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# KINETICS OF ANODE PROCESSES IN *CHROMISPEL - C* ELECTROLYTE FOR CHROMIUM PLATING

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## ABSTRACT

The kinetics of anode process running in Chromispel – C non-standard chloride electrolyte for chromium plating has been studied. The anodes investigated are prepared from platinum, silver, lead, PbCa 0.11% alloy and M10 and P25 ceramal alloy. The processes running on the anode are identified. The distribution of the total current among anode reactions is established. The effect of electrolyte concentration, anode material, current density and temperature on current distribution is studied.

The potential dynamic curves are recorded under varying operation conditions of chromium plating and the general I vs. E dependence established. The values of the corresponding corrosion potentials $E_c$, potentials $E_1$ and $E_2$ as well as the limiting currents $I_1$ and $I_2$ for the first and second step of the I vs. E curve are determined.

The activation energy is calculated using the temperature-kinetic model and the mechanism of electrode polarization established.

Platinum and P25 ceramal alloy are recommended as suitable anode materials.

*Keywords: Chromium plating, anode materials, cermal alloy, electrodeposition.*

## INTRODUCTION

The majority of plants around the world use the standard chromium bath while chrome plating (containing chromium trioxide 250 g.L$^{-1}$ and 2.5 g.L$^{-1}$ sulfuric acid). In this bath, chromium deposits with current efficiency not higher than 10 – 12%. This low efficiency is one of the reasons to constantly search for new, more effective components and techniques of chrome plating.

*“Chromispel”* baths can be referred to the new electrolytes. They are characterized with exceptionally high content of chromium trioxide (up to 1600 g.L$^{-1}$) and there the sulfate anions are replaced with halogens ($Cl^-$, $I^-$). The perceptiveness of these electrolytes is determined by the fact that they create possibility for electroplating of layers with current efficiency 60 to 70% at room temperature /1-5/.

The practical usage of *Chromispel* electrolytes is made difficult because of the lack of suitable anode materials. They are supposed to possess not only high resistance to corrosion in the aggressive media of the chrome bath, but to guarantee suitable distribution of the total anode current, i.e. a small quantity of chlorine should be precipitated over them and the oxidation of the trivalent chrome ions should run with such a speed, at which they do not accumulate in the chromium bath.

In the NAFTA countries in a report, represented to the Senate of USA it is commented that during 2004 the galvanic production decreased with 75% in comparison to 2000, because of the export of a big part of the automobile production in China. In order to avoid these important economical problems it is recommended to galvanic specialists to search for new materials and new technologies of chrome plating.

## EXPERIMENTAL CONDITIONS AND SET-UP

### *Preparation of Chromispel – C electrolytes*

Electrolytes with different content of $CrO_3$ were prepared:

° electrolyte of *standard* concentration - $CrO_3$ *250* g.L$^{-1}$

° electrolyte of *middle* concentration - $CrO_3$ *500* g.L$^{-1}$

° electrolyte of *high* concentration - $CrO_3$ *750* g.L$^{-1}$.

To each of them it was added a different quantity of hydrochloric acid in $CrO_3$ : $Cl^-$; 15:1, 20:1, 25:1, 30:1 ratio.

### *Experimental conditions for collecting and separating of the anode gas*

For the defining of the composition of the anode gasses at deposition of chrome from chloride electrolyte it was used the Orsa apparatus, equipped with burette and absorption vessel only for the chlorine. The volume of oxygen was determined as a different from the total volume of the anode gasses and the volume of the absorbed chlorine by the absorbent agent.

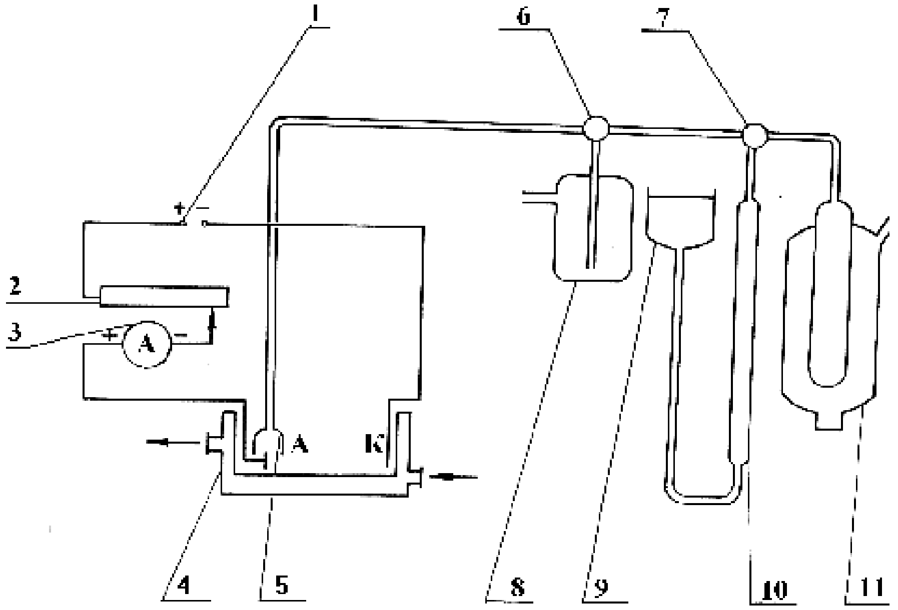

**Figure 1.** *Scheme of the experimental conditions: 1– rectifier; 2 – rheostat; 3 – ampere meter; 4 – galvanic cell; 5 – collective bell for anode gases; 6, 7 – three-way taps; 8 – hydraulic shutter; 9 – pressure vessel; 10 – measuring burette; 11 – absorber*

***Experimental conditions for taking down of the polarization curves***

In order to take down the polarization curves we used: RADELKIS potentiostat OH - 405 type, XY – RECORDER and reference Calomel electrode. The cathode was a copper plate, for the anode we used platinum.

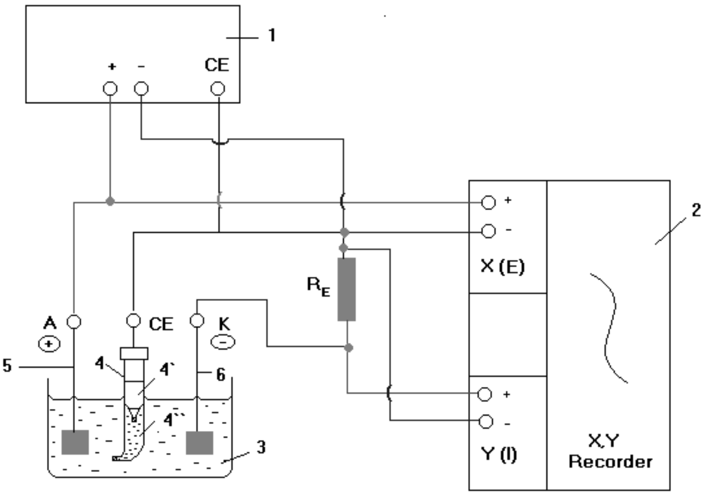

**Figure 2.** *Scheme of the equipment for recording polarization curves in potentiostatic regime: 1 - potentiostat; 2 – recorder; 3 – electrolysis bath; 4 – reference electrode (Calomel electrode); 4` - salt bridge; 5 - anode; 6 – cathode;* $R_E$ *– high ohm resistance*

## RESULTS AND DISCUSSIONS

Platinum was chosen to be an anode because of its high electrochemical stability in *Chromispel – C* electrolyte. This anode material guarantees the cleanness of the experiment, which means that in the electrolyte there will not be any foreign ions, apart of those included in its composition. While chrome plating with *Chromispel – C* electrolytes a minimum of three partial reactions run – evolution of oxygen, evolution of chlorine and oxidation of trivalent chromium ions to hexavalent ones.

$$1)\ 2Cl^- - 2e^- \rightarrow Cl_2$$

$$2)\ 4OH^- - 4e^- \rightarrow O_2 + 2H_2O$$

$$3)\ Cr^{3+} - 3e^- \rightarrow Cr^{6+}$$

The smallest part of the total anode current is spent on evolution of chlorine and the biggest possible one for the obtaining of oxygen (Figure 3). The chrome plating conditions influence that distribution. The high anode density leads to the increase of $A_{Cl_2}$ and $A_{O_2}$ and to decreasing of that of $A_{Cr^{3+}/Cr^{6+}}$.

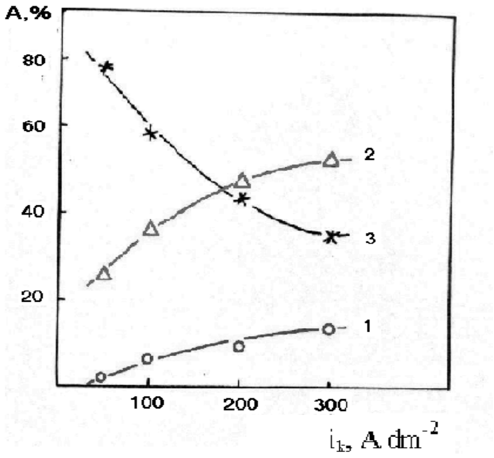

**Figure 3**. *Current efficiency for the three anode partial reactions on platinum anodes in medium concentration of Chromispel –C electrolyte, calculated in percentage; 1 – curve for separating of chlorine, 2 – for oxygen, 3 – for oxidation of trivalent chrome ions to hexavalent ones*

It was established that the presence of 2 to 6 g trivalent chrome ions influence slightly on the electrochemical evolution of oxygen and oxidation of trivalent chrome ions to hexavalent chrome ions, at the same time lowers abruptly current efficiency $A_{Cl_2}$ (Figure 4).

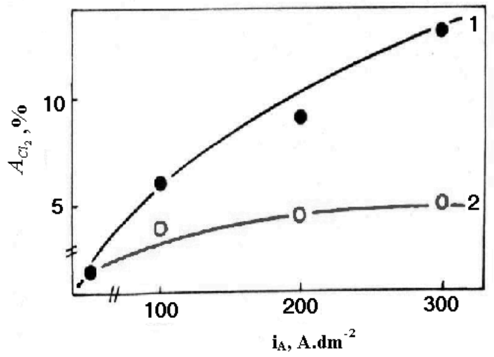

**Figure 4**. *Influence of the trivalent chrome ions on current efficiency of the reaction* $2Cl^- - 2e^- \rightarrow Cl_2$ *in medium concentration of Chromispel – C electrolyte at 20ºC; 1 – without* $Cr^{3+}$*, 2 – with 6* $g.L^{-1}$ $Cr^{3+}$

By taking down potential dynamic curve the polarization dependencies are studied in *Chromispel – C* electrolytes for platinum anodes. The influence of the factors was studied – concentration of chromium trioxide and hydrochloric acid, temperature, influence of trivalent chrome ions and nature of the anode material. The value of the corrosion potential has been estimated ($E_c$) as function of those factors. It is from 1,19 to 1,29 V and is little influenced by the conditions of electrolysis (Tables 1, 2, 3).

**Table 1**. *Values of* $E_c$*, measured in Chromispel – C electrolyte with a concentration of 250* $g.L^{-1}$ *and platinum anode, calculated according to Calomel electrode*

| $t^0$ C | $CrO_3$:$Cl^-$ | $E_c$, V | $CrO_3$:$Cl^-$ | $E_c$, V | $CrO_3$:$Cl^-$ | $E_c$, V | $CrO_3$:$Cl^-$ | $E_c$, V |
|---|---|---|---|---|---|---|---|---|
| 20 | 15:1 | 1,2471 | 20:1 | 1,2071 | 30:1 | 1,2571 | 35:1 | 1,2171 |
| 30 | | 1,2105 | | 1,1905 | | 1,2105 | | 1,2205 |
| 40 | | 1,2040 | | 1,2640 | | 1,2340 | | 1,1740 |
| 50 | | 1,1875 | | 1,2375 | | 1,2275 | | 1,2275 |

**Table 2**. *Values of* $E_c$*, measured in Chromispel – C electrolyte with a concentration of 500* $g.L^{-1}$ *and platinum anode, calculated according to Calomel electrode*

| $t^0$ C | $CrO_3$:$Cl^-$ | $E_c$, V | $CrO_3$:$Cl^-$ | $E_c$, V | $CrO_3$:$Cl^-$ | $E_c$, V | $CrO_3$:$Cl^-$ | $E_c$, V |
|---|---|---|---|---|---|---|---|---|
| 20 | 15:1 | 1,2571 | 20:1 | 1,2671 | 30:1 | 1,2471 | 35:1 | 1,2271 |
| 30 | | 1,2205 | | 1,2105 | | 1,2105 | | 1,2105 |
| 40 | | 1,2640 | | 1,2940 | | 1,2040 | | 1,2140 |
| 50 | | 1,2475 | | 1,2275 | | 1,2275 | | 1,2275 |

**Table 3**. *Values of* $E_c$*, measured in Chromispel – C electrolyte with a concentration of 750* $g.L^{-1}$ *and platinum anode, calculated according to Calomel electrode*

| $t^0$ C | $CrO_3$:$Cl^-$ | $E_c$, V | $CrO_3$:$Cl^-$ | $E_c$, V | $CrO_3$:$Cl^-$ | $E_c$, V | $CrO_3$:$Cl^-$ | $E_c$, V |
|---|---|---|---|---|---|---|---|---|
| 20 | 15:1 | 1,2371 | 20:1 | 1,2971 | 30:1 | 1,2871 | 35:1 | 1,2771 |
| 30 | | 1,2705 | | 1,2905 | | 1,2605 | | 1,2605 |
| 40 | | 1,3040 | | 1,2940 | | 1,2940 | | 1,2840 |
| 50 | | 1,3075 | | 1,2975 | | 1,2975 | | 1,2975 |

It has also been found the general type of the anode polarization curve for platinum anode (Figure 5). It is characterized with two steps, the first of which is more clearly expressed and the limit current $I_1$ corresponds to it, while the second corresponds to current $I_2$. $I_1$ is changed from $0,55*10^{-3}$ A to $5*10^{-3}$ A, but $I_2$ has values of $3,9*10^{-3} - 37*10^{-3}$ A.

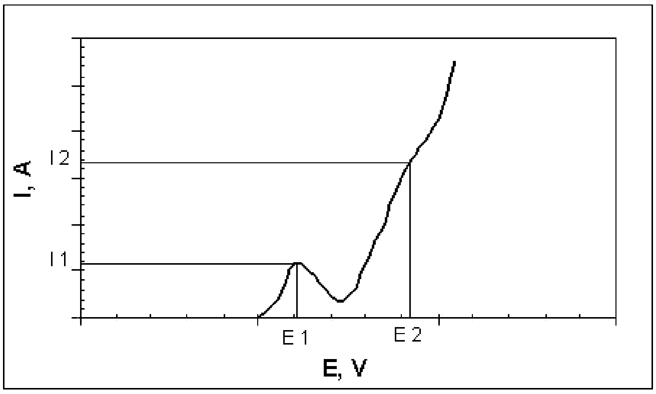

**Figure 5.** *General type of the anode polarization curve, taken down at 20ºC in Chromispel – C electrolyte*

The potential corresponding to $I_1$ is very close to the standard potential of the reactions – discharging of oxygen and oxidation of trivalent chrome ions to hexavalent ones. This proximity does not let us clarify which of the two reactions starts first.

$$2H_2O \rightarrow O_{2(г)} + 4H^+ + 4e^-, \qquad E^0=1,229V$$

$$7H_2O + 2Cr^{3+} \rightarrow Cr_2O_7^{-2} + 14H^+ + 6e^-, \qquad E^0=1,33V$$

Through experiment it has been proved that the lower the potential of the electrode has been, the higher $A_{O_2}$ has been. With the increasing of the potential and current the quantity of the discharged gas chlorine increases, that's why we can say with certainty that the second step corresponds to the discharging of chlorine.

$$2Cl^- - 2e^- \rightarrow Cl_2$$

**Table 4.** *Anodic current efficiency for the separate anode reactions in Chromispel – C, 500 g.L$^{-1}$ CrO$_3$, CrO$_3$:Cl$^-$=20:1, t=20$^0$C*

| $\tau$ , h | I, A | E, V | i, A.dm$^{-2}$ | $V_{Cl_2}$ , ml | $V_{O_2}$ , ml | $A_{Cl_2}$ ,% | $A_{O_2}$ ,% | $A_{Cr^{3+}/Cr^{6+}}$ ,% |
|---|---|---|---|---|---|---|---|---|
| 5 | 0.12 | **1.7** | 4 | 8 | 12 | 3.19 | **9.57** | 87.24 |
| 2.5 | **0.21** | **1.9** | 7 | **33.8** | 1.2 | 15.4 | 1.1 | 83.5 |

The obtained values of the potentials for the first and second step $E_1$ and $E_2$ from the polarization curves are higher than the corresponding standard potentials. This is to say that the electrochemical processes, running on the anode, are connected with significant polarization.

Through using of temperature – kinetic method it has been calculated $E_a$ and it has been determined the nature of the electrode polarization. The types of polarization are concentration, electrochemical and phase. At concentration polarization $E_a$ of 8380 – 25140 $J.mol^{-1}$ and it does not change with alteration of the potential. For the first step the numerical values correspond to the concentration polarization but with the alteration of the potential $E_a$ is changed which is an evidence of electrochemical hindrance.

**Table 5.** *Values of Ea calculated from the dependency* $\ln i_1 - 1/T$ *in Chromispel – C electrolyte with concentration of* $250 g.L^{-1}$ $CrO_3$

| $CrO_3:Cl^-$ | Values of E trough which isopotential lines pass, V | $E_a$, $J.mol^{-1}$ |
|---|---|---|
| 15:1 | 1,125 | 4365 |
| | 1,25 | 35334 |
| | 1,375 | 12877 |
| 20:1 | 1,125 | 3118 |
| | 1,275 | 2494 |
| | 1,4 | 2078 |
| 30:1 | 1,15 | 7690 |
| | 1,25 | 6651 |
| | 1,45 | 3326 |
| 35:1 | 1,175 | 8730 |
| | 1,35 | 13302 |
| | 1,475 | 3949 |

$E_a$, which corresponds with the reaction of the chlorine evolution, is several times bigger than the one for the evolution of oxygen, but its numerical values are still in the limits, typical for concentration polarization.

**Table 6.** *Values of* $E_a$ *calculated from the dependency* $\ln i_2 - 1/T$ *in Chromispel –C with concentration of* $250 g.L^{-1}$ $CrO_3$, $CrO_3:Cl^-=20:1$

| Values of E trough which isopotential lines pass, V | $E_a$, $J.mol^{-1}$ | tgα |
|---|---|---|
| 1,75 | 17460 | 2100 |
| 1,85 | 19538 | 2350 |
| 1,925 | 21201 | 2550 |

As the influence of the nature of the anode material is essential for the kinetics of the anode processes, we have paid attention to pure silver anodes, pure lead ones and the alloy PbCa (0,11% Ca) which was especially designed for this research by the Bulgarian Academy of Sciences. Metal ceramal alloys M 10 and P 25 were observed too (Figure 6). It was also found that the lowest $E_c$ is in the alloy PbCa (0,11%Ca) (-0,32V), and the highest is that of M 10 (0,63V).

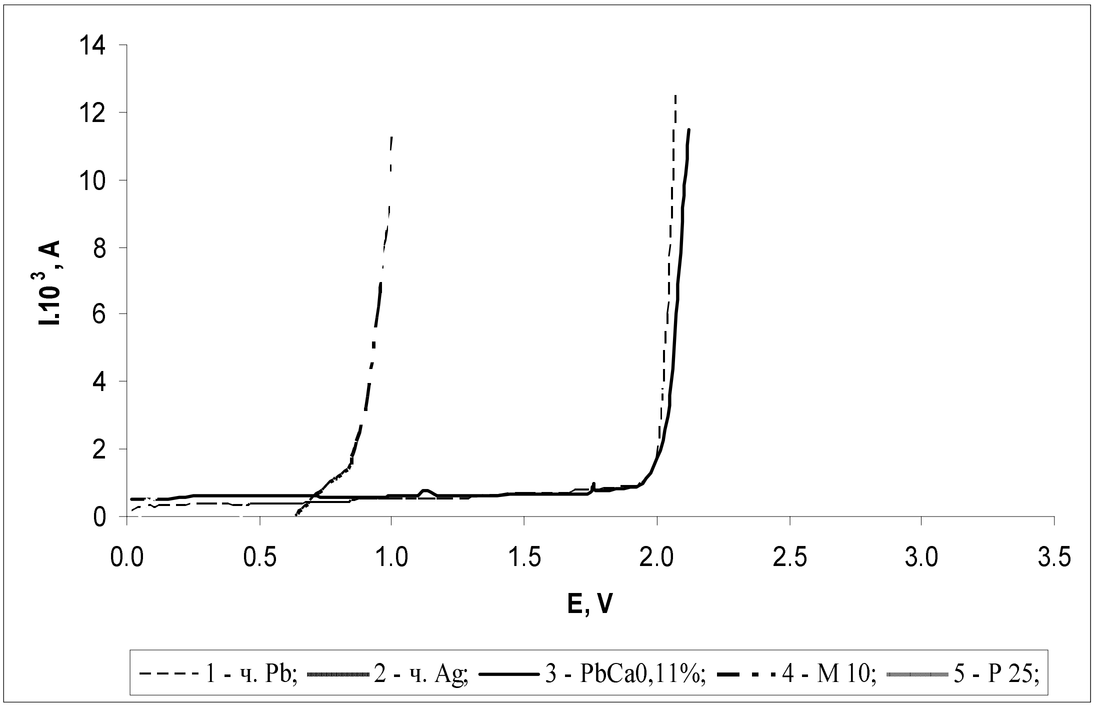

**Figure 6.** *Polarization dependencies of different anode materials, taken down at 20ºC in Chromispel – C, 250g.*$L^{-1}$ $CrO_3$, $CrO_3:Cl^-=20:1$

The line of the curve of the polarization dependencies shows that pure silver is very quickly polarized, as well as polychrome acids influence it. The anode starts to destroy and these chemical and electrochemical interactions define the complex aspect of the polarization dependency.

Although slower, the anodes of lead and lead alloys also destroy. This typical chemical instability of theirs, as well as their high polarization make them unsuitable as anodes in *Chromispel – C*.

Out of the five different observed anode materials the most preferable one should be the metal ceramal alloy P 25, whose stability in *Chromispel – C* is almost equal to that of the platinum.

## SUMMARY

- The total current distribution among separate anode reactions is determined.
- Potential dynamic curves are recorded under varying experimental conditions. The general course of platinum anode polarization curve and a mechanism of the anode process are proposed.
- The values of corrosion potential ($E_c$) and of potentials $E_1$ and $E_2$ as well the corresponding limiting currents $I_1$ and $I_2$ for the first and second step of polarization curve are determined.
- $E_a$ is calculated according to the temperature-kinetic method and the nature of the electrode polarization was determined.

- The most suitable anodes to operate in *Chromispel – C* electrolytes appear to be Pt ones as well as anodes prepared from metal ceramal alloy P 25.

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