode layer.

Key words: Electrodeposition, trivalent chromium bath, hard chromium, polyvinylpyrrolidone

1. Introduction

Since chromium electrodeposits are distinguished by their exceptional properties (such as high wear and corrosion resistance, high hardness, and low friction coefficient), hard chromium electroplating is widely used in modern industry. As a rule, the thickness of the hard chromium coatings is in the range from several tens to several hundred micrometers. Generally, chromium is deposited from hexavalent chromium baths containing extremely toxic compounds of Cr(VI). Increasing attention to the environmental problems stimulates development of chromium deposition technologies on the basis of Cr(III) compounds as an ecofriendly alternative to the usual hexavalent chromium baths.

A number of attempts were made recently to develop effective trivalent chromium baths.^{1–13} It should be stressed that the baths proposed are not always sufficiently stable. Additionally, it is difficult to deposit thick chromium layers from trivalent chromium baths.

As was shown previously,^{14,15} the surface appearance of the coatings deposited from trivalent chromium baths deteriorates with the deposition time because the colloidal particles of the Cr(III) hydroxide formed in the near-electrode layer cover the cathodic surface and are incorporated into the deposit structure. As a result, current efficiency decreases and coatings crack and become dark. It was stated¹⁶ that certain organic surfactants, which are selectively adsorbed on chromium(III) hydroxide, optimize the grain size of the hydroxide sol and allow growth of the maximum thickness of high-quality Cr deposits, but only up to 5–10 μm .

We suppose that using water-soluble polymers can be more effective and promising in order to obtain

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thick Cr coatings from a trivalent chromium bath. Indeed, a beneficial effect of polyethylene glycol on the trivalent chromium deposition process was recently established.^{17,18}

In the present work, we describe the main results of our investigations devoted to the study of a hard chromium electroplating process using a trivalent sulfate chromium bath containing some polyvinylpyrrolidones (PVPs) as water-soluble polymeric additives.

2. Experimental

For the chromium deposition, the following basic sulfate-formate bath was used^{14–16} (mol L^{-1}): 0.5 $\text{KCr}(\text{SO}_4)_2$, 0.75 HCOOH , 2 $(\text{NH}_4)_2\text{SO}_4$, 0.5 H_3BO_3 ; pH 3.

Chromium deposition was performed under a steady-state value of current density in a temperature-controlled glass cell without separation of electrode compartments. A titanium-manganese dioxide anode (TMDA) served as the anode. On the TMDA, the electrooxidation of Cr(III) ions to Cr(VI) occurs at a comparatively low rate.¹⁹

The working electrode, made of copper foil with a surface area $S = 0.018 \text{ dm}^2$, was embedded in a Teflon holder. Prior to each experiment, the surface of the working electrode was treated with magnesium oxide and then rinsed with hydrochloric acid solution and distilled water.

The current efficiency of chromium electrodeposition was calculated by comparing the weight gain of the working electrode with the cathode of a copper coulometer connected in series.

The concentration of Cr(III) ions in the bath was determined by spectrophotometric method. The pH value was controlled by common potentiometric method. If needed, the pH of the solutions was adjusted to the required value by addition of H_2SO_4 or NH_4OH .

The effect of water-soluble polymers on the aggregative stability of the $\text{Cr}(\text{OH})_3$ sol was studied by turbidimetric analysis. The $\text{Cr}(\text{OH})_3$ sol was obtained by adding some portions of NaOH solution to the 250-times diluted basic trivalent chromium electrolyte up to pH 8.5. Then a polymer additive solution was added and the optical density was measured by means of a photoelectric colorimeter KFK-2-UkhL-42 (the cell thickness was 5 mm, the wavelength was 540 nm, the reference liquid was distilled water).

The morphology of the deposits was investigated by scanning electron microscopy (EVO 40XVP). The samples used in the SEM study were electroplated on the electropolished Cu-substrate.

The hardness of chromium coatings was determined using a PMT-3 set-up at a load of 100 g and the coating thickness of no less than 20 μm .

3. Results and discussion

3.1. Chromium electrodeposition, morphology of chromium deposits and their hardness

It was stated in preliminary experiments that bright chromium deposits approximately 1 to 5 μm thick may be obtained from the basic trivalent chromium bath (without polymeric additive). However, the surface appearance of the coatings deteriorates with the deposition time, and thick coatings have a high tendency to crack and are somewhat rough. In addition, after 5–10 min of electrolysis, we observed a decrease in the current efficiency of chromium deposition.

We tried to solve this problem in the present work using some water-soluble polymers and tried several PVPs with different molecular weights as polymeric additives.

PVP is a water-soluble polymer made from the monomer N-vinylpyrrolidone. It is generally used as a

synthetic blood plasma substitute and in the cosmetic, drug, and food-processing industries.²⁰ As concerns its main properties, PVP is soluble in water as well as other polar solvents. It has excellent wetting properties in solution. Figure 1 gives the chemical structure of PVP.

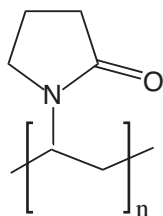


Figure 1. Chemical structure of polyvinylpyrrolidone.

The dependences of current efficiency of chromium deposition versus PVP content in the bath are shown in Figure 2.

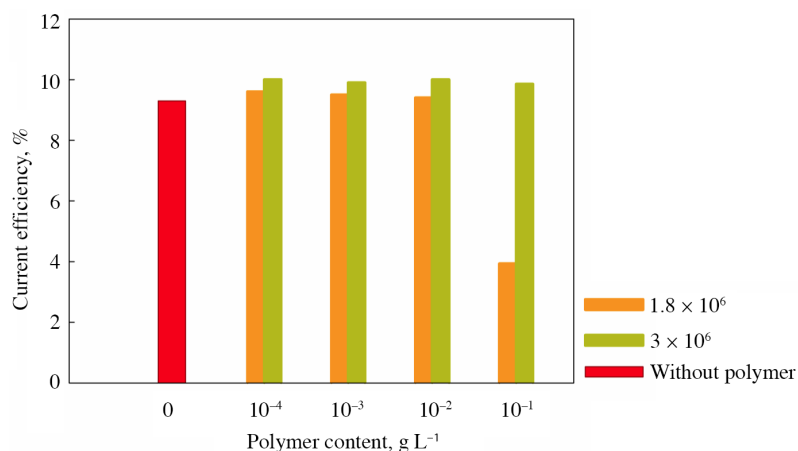


Figure 2. Effect of polyvinylpyrrolidone content on current efficiency of chromium electrodeposition reaction at different polymer average molecular weights (1.8×10^6 or 3×10^6). Deposition time 2 h; current density 15 A dm^{-2} ; temperature $30 \text{ }^\circ\text{C}$.

The current efficiency exhibits a maximum value at the polymer concentration of about 0.01 g L^{-1} . At this concentration, rather smooth coatings with the thickness of several tens of micrometers are obtained. When the concentration of polymer increases (up to 0.1 g L^{-1} and more), the current efficiency of chromium electrodeposition diminishes and the coatings become dark. An increase in average molecular weight of polymer results in improvement in the surface appearance of deposits.

It must be stressed that in the bath under study the rate of metal deposition is practically independent of the deposition time (Figure 3) and thick chromium coatings can be easily obtained. It is a very important advantage of the electroplating process proposed.

Figure 4 shows the surface morphology of the chromium deposits under study. The surface of the coatings is smooth with spheroid inclusions. The Cr-coatings obtained from the bath containing PVP are brighter, smoother, and more uniform compared with those deposited from the bath without polymer additive.

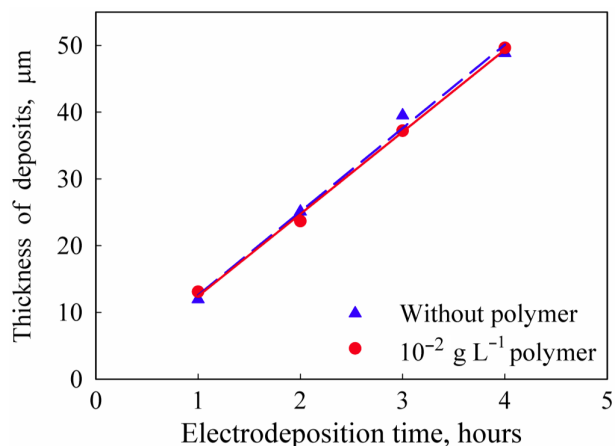


Figure 3. Dependences of thickness of deposits on deposition time. Current density 15 A dm^{-2} ; temperature 30°C . Polymer average molecular weight 3×10^6 .

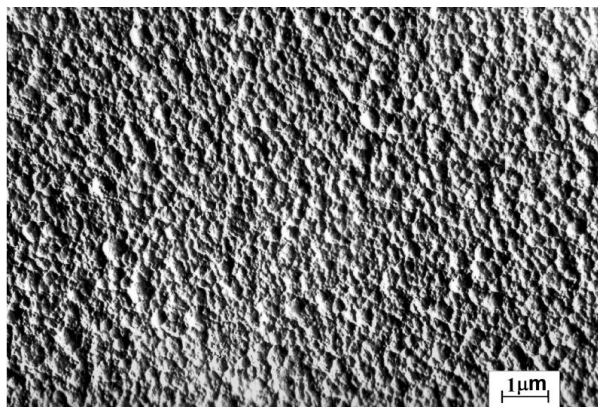


Figure 4. SEM image of surface morphology of the Cr-deposit obtained from the bath with 0.01 g L^{-1} PVP (average molecular weight 3×10^6).

It should be observed that the hardness of deposits under consideration proved to have values somewhat lower than those typical of the "usual" coatings deposited from hexavalent chromium baths (Table). With an increase in the current density, the hardness of deposits decreased.

Table. Hardness of Cr deposits obtained from the trivalent chromium bath with 0.01 g L^{-1} PVP additive (average molecular weight 3×10^6).

Current density, A dm^{-2}	Hardness, HV
10	720
15	690
20	660

Thickness of deposit $\sim 25 \mu\text{m}$

3.2. Effect of PVP on aggregative stability of the $\text{Cr}(\text{OH})_3$ sol

The changes in the surface morphology of deposits caused by the polymer additive could have resulted from the effect of PVP macromolecules on the aggregative stability of the $\text{Cr}(\text{OH})_3$ sol formed in the near-electrode layer. To verify this assumption, we performed a turbidimetric study of the $\text{Cr}(\text{OH})_3$ sol in the presence of PVP.

The time dependence of the measured absorbance of the sol in the system without polymeric additive is represented as a curve with a weakly pronounced maximum (Figure 5, curve 1). According to the well-known equation,²¹

$$D = k\nu V^2,$$

where D is the value of the sol absorbance, ν is the particle concentration in the dispersed system, V is the average particle volume, and k is a certain constant.

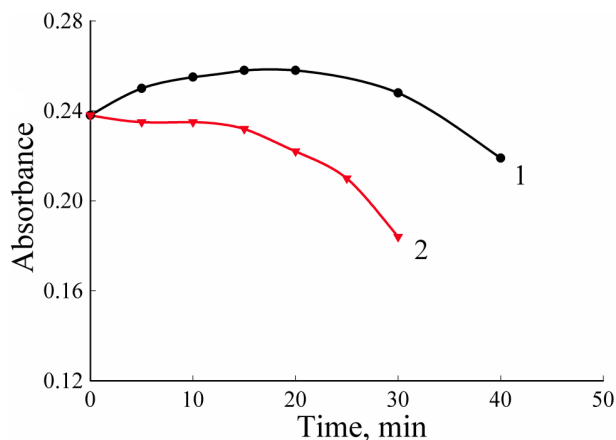


Figure 5. Time dependence of the absorbance of $\text{Cr}(\text{OH})_3$ sol: (1) without PVP, and (2) with 0.01 g L^{-1} PVP (average molecular weight 3×10^6).

The bell shape of the D vs. time curve can be associated with the processes of coagulation and subsequent sedimentation of the dispersed phase, which occur in time.

When PVP was introduced into the $\text{Cr}(\text{OH})_3$ sol, absorbance of the dispersed system decreased sharply (Figure 5, curve 2). This phenomenon was stated to be typical of PVP additives with different average molecular weight in a wide range of its concentration (from 10^{-5} to 10^{-1} g L^{-1}), being caused by the acceleration of both flocculation and coagulation followed by the sedimentation of colloid particle to form a sediment in the cell bottom. Hence, PVP is an effective flocculant that promotes the aggregation of the $\text{Cr}(\text{OH})_3$ particles. As a result of the flocculation effect of PVP, coarsely dispersed $\text{Cr}(\text{OH})_3$ particles are formed. We suggest that incorporation of $\text{Cr}(\text{OH})_3$ particles into the chromium electrodeposit may be considered a typical example of formation of composite coatings containing nanoparticles in a metal deposit. It is known that in such a case as the size of nanoparticles becoming greater, less can be incorporated into a metal deposit per unit volume.²² In addition, PVP macromolecules may adsorb at the electrode surface, thus impeding the incorporation of the $\text{Cr}(\text{OH})_3$ nonmetal phase into the deposit. Apparently, these phenomena are the reasons for the improvement of the coating surface appearance as well as stabilization of the value of current efficiency in long-term electrolysis.

4. Conclusions

The presence of PVP additive in sulfate trivalent chromium bath results in improvement of the surface appearance of chromium electrodeposits. Coatings with the thickness of several tens of micrometers may be obtained from the bath under consideration, the current efficiency of metal electrodeposition reaction being practically constant during relatively long-term electrolysis. As a result, an actual problem of thick Cr-coating electrodepositing from Cr(III) baths may be solved by using PVP additives. PVP macromolecules affect the aggregation of the $\text{Cr}(\text{OH})_3$ colloidal particles formed in the near-electrode layer during chromium deposition.

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