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Anodic behaviour of gold in cyanide solution

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The anodic dissolution of gold in concentrated potassium cyanide solution was studied. Four regions of passivation were observed: at −0·6 V, +0·1 V, +0·4 V and +0·7 V versus SCE. The passive phenomena were explained in terms of the interaction of hydroxyl ions with the gold surface.

1. Introduction

The dissolution of gold in dilute cyanide solution by chemical or electrochemical methods has been studied by many workers [1–3] as cyanidation of gold in such media is of importance in mineral processing. The dissolution of gold in concentrated cyanide solution is, however, also industrially important since gold potassium cyanide is the chief ingredient of the gold electroplating bath.

The overall reaction of gold dissolution in cyanide solution is

$$Au + 2CN^- \longrightarrow Au(CN)_2^- + e^-; \quad E^0 = 0{\cdot}60\,V \tag{1}$$

and the reaction mechanism [4] is

$$Au + CN^- \xrightarrow{rds} (AuCN)_{ads} + e^- \tag{2}$$

$$(AuCN)_{ads} + CN^- \rightleftharpoons Au(CN)_2^-. \tag{3}$$

However, the reaction goes through several passivations [5, 6], whose nature is not yet quite clear.

Recently, Bewick [7, 8], Yeager [9] and McIntyre [10] studied the surface phenomena at gold electrodes in aqueous acid by reflectance spectroscopic methods. These results are not, however, directly applicable for the identification of the anodic film on gold in a cyanide system.

The object of this study was to explain the anodic response of gold in concentrated potassium cyanide solutions.

2. Experimental

A rectangular lucite cell was evenly divided into two compartments (4 cm × 4 cm × 8 cm) by a piece of cation exchange membrane (MC 3470, Ionac Co). A pure gold disc (99.9%, 1·5 cm diameter) was attached to the wall of the anode compartment while a platinum plated titanium mesh was used as the cathode. The distance between the electrodes was 7 cm. A saturated calomel electrode was used as the reference electrode with the tip of the luggin tube approximately 0·2 cm below the gold anode disc. The electrolyte was thoroughly de-oxygenated by nitrogen purging.

Anodic polarization data were collected by a potential scanning method. A scanning potentiometer (Model SMP 72, Wenking) was adopted to provide the potential signal, which was connected to a potentiostate (Model HP 72, Wenking). A *X–Y* recorder (Model 70 44 A, Hewlett-Packard) recorded all the results.

The gold discs after a proper cleaning, annealing and pickling procedure were dipped in the potassium cyanide electrolyte for an hour to reach equilibrium. The potential of the disc was then scanned at 50 mV s^{-1}. The potential was kept between −1·0 V and +1·0 V versus SCE. The temperature was controlled at 30 ± 2° C.

Reagent grade chemicals were used to prepare the electrolyte solutions.

3. Results and discussion

Fig. 1 shows that the polarization curve of gold in concentrated KCN solution is similar to that in dilute KCN solution obtained by Cathro [5]. At −0·6 V, +0·1 V and +0·4 V, the gold surface becomes passive. Over +0·4 V, the surface was covered with a brownish film.

When the KCN concentration exceeded 1·0 M,

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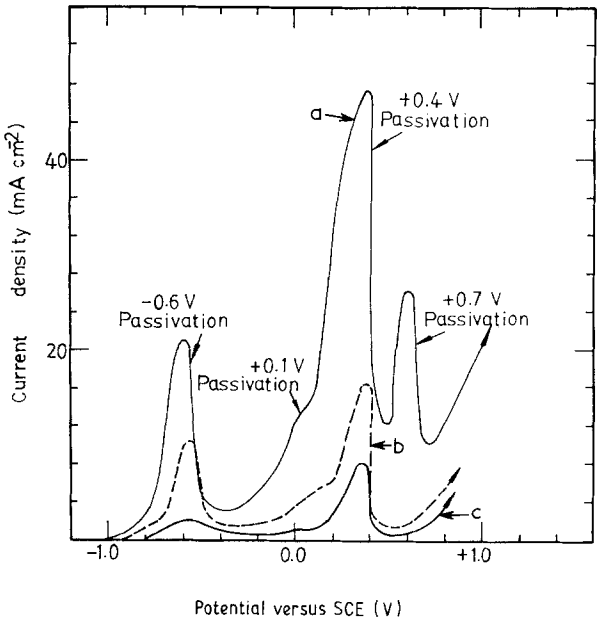

Fig. 1. Anodic polarization curves of gold in concentrated cyanide solutions. (a) 1·0 M KCN; (b) 0·5 M KCN; (c) 0·2 M KCN (scan rate 50 mV s^{-1}).

another passive region occurred at 0·7 V. Above 0·7 V, part of the film diffuses into solution and oxygen evolution starts.

MacArthur [6] thought the passive region at −0·6 V was due to the slowness of Reaction 3. Since it is generally considered that Reaction 2 is the rate-determining step, this explanation seems doubtful. Cathro [5] attributed it to

$$Au + nOH^- \longrightarrow AuO_{n/2} + n/2\,H_2O + ne^- \quad (4)$$

but since most gold oxides are very unstable [11], it also seems unlikely that Reaction 4 should occur at such low potential.

It can be observed from Fig. 2 that the concentration of hydroxyl ions affects strongly the passivation at −0·6 V. Hence it could be the adsorption of hydroxyl ions on the surface which blocks the reaction.

As for the passive region at 0·1 V, MacArthur speculated that it was due to the formation of Au_2O_3. However gold oxide or hydroxide should only occur at higher potential by the theoretical

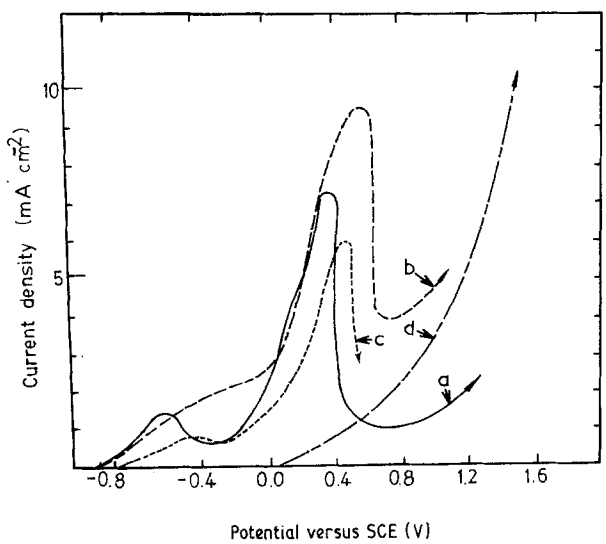

Fig. 2. Effect of pH value on gold passivation. (a) 0·2 M KCN, pH 12·8; (b) 0·2 M KCN + phosphate buffer, pH 8·1; (c) 0·2 M KCN + acetate buffer, pH 5, (d) 0·1 M KOH buffer, pH 5 (scan rate 50 mV s^{-1}).

calculation. It is possible that the passivation is caused by the oxygen evolution which occupies the active sites on the gold surface. Barnartt [12] found that at a pH of 1, the equilibrium potential of Reaction 5 with respect to SCE is + 0·59 V.

$$OH^- \longrightarrow 1/4\,O_2 + 1/2\,H_2O + e^- \quad (5)$$

Hence in cyanide solution, where the pH is about 13 the equilibrium potential will be − 0·12 V. Our own experiment with pure 0·1 M KOH electrolyte (see Fig. 2) shows that oxygen evolution starts at 0·05 V which is very close to 0·1 V. When the solution was saturated with air, however, the *I–E* curve did not change. On the other hand Lebedev [13] found that oxygen (1 atm) had a significant effect on the passivation at this region.

As regards the passivation at 0·4 V, MacArthur [6] and Cathro [5] both attributed it to the formation of Au_2O_3 which blocks the reaction surface. More recently Ogura [14] and Frankenthal [15] claimed the real product should be $Au(OH)_3$. The reaction is

$$2Au + 3H_2O \longrightarrow Au(OH)_3 + 3H^+ + 3e^- \quad (6)$$

The standard potential is + 1·363 V so at pH 13 *E* is + 0·36 V versus SCE which is fairly close to 0·4 V. Consequently the assumption that $Au(OH)_3$ forms and blocks the active site of the gold surface seems to be reasonable at this potential.

The $Au(OH)_3$ formed is non-adhesive and fragments of the film flake off the surface. Current efficiency measurements show that Reaction 1 is still the main reaction. When the KCN concentration reaches 1 M, enough cyanide ions will penetrate the film to maintain the current. Only when the potential is raised to 0·7 V is a thicker film formed which blocks the dissolution reaction completely.

Hence the anodic behaviour of gold in concentrated cyanide solution is similar to that in acidic chloride solution [15, 16]. In the chloride system, Frankenthal [15] maintained that the passive behaviour is the result of the competing adsorption of chloride ions and hydroxyl ions. The adsorption of chloride ions facilitates the dissolution of gold while the adsorption of hydroxyl ions causes passivation. Similar reasoning can be applied to gold in the cyanide system. The adsorption of cyanide facilitates the dissolution of gold while the adsorption of hydroxyl ions causes passivation.

Acknowledgement

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