Effect of Thallium Ions on Anodic Dissolution of Gold in Alkali–Cyanide Electrolytes at Potentials More Positive Than the NHE Potential

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Abstract—The gold dissolution rate $i$ in solutions containing 0.1 M KOH, 0.1 M KCN, and $2.5 \times 10^{-7}$ to $1.5 \times 10^{-5}$ M TINO$_3$ is studied as a function of potential $E$ of the electrode whose surface is renewed prior to each experiment, the TINO$_3$ concentration $c$, and the time $t$ of the electrode contact with solution. At $c$ exceeding 0.5 $\times$ 10$^{-5}$ M and $t = 0$, the rate is 1.5–2 times that at $c = 0$. Initial portions of $i$ vs. $t$ curves in the absence and presence of TINO$_3$ coincide only at $c$ below 10$^{-6}$ M. Potentiostatic and potentiodynamic measurements show that, at positive $E$, only small coverages of the electrode surface with thallium are obtained, which make no impact on $i$ at $E < 0$ and heavily increase it at $0 < E < 0.3$ V. The discovered effects are attributed to the formation, during the adsorption of oxidized thallium forms, of dipoles comprising thallium adions and gold atoms. Presumably, the dipoles face the gold with their negative ends and make the potential of zero free charge more negative.

INTRODUCTION

Neutral cations, which take no part in the overall electrode process, frequently heavily affect the electrode polarization and properties of deposits that form in these conditions [1–5]. The works of N.T. Kudryavtsev made a considerable contribution to studies of the mechanism of this phenomenon. As shown in [1, 5], microscopic amounts of lead, mercury, and tin drastically influence the zinc electrodeposition from zincate solutions and the quality of the coatings. In other works performed under his guidance, it was noted that the nature and concentration of alkali metal cations alter the electrode kinetics in cyanide silver-plating electrolytes [6–9] and the deposit structure [10].

The nature and concentration of alkali metal cations in alkali–cyanide solutions affect not only the silver plating process, but the gold dissolution as well [11–13]. Microscopic amounts of such cations as Tl$^+$, Pb$^{2+}$, Hg$^{2+}$, and Bi$^{3+}$ affect the gold dissolution even stronger [14, 15]. The effect of microscopic amounts of Tl$^+$ on the gold dissolution at negative potentials $E$ was considered in [16–18]. In the present work, we consider the effect of Tl$^+$ at positive $E$.

EXPERIMENTAL

To study potentiodynamically the gold behavior, we used a three-electrode electrochemical cell (the electrode in the cell could be renewed by cutting off its surface layer [19]) and a computer-controlled electrochemical interface [20]. These devices allowed us to perform any $i$, $E$, and $t$ measurements with potential scanned at rates $v$ of 0.001 to 10 V s$^{-1}$ and refer the results to controlled times $t$ of the electrode contact with solution after renewing its surface, thus providing information about the process at certain coverages of the surface by a catalytically active adsorbate [19].

To take measurements, the circuit was closed at $t = 0.2$ s after the surface renewing, and an initial potential of the working electrode was established. Immediately afterwards (or after a fixed time period $\Delta t$ after the renewal, which is given in the description of a relevant experiment, and prior to scanning the electrode potential) the potential was scanned and a voltammetric curve was recorded, or a current was passed and its dependence on $t$ was fixed at $E = $ const.

The standard potential of gold in cyanide solutions is $–0.61$ V [21]. At dicyanoaurate and cyanide ion concentrations of 0.01 and 0.1 M, respectively, the equilibrium potential is close to the standard one. If the Tl$^+$ concentration in an alkali solution$^1$ is about $10^{-5}$ M or lower, thallium phase forms at $E$ below $–0.65$ V [22]. Therefore, for the initial potential at which gold undergoes no dissolution yet and no thallium phase forms either, we selected $–0.61$ V. Potentials were measured relative to a silver–silver chloride electrode and then recalculated to a normal hydrogen electrode (NHE). All the potential values in this paper are referred to NHE. The electrode surface area was $5 \times 10^{-3}$ cm$^2$. The temperature was thermostated at 23°C.

$^1$ Ions Tl$^+$ form no strong complexes with cyanide ions [17, 18].
The working solutions contained different amounts of KOH, KCN, and Tl(NO₃)₂. To stabilize the equilibrium potential, we introduced 0.01 M KAu(CN)₂. Solutions were prepared using twice-distilled water; KCN of analytical grade (Czechoslovakia); KAu(CN)₂ and Tl(NO₃)₂ of reagent grade; and KOH of ultra-high purity grade. To remove oxygen, solutions were bubbled with electrolytic hydrogen for two hours, which reduced currents caused by the oxygen reduction to 10–15 μA cm⁻² [23].

RESULTS AND DISCUSSION

As seen from potentiodynamic polarization measurements (Fig. 1), in accordance with [24,25], in the absence of thallium ions (curve 1), the gold dissolution currents are very low in the potential region extending from –0.6 to 0 V. At more positive potentials, the current with \( E \) increases, but after reaching a maximum at about 0.35 V, the increase is replaced by a decrease, albeit barely noticeable, which is explained in [24] by deceleration of the gold dissolution process as a result of concurrent adsorption of cyanide and hydroxide ions, although the adsorption rate of hydroxide ions is not high. Consequently, at high \( v \), the decrease is barely perceptible or is absent altogether, as is the case with a curve recorded after periodical (every six seconds) renewal of the surface in the course of recording a polarization curve (PC) [16]. A further potential scan leads to another increase in the current until \( E = 0.55 \) V, after which passivation occurs, which is caused by the formation of gold(III) oxides [25,26].

We admit that the heights and some details of these maximums are sometimes irreproducible quantitatively, because of the influence exerted by products of decomposition of cyanide ions [25]. In particular, they depend on the way the solution was prepared (from dry KCN or a concentrate obtained by distilling HCN into a KOH solution) and its storage time before use. This is especially true for \( E > 0.4 \) V. Because of this, in what follows, we will analyze the anodic behavior of gold only at potentials less than 0.4 V.

In Fig. 1 (curve 2), we present results of polarization measurements performed immediately after renewing the gold surface in KCN solution with additive of \( 1.5 \times 10^{-5} \) M Tl(NO₃)₃. Keeping a renewed electrode at the equilibrium potential for 100–150 s yields a similar curve. This implies that, to the first approximation, during measurements at \( v = 0.002 \) V s⁻¹, the electrode is at adsorption equilibrium by Tl⁺ [17,18]. Comparing curves 1 and 2 shows that the presence of Tl(NO₃)₃ dramatically alters PC at potentials ranging from –0.61 to nearly 0.5 V. Specifically, in the presence of Tl(NO₃)₃, maximums \( A \) and \( B \) appear in PC at, respectively, negative and positive potentials. The effect of Tl⁺ on the anodic dissolution of gold at negative potentials was described at great length in [16–18]. Maximum \( A \) was attributed to the accumulation of some catalytically active thallium species (practically in the form of adatoms) on the electrode. To the first approximation, all other conditions being the same, the maximum height is proportional to the surface density of thallium species. The decrease in the current, which follows the maximum, was explained by the ionization and partial removal of adsorbed thallium from the gold surface [17].

One could have assumed that maximum \( B \) also reflects the accumulation of some catalytically active thallium compounds (other than adatoms) on the electrode in the course of scanning the potential, at certain values of it. The evidence proffered for the feasibility of such an assumption comes from radiochemical measurements of concurrent adsorption of thallium and cyanide ions [27]. According to the measurements, with an decrease in a negative value of potential, the thallium adsorption on gold from alkali–cyanide solutions steadily diminishes and at \( E = 0 \) V reaches very small values (\( \theta < 0.1 \)). However, near maximum \( B \) (\( 0 < E < 0.2 \) V), the thallium adsorption again increases with potential. We have no information on the concurrent adsorption of thallium and cyanide ions at \( E > 0.2 \) V. By analogy with the explanation devised for the process development near maximum \( A \), one could have assumed that the decrease in the current after maximum \( B \) is also connected with the removal of thallium from the gold surface.

More likely than not, at \( E > 0 \) V, the catalytically active species in question are some adsorbed oxidized forms of thallium ions, for example, compounds of Tl(III) [22]. As we have already mentioned, maximum \( B \) may reflect the accumulation of some catalytically active thallium compounds on the electrode in the course of scanning the potential. This is indicated by the decrease in the height of maximum \( B \) with increasing \( v \) (i.e. with decreasing \( i \)) in this potential range. A similar dependence is true for maximum \( A \).