

MECHANISM OF CHEMICAL GOLD PLATING FROM A BOROHYDRIDE ELECTROLYTE

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UDC 621.1793.3

Borohydrides of the alkali metals can be used for the production of gold chemical coatings [1, 2]. Thus, fine-grained coatings up to 7-10 μ thick are deposited on nickel, cobalt, Kovar, copper, and gold substrates, from an electrolyte with composition (g/liter): $\text{KAu}(\text{CN})_2 - 6$, $\text{KOH} - 7$, $\text{KCN} - 6.5$, $\text{NaBH}_4 - 0.4$ [2]. The rate of deposition on a gold substrate is constant, 1.5 μ/h . On other metals, especially on nickel, it initially is several times as high and reaches the indicated constant value after 20-30 min.

For a study of the mechanism of the process on a gold electrode, the potentiostatic polarization curves of the cathodic deposition of gold from an electrolyte of the composition cited above without borohydride and of the anodic oxidation of sodium borohydride in a solution without gold and cyanide ions were taken (Fig. 1).

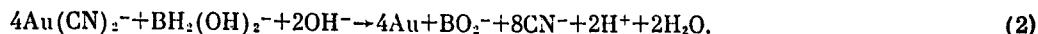
The curves intersect at the potential -0.53 V, which is very close to the static potential of the electrode in the process of chemical gold plating, which under our conditions proved equal to -0.50 V. The current density at the point of intersection $4 \cdot 10^{-4}$ A/cm² is equivalent to a rate of deposition of gold of 1.5 μ/h , which also coincides with the actual rate of deposition in chemical gold plating (see above). This is evidence of an electrochemical mechanism of the chemical deposition of gold on a gold substrate. Evidently the reduction reaction does not require direct contact of the complex ions of gold and ions of the reducing agent, but proceeds by an exchange of electrons through the substrate metal.

Certain researchers [3-5] believe that the reducing agent is not the BH_4^- ion, but products of its hydrolysis: the ions BH_3OH^- , $\text{BH}_2(\text{OH})_2^-$, $\text{BH}(\text{OH})_3^-$.

Our analytical measurements of the amount of reduced gold, consumed sodium borohydride, and the volume of hydrogen liberated, both in the summary process and on account of hydrolysis, have shown that the reaction of reduction of gold ions is closest to the processes:



and



Thus, for reaction (1) the analytical determinations show a 24-37% excess of the experimental data over the calculated values, while for reaction (2) there is a 4-10% decrease.

The molecular hydrogen liberated in the process of chemical gold plating is formed only on account of the reaction of hydrolysis of borohydride, and not as a result of the occurrence of a redox reaction.

This is explained by the data of [2] on the influence of the concentration of alkali and sodium borohydride on the rate of chemical deposition of gold.

Actually, for a stable occurrence of the process of chemical gold plating without decomposition of the electrolyte, the KOH concentration in it should be no lower than 6-7 g/liter. When the concentration is increased to 10 g/liter, the rate of deposition drops to a third, while at 15-20 g/liter there is practically no deposition. According to Davis [6], as the OH^- ion concentration is increased, hydrolysis becomes more difficult. The consequent decrease in the concentration of intermediate hydrolysis products should also lead to a decrease in the rate of gold plating. According to the data of [7], at pH 13 the BH_4^- ion is little subject to hydrolysis, and, correspondingly, the deposition practically ceases.

Translated from *Zashchita Metallov*, Vol. 12, No. 6, pp. 724-726, November-December, 1976. Original article submitted September 27, 1974.

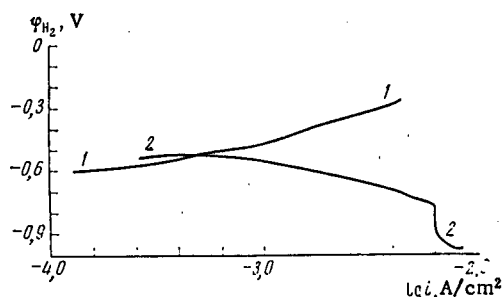


Fig. 1. Polarization curves on a gold electrode: 1) anodic oxidation of NaBH_4 ; 2) cathodic deposition of gold.

The amount of hydrolysis products also increases with increasing borohydride concentration. However, an excess accumulation of them is unobtainable: The reduction reaction begins to occur in the volume of the electrolyte.

Up to 20% of the gold precipitates from a solution containing more than 0.8 g/liter sodium borohydride, after boiling. After filtration of the solution and the addition of potassium dicyanoaurate in an amount equal to the deposited gold, the electrolyte becomes stable and operates stably at a temperature of 95–97°. Probably an optimum content of hydrolysis products, capable of being oxidized only on the catalytically active surface of the metal, is established in it.

The increased initial rate of chemical gold plating on nickel, copper, and cobalt substrates can be explained by the catalytic influence of the material of the substrate, which then is covered by a layer of gold.

There is information that the anodic treatment of copper in alkaline solution [8] and the incorporation of boron into a nickel coating [9] increase the rate of hydrolysis of sodium borohydride. In our experiments, preliminary anodic polarization of copper in a 0.1 N solution of KOH at $D_a = 0.05 \text{ mA/cm}^2$ led to an increase in the initial rate of deposition from 0.1 to 0.3 μ .

On nickel, obtained from a borohydride electrolyte, it is also higher than on nickel deposited from a hypophosphite electrolyte.

The catalytic influence of the substrate on the rate of deposition of gold is confirmed by the lengthening of the initial period with a high rate of the process in the case of an increase in the porosity of the gold deposits, achievable, for example, by the introduction of certain saturated hydrocarbons into the solution.

The polarization curve of the anodic oxidation of sodium borohydride on a nickel electrode, in contrast to gold, has a peak of the current at a potential of about +0.2 V. With increasing alkali concentration in the electrolyte, the peak decreases, while when potassium cyanide is introduced into the solution, at the same time it is shifted in the direction of more negative values of the potential. The existence of two peaks was detected on the copper anode: at a potential of +0.1 and +0.3 V. The first decreases with decreasing temperature and with increasing alkali concentration in solution. The second increases somewhat with increasing KOH concentration.

The optimum concentration of potassium cyanide, 6.5 g/liter, provides for the highest rate of the process with stability of the electrolyte. Increasing its content above 7 g/liter leads to a decrease in the rate of gold plating, while above 13 g/liter it leads to a virtual cessation of it. CN^- ions, which possess a high adsorption capacity and are a strong catalytic poison [10], in an excessive concentration poison the catalytic surface of the substrate, displacing from it the ions that participate in the deposition of gold.

Hence, the data obtained permit us to conclude that in chemical gold plating with the use of sodium borohydride as a reducing agent, the basic reducing agents are the intermediate products of hydrolysis of BH_4^- ions, most likely BH_3OH^- and $\text{BH}_2(\text{OH})_2^-$ ions. The deposition of gold occurs as a result of coupled electrochemical reactions: The oxidation of BH_3OH^- and $\text{BH}_2(\text{OH})_2^-$ ions and the reduction of $\text{Au}(\text{CN})_2^-$ with transfer of electrons through the surface of the substrate metal.

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PRODUCTION OF TUNGSTEN COATINGS BY ELECTROLYSIS OF OXYCHLORIDE MELTS BASED ON AN EQUIMOLAR KCl-NaCl MIXTURE

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UDC 541.135.3

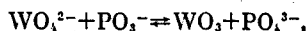
Salt halide melts, used for the production of solid cathodic deposits of tungsten, are either aggressive [1, 2] or expensive ($\text{CsCl}-\text{Cs}_2\text{WCl}_6$) and require special synthesis [3]. Electrolysis from them must be conducted in an inert atmosphere. Chloride-oxide melts based on calcium compounds ($\text{CaCl}_2-\text{CaWO}_4-\text{CaO}$) are more convenient, but they require a high temperature [4]. On account of the poor solubility of these electrolytes in water, it is very difficult to wash the cathodic deposits free of entrapped salts.

To obtain solid cathodic deposits of tungsten, we tested solutions of sodium tungstate in a low-melting equimolar mixture of KCl-NaCl in air. The temperature of electrolysis was 700°C. The cathode was a copper plate, preliminarily treated with dilute nitric acid. The electrolytes were prepared from dry remelted salts.

The quality and composition of the deposits was monitored by x-ray diffraction study [5] and microscopic observations (MIM-7 microscope) of the surfaces and sections of the coatings obtained.

According to the data of thermal analysis, the mutual system of sodium and potassium chlorides and tungstates ($\text{Na}, \text{K} \parallel \text{Cl}, \text{WO}_4$) is characterized by unlimited solubility of the components [6]. Considering the good solubility of sodium tungstate in a chloride melt KCl-NaCl, we studied the influence of its concentration on the cathodic deposition of tungsten within wide limits (2-20 mole %) at 4-6 mole % intervals. The most stable electrolytes, in the electrolysis of which solid tungsten coatings are formed, contain 8-10 mole % tungstate. In this case, good cohesion with the copper substrate and the formation of a uniform solid deposit are observed at a current density of 0.05-0.1 A/cm² (Table 1).

According to the modern concepts of acids and bases in melts, the WO_4^{2-} anion behaves like a weak base in molten chlorides [7]. However, electrodeposition of the metal is more easily performed from an acid particle containing a smaller number of oxygen atoms [8]. Therefore, it is advisable to produce cathodic deposits of tungsten from an acidified chloride melt. Sodium metaphosphate, facilitating the electrodeposition of tungsten through the acid-base equilibrium



was used as the acid.

The concentration of the metaphosphate additive was varied from 0.1 to 8.0 mole %. An addition of 0.25 mole % proved optimum. The current density necessary for the production of fine-crystalline cathodic deposits