Automatic Control of the Solution in Trivalent Chromium Plating Process

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Stable operation of chromium plating solutions based on trivalent-chromium compounds needs continuous or frequent replenishment: additions of chromium salts and alkalies. It leads to excessive built-up of salts (e.g. sodium or ammonium sulfate). A combination of two anodes placed in two half-cells with appropriate ion-exchange membranes enables easy and economic automatic control of the concentrations of chromium ions, sulfates and pH-value in the plating solution. Any losses of organic components, such as formic acid, and formation of chromate due to anodic oxidation are also eliminated. Higher cathodic current efficiency is reached due to the prevention of the incomplete reduction of Cr^{3+} to Cr^{2+} followed by the reverse anodic oxidation of Cr^{2+} to Cr^{3+}.

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Introduction

Trivalent chromium plating process is using only insoluble anodes. Therefore addition of chromium salt (usually chromium sulfate or chloride) is necessary. Rapid lowering of pH value of the plating solution results from the built-up of sulfates or chlorides (i.e. sulfuric or hydrochloric acid) in the course of plating process since cathodic discharge of one equivalent of Cr^{3+} ions releases one equivalent of free acid. Apart from that evolution of chlorine gas, anodic oxidation of Cr^{3+} and organic components of the solution may happen at insoluble anodes.

Sulfate-type Bath

All above disadvantages of trivalent chromium plating can be overcome in sulfate-type bath by separating an insoluble anode with an anionic membrane. It allows to change the pH value of plating solution in the desirable direction [1]. The direction of this change is determined by the concentration of sulfuric acid in the anolyte. Constant pH corresponds to a steady-state process, i.e. to equal rates of the transfer of hydrogen ions through the membrane and their discharge at the cathode. When the current passes through the electrolytic cell, the equality of these rates will take place only, if the current efficiency for hydrogen evolution is equal to the transport number of hydrogen ions through the membrane. Hydrogen current efficiency depends practically on every parameter of the plating process: composition of the plating solution, especially, its pH, Cr^{2+}/Cr^{3+} ratio, temperature and current density. The transport number of H^+ ions is strongly effected by the concentration of sulfuric acid in the anolyte: in the course of the electrolysis sulfuric acid is continuously building up in the anolyte. Therefore, it would be practically impossible to balance the input and the consumption of hydrogen ions in the plating solution by using single anionic membrane.

Simultaneous operation of an anionic and a cationic membranes (Fig. 1)

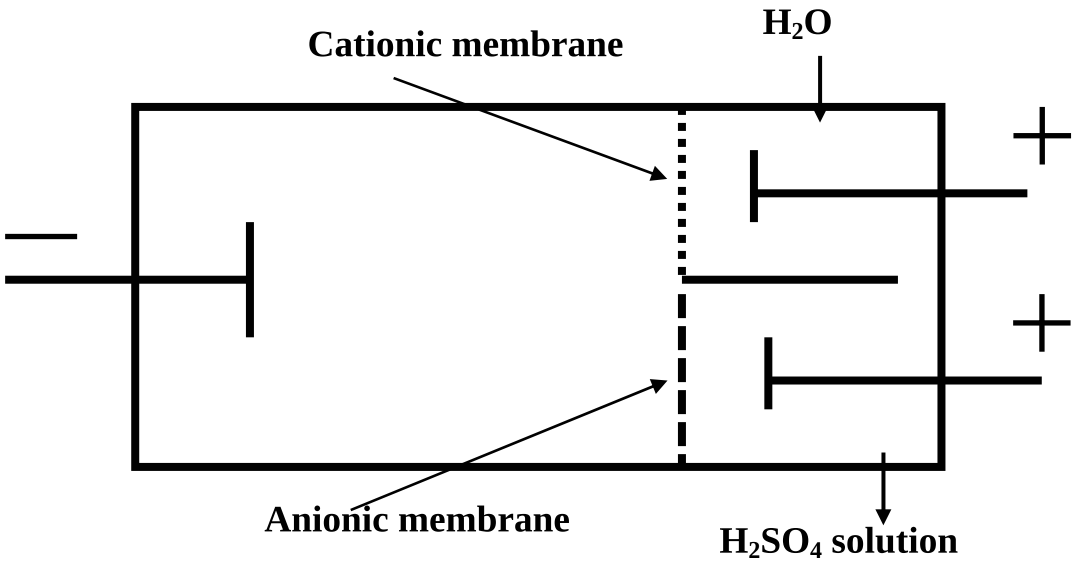

Fig. 1. Chromium plating cell with one cationic and one anionic membranes

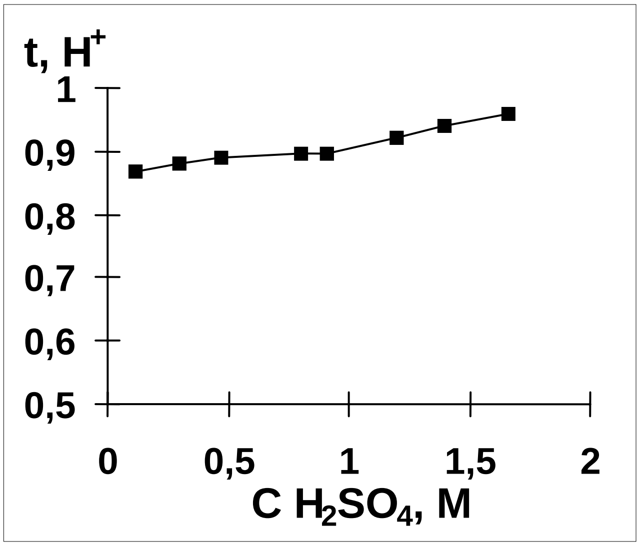

Fig. 2 - Transport number of H^+ *ions vs. the concentration of sulfuric acid in the anolyte. Anodic chamber with the cationic membrane.*

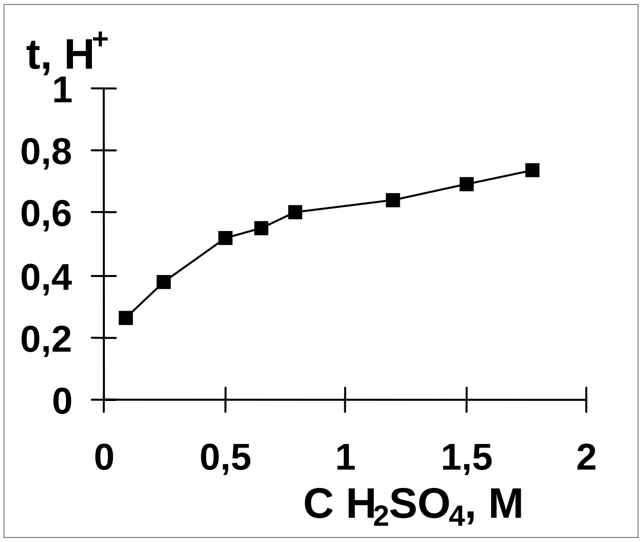

Fig. 3 - Transport number of H^+ *ions vs. the concentration of sulfuric acid in the anolyte. Anodic chamber with the anionic membrane.*

and controlled distribution of the total electric charge passed through each of them allows to maintain constant pH or to change it arbitrarily irrespectively of the cathode current efficiency and varying concentration of the sulfuric acid in the anolyte:

$$Q_\Sigma = Q_c + Q_a \qquad (1)$$

Here Q_Σ is total electric charge passed through the cell, i.e. through the cathode;
Q_c and Q_a are the charges passed through the cationic (c) and anionic (a) membranes. Transport number of hydrogen ions depends on the type of the membrane and on the concentration of sulfuric acid. It follows from the curves in Figs 2 and 3 that at very low current efficiency of chromium constant pH of the plating solution will correspond to Q_c approaching Q_Σ. At higher current efficiency for chromium (about 30%) Q_a will be close to Q_Σ at higher concentrations of sulfuric acid in the anolyte, while at lower concentrations (below 1 N) both Q_a and Q_c should be close to 50 % of Q_Σ. If both anodes are connected in parallel, one part of the total current passes through the cationic membrane, and another part passes through the anionic membrane:

$$I_\Sigma = I_c + I_a \qquad (2)$$

The pH value of the plating solution will be gradually rising up or lowering down depending on the current relationship between the input of hydrogen ions (through the two membranes) and their consumption at the cathode. As soon as pH approaches its upper or lower admissible limit one of the anodes should be disconnected. Then the pH starts to change in the opposite direction. When it approaches the opposite limit both anodes will start to operate simultaneously in parallel.

During the operation of chromium plating tank the concentration of sulfuric acid in the anolyte is gradually increasing: the built up of sulfuric acid in the long term operation should be equivalent to the amount of deposited chromium metal and the amount of chromium sulfate added to the bath. So at certain moment the anolyte should be diluted to such an extent, which will bring Q_c/Q_a ratio back to its initial value which should be close to unity.

Chloride-type Bath

There is no principal difference between the operation of sulfate- and chloride-type baths: in both cases pH control and removal of anions in amounts equivalent to the amounts of deposited metal and added chromium salt are achieved by the electrolytic transfer of anions through membranes. However the use of hydrochloric acid as an anolyte (similarity to sulfuric acid in sulfate-type solutions) creates a problem of the formation of chlorine-oxygen mixture at the anode, current efficiency or chlorine under steady-state conditions being equal to the transport number of chloride ions:

$$\text{C.E.}_{\text{Cl}_2}/100 = t_{\text{Cl}^-} \qquad (3)$$

Here $\text{C.E.}_{\text{Cl}_2}$ is current efficiency of chlorine and t_{Cl^-} is the transport number of chloride ions. Fortunately the transport number of chloride ions through the cationic membrane is very low. Therefore separation of the anode from the plating solution by the cationic membrane can be used in order to decrease the input of Cl^- into the anolyte. Small amounts of chlorine evolved from the anolyte separated by the cationic membrane can be easily removed from oxygen-chlorine mixture. Major amounts of chloride ions, which should be removed from the plating solution, pass through the anionic membrane and are accumulated in the space between the anionic and the cationic membranes (as HCl) (see Fig. 4).

The solution at the anodic side of the anionic membrane is separated from the anolyte by another cationic membrane in order to minimize the formation of chlorine gas.

Summary

The use of two anodes separated from the plating solution by one cationic and one anionic membranes enables to introduce automatic control of the composition of trivalent chromium plating solution and to eliminate undesirable effects of anodic side reactions.

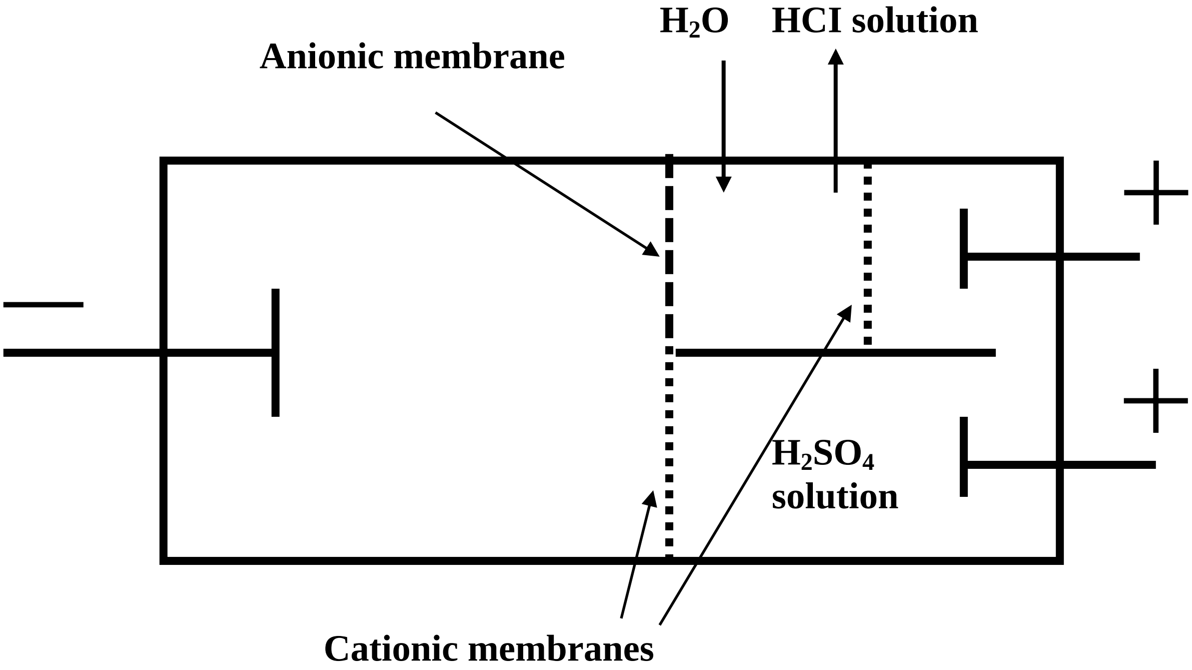

Fig. 4. Plating cell with one anionic and two cationic membranes.

Reference

[1] Sergei S. Kruglikov, Vladimir N. Kudryavtsev, Dmitri Yu. Turaev, Vitali V. Kuznetsov. Proc. AESF SUR_FIN' 2002, p, 560-566