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DISSOLUTION THEORY OF GOLD IN ALKALINE THIOUREA SOLUTION(Ⅰ) ①

Anodic Behavior on Gold in Alkaline Thiourea Solution Containing Na_2SO_3

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ABSTRACT Anodic polarization behaviors of gold and its associated elements, e.g., silver, copper, nickel and iron, in the alkaline thiourea solution with and without Na_2SO_3 were examined. The results showed gold is hardly dissolved in the solution with Na_2SO_3 because of the passivation of elemental sulfur produced by irreversible decomposition of alkaline thiourea; however, the additive Na_2SO_3 improves the stability of thiourea in alkaline media, greatly increases anodic current of gold and accelerates the selective dissolution of gold in the alkaline thiourea solution, without changing the passivation states of the associated elements of gold. Also the factors affecting the polarization of gold anode were investigated in detail, and it was found that, the Na_2SO_3 obviously decreases polarization potential of gold and the apparent activation energy of gold dissolution, and the controlling step of the dissolution of gold anode in the alkaline thiourea solution is changed from the anode dissolution reaction to the solute diffusion. The mechanism for accelerated dissolution of gold in the alkaline thiourea solution with Na_2SO_3 was considered as electrochemical reduction and catalysis, over the Na_2SO_3 concentration of 0.01 ~ 0.5 mol/L, at the potential of 0.34 ~ 0.44 V.

Key words alkaline thiourea sodium sulfite polarization behavior gold

1 INTRODUCTION

Since thiourea was utilized as the lixiviant of gold early in 1932[1], extracting gold from ore or scrap by acidic thiourea solution has been widely studied all over the world[2,3]. The mechanism for dissolving gold by thiourea was generally considered as that thiourea in acidic media is easy to produce formamidine disulfide, which plays a very important role acting as an oxidant for dissolving gold, and then thiourea as a ligand complexes directly with gold ion[4]. In order to resolve the problem of acidic thiourea consumed excessively in dissolving gold, it was regarded as two important aspects that the initial concentration of thiourea and the mix potential of the solution should be controlled reasonably[5]. Also it was reported[6,7] that sulfur dioxide can prevent thiourea from decomposing irreversibly, and the relationship equation between the dissolution rate of gold and consumption of thiourea was obtained. In addition, some other weak reductants, e.g., H_2S and its salts, $Na_2S_2O_4$, $Na_2S_2O_3$, were used as the additives in accelerating dissolution of gold in the acidic thiourea solution[8].

However, it was considered that formamidine disulfide is an efficient oxidant only at pH less than 1.7, and gold dissolves with thiourea only in acidic media[9]. Generally, gold ore or scrap contains gold, silver, copper, nickel, iron

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and many other elements. Also, these associated elements of gold dissolve easily in the acidic thiourea solution, which results in the excessive consumption of thiourea. In addition, the equipments for extracting gold are easily corroded in acidic media.

Therefore, it has been attempted that gold dissolved in an alkaline thiourea solution, with the aim at resolving the defects on the dissolution of gold in the acidic thiourea solution. But studies on the dissolution of gold and its associated elements in an alkaline thiourea solution were seldom reported till now, because thiourea is very unstable in alkaline media[10]. It was found that the addition of Na_2SO_3 stabilized alkaline thiourea solution in our work. The polarization behaviors of gold anode in the alkaline thiourea solution adding Na_2SO_3 are discussed in this paper.

2 EXPERIMENTAL

The sheets of gold, silver, copper, nickel and iron of purity 99.9 % with an area of 1.0 cm × 1.0 cm were polished by 7 μm abrasive paper, and used as the working electrode. The solutions with various concentrations were prepared by dissolving recrystallized thiourea, sodium sulfite into distilled water. The solution pH was adjusted with H_2SO_4 or NaOH. The electrochemical polarization was performed using a typical three electrode system, consisting of a metal working electrode, a platinum wire as counter electrode, and a saturated calomel electrode as the reference electrode through a Luggin probe with a potentiostat. The volume of the solution used in the experiments was 200 mL and the cell was maintained in a thermostatical water bath to keep constant temperature. Agitation of the solution was accomplished with a magnetic stirrer to ensure stationary diffusion of the solution.

3 RESULTS AND DISCUSSION

3.1 Effect of Na_2SO_3 on polarization of gold anode in alkaline thiourea solution

The Na_2SO_3 enhances the polarization of the gold anode in the alkaline thiourea solution, as is shown in Fig.1.

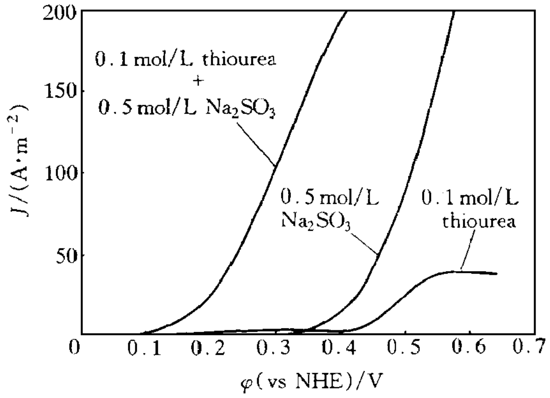

Fig.1 Polarization curves of the gold anode in different solutions at pH 12.5, 323 K and 10 mV/s

It can be seen from Fig.1 that the anodic polarization currents of gold in the potential range of 0.1 ~ 0.34 V approximate to zero in 0.1 mol/L thiourea solution and 0.5 mol/L Na_2SO_3 solution of pH 12.5, respectively. However, the anodic current in the mixed solution of 0.1 mol/L thiourea and 0.5 mol/L Na_2SO_3 solution increases greatly, reaches about 140 A/m^2. This illustrates obviously that there might exist some electrochemical reactions between thiourea and Na_2SO_3, shown in the following reactions:

$$SO_3^{2-} + 2OH^- - 2e = SO_4^{2-} + H_2O \qquad (1)$$

$$\varphi_1 = -0.103 - 0.0591\,pH + 0.0295\lg[SO_4^{2-}] - 0.0295\lg[SO_3^{2-}]$$

$$2CS(NH_2)_2 + 2OH^- - 2e = NH_2(NH)CSSC(NH)NH_2 + 2H_2O \qquad (2)$$

$$\varphi_2 = 0.42 + 0.0295\lg[(CS(N_2H_3))_2] - 0.0591\,pH - 0.0591\lg[CS(NH_2)_2]$$

Reaction (3) is rewritten through the deducting of reaction (1) and reaction (2).

$$SO_3^{2-} + NH_2(NH)CSSC(NH)NH_2 + H_2O \rightleftharpoons SO_4^{2-} + 2CS(NH_2)_2 \qquad (3)$$

According to the equation $\Delta G = -nFE$, the thermodynamic equation corresponding to reaction (3) can be obtained as

$$\Delta G_3 = \Delta G_1 - \Delta G_2 = -2F(-0.523 + 0.0295\lg K) \qquad (4)$$

When reaction (3) is in equilibrium, namely $\Delta G_3 = 0$, its equilibrium constant K is $10^{17.73}$, which indicates clearly that the equilibrium of reaction (3) shifts easily to the positive only based on the reaction thermodynamics.

As a result, the above electrochemical reactions increase greatly the anodic current, also prevent thiourea in alkaline media from further decomposing. This illustrates that the Na_2SO_3 improves obviously the stability of thiourea in alkaline media. As described in our previous work[11], the additive Na_2SO_3 also increases relatively the efficient concentration of thiourea, and enlarges the anodic current of gold in the alkaline thiourea solution.

3.2 Anodic behaviors of gold and its associated elements in alkaline thiourea solution containing Na_2SO_3

The anodic polarizations were investigated for gold, silver, copper, nickel and iron in 0.1 mol/L thiourea solution with and without 0.5 mol/L Na_2SO_3. The results are shown in Fig.2 and Fig.3, respectively.

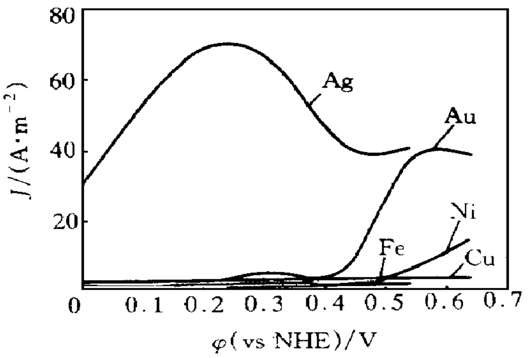

Fig.2 Polarization curves of Au, Ag, Cu, Ni and Fe anodes in 0.1 mol/L thiourea solution at pH 12.5, 323 K and 10 mV/s

The polarization currents of copper, nickel and iron in the alkaline thiourea solution without Na_2SO_3 are almost zero from Fig.2. The polarization curve of silver attends an obvious polarization peak at the potential of 0.24 V, which is the symbol of the passivation. The polarization current of gold is small, also gold is passivated near the potential 0.54 V. The gold electrode after polarization was examined for the composition of the product on gold surface by X-650 micrograph, which contains 3.98% (mass fraction) elemental sulfur. This turns out that gold in the alkaline thiourea solution is easily passivated by the elemental sulfur, because of the irreversible decomposition of thiourea in alkaline media.

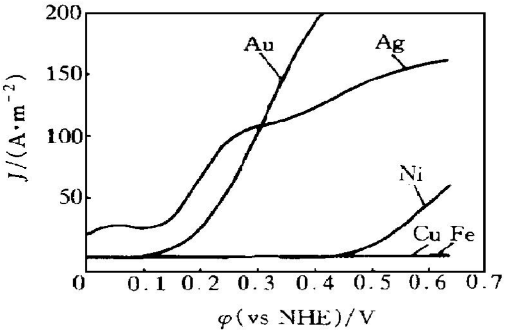

Fig.3 Polarization curves of Au, Ag, Cu, Ni and Fe anodes in 0.1 mol/L thiourea solution containing 0.5 mol/L Na_2SO_3 at pH 12.5, 323 K and 10 mV/s

From Fig.3, the anodic current of silver is large at the beginning of the polarization in the alkaline solution with Na_2SO_3, then is weakened gradually because of passivation. Like that without Na_2SO_3, the polarization currents of copper, nickel and iron approximate to zero. And the anodic current of gold enlarges greatly at a potential larger than 0.3 V, also is larger than that of other metals, which shows that gold is dissoluble selectively in the alkaline thiourea solution containing Na_2SO_3.

Therefore, adding Na_2SO_3 into the alkaline thiourea solution of pH 12.5 enhances greatly the anodic polarization current of gold, but does not change the passivation states of its associated elements.

3.3 Factors affecting polarization of gold in alkaline thiourea solution containing Na_2SO_3

3.3.1 Concentration of thiourea

The effect of thiourea concentration on polarization of gold anode in thiourea solution of pH

12.5 with 0.5 mol/L Na_2SO_3 at 323 K is presented by Fig.4.

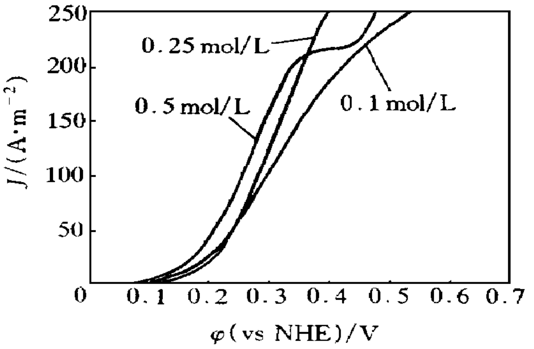

Fig.4 Effect of variable thiourea concentration on polarization of gold anode in thiourea solution with 0.5 mol/L Na_2SO_3 at pH 12.5, 323 K and 10 mV/s

From Fig.4, the anodic polarization current of gold increases with thiourea concentration at the beginning, and then polarization curve of gold in 0.5 mol/L thiourea solution attends a platform at the potential 0.34 V because of passivation. Increasing the concentration of thiourea makes the concentration of formamidine disulfide higher, which accelerates the dissolution of gold. However, excessively high concentration of thiourea results in branch reaction of formamidine disulfide to produce element sulfur passivating gold surface and reduces polarization current of gold in the alkaline thiourea solution. The proper thiourea concentration for dissolving gold efficiently was regarded as 0.1 mol/L.

3.3.2 Concentration of Na_2SO_3

Fig.5 shows the effect of Na_2SO_3 concentration on anodic polarization of gold in 0.1 mol/L thiourea solution of pH 12.5.

It can be seen from Fig.5 that the valid concentration of thiourea increases with the concentration of Na_2SO_3, and the dissolution trend of gold enhances. But excessively high concentration of Na_2SO_3 decreases the mix potential of the solution, which causes the anodic current of gold to reduce.

According to the Vant't Hoff's method[12], $J = K \cdot c^n$, the reaction order can be calculated from the Eqn.(5)

$$\lg J = K' + n \cdot \lg c(Na_2SO_3) \qquad (5)$$

It can be drawn from Fig.6 that the reaction that the Na_2SO_3 participates in anodic dissolution of gold in the alkaline thiourea solution is of the first order at the Na_2SO_3 concentration of 0.1 ~ 0.75 mol/L and the potential of 0.24 V. When the potential is 0.34 ~ 0.44 V, the reaction order is 1 at the Na_2SO_3 concentration of 0.01 ~ 0.5 mol/L. And that is 1 at the potential of 0.14 V, the Na_2SO_3 concentration of 0.25 ~ 0.75 mol/L. Therefore, the Na_2SO_3 plays the

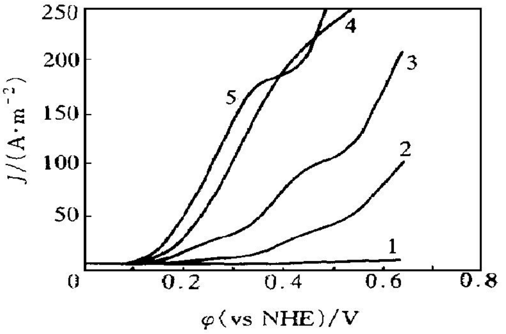

Fig.5 Effect of Na_2SO_3 concentration on polarization of gold anode in 0.1 mol/L thiourea solution at pH12.5, 323K and 10 mV/s

1 — $c(Na_2SO_3) = 0.01$ mol/L;
2 — $c(Na_2SO_3) = 0.1$ mol/L;
3 — $c(Na_2SO_3) = 0.25$ mol/L;
4 — $c(Na_2SO_3) = 0.5$ mol/L;
5 — $c(Na_2SO_3) = 0.75$ mol/L

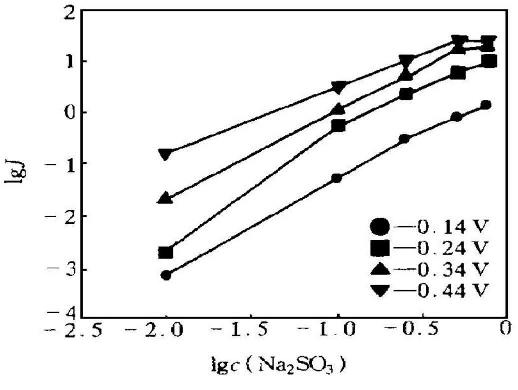

Fig.6 Relationship between lg$J$ and lg$c$(Na_2SO_3)

role of electrochemical reduction and catalysis under the described conditions.

3.3.3 Temperature

The effects of temperature on the polarization of gold anode in the alkaline thiourea solution with and without Na_2SO_3 at pH 12.5 are shown in Fig.7 and Fig.8, respectively.

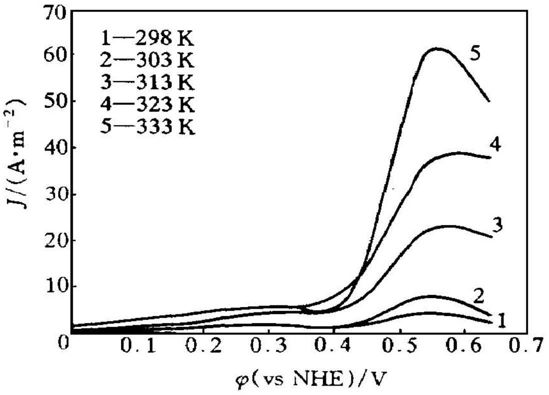

Fig.7 Effect of temperatures on polarization of gold anode in 0.1 mol/L thiourea solution at pH 12.5 and 10 mV/s

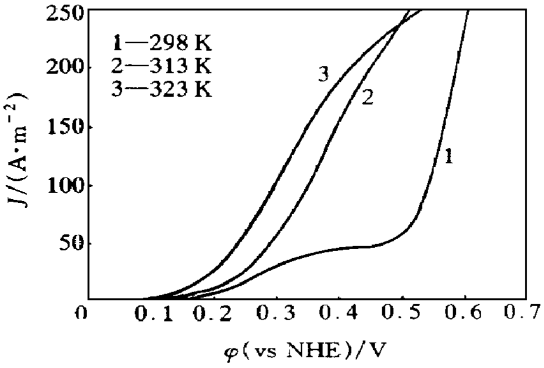

Fig.8 Effect of temperatures on polarization of gold anode in 0.1 mol/L thiourea solution containing 0.5 mol/L Na_2SO_3 at pH 12.5 and 10 mV/s

It can be seen from Fig.7 that the anodic current of gold in 0.1 mol/L thiourea solution without Na_2SO_3 is small. However, an obvious peak attends for each polarization curve at the potential of about 0.54 V. This shows that dissolution trend of gold increases slowly with temperature at the potential less than 0.54 V, and decreases obviously at the potential more than 0.54 V, because of the passivation of elemental sulfur produced by the decomposition of thiourea in alkaline media, as in the former description.

It was assumed that the polarization current of gold in the alkaline thiourea solution represents the dissolution rate of gold. According to the Arrhenius formula, $\ln J = k - E/RT$ (where, J is current density representing the dissolution rate of gold, k is reaction rate constant of gold dissolution, E is apparent activation energy of gold dissolution), the relationship between $\ln J$ and $1/T$ can be obtained at the potential of 0.24 V and 0.54 V. The relationship is complicated at 0.24 V, which indicates that the polarization current may represent the adsorption of thiourea on the surface of gold. And the relationship at 0.54 V is consistent with a linear eqn., $y = -6.7 \times 10^{-3} x + 21.9$, in which the apparent activation energy of gold dissolution was calculated to be 55.6 kJ/mol. Thus, it was concluded that the process for dissolving gold at the potential of 0.54 V is governed by the dissolution reaction step of gold anode in the alkaline thiourea solution without Na_2SO_3. Also, the dissolution trend of gold at 323 K is 5.7 times more than that at 298 K.

Therefore, temperature affects the dissolution of gold anode, but the potential is the critical factor affecting the dissolution of gold anode in the alkaline thiourea solution without Na_2SO_3. Actually, gold is difficult to be dissolved in the alkaline thiourea solution, because of little polarization at the potential lower than 0.54 V and the coverage of elemental sulfur produced in the decomposition of thiourea in alkaline media at the potential higher than 0.54 V.

Fig.8 shows that the polarization current of gold in the alkaline thiourea solution in the presence of Na_2SO_3 increases obviously with elevating the temperature at the potential below 0.5 V. However, with shifting the potential to the positive, the polarization curves of gold at different temperatures attend intersections, which indicates that excessively high temperature over 323 K causes the slight decomposition of thiourea in alkaline media at the potential over 0.5 V. The temperature has the remarkable influences on the polarization of gold in the alkaline thiourea solution with Na_2SO_3.

Similarly, according to the Arrhenius formula, $\ln J = k - E/RT$, the relationship of $\ln J$ at 0.24 V versus $1/T$ is a linear equation, $y = -4.9 \times 10^3 x + 16.8$. Based on this, the apparent activation energy of the dissolution of gold in the alkaline thiourea solution containing 0.5 mol/L Na_2SO_3 was calculated to be 40.7 kJ/mol, which is much smaller than that of without Na_2SO_3. However, when the potential is 0.54 V, the relationship between $\ln J$ versus $1/T$ is not linear. Gold is passivated by sulfur because of irreversible decomposition of alkaline thiourea at the higher potential. This turns out that adding Na_2SO_3 into the alkaline thiourea solution reduces obviously anodic polarization potential of gold, decreases the reaction activation energy of gold dissolution. Also the additive Na_2SO_3 changes the controlling step of the process for dissolving gold in the alkaline thiourea solution from the dissolution reaction of gold anode to the solute diffusion.

3.3.4 Scanning rate

Fig.9 shows the effect of scanning rate on polarization of gold anode in the thiourea solution containing Na_2SO_3 at pH 12.5. From Fig.9, it can be seen that the polarization current of gold increases with reducing scanning rate at the potential below 0.38 V. Small scanning rate causes electrochemical reaction time between Na_2SO_3 and thiourea to extend and the valid concentration of thiourea to enhance. Thus, the anodic current of gold increases. However, the polarization curves at the scanning rate of 10 mV/s and 100 mV/s attend by intersection at 0.38 V and 0.25 V respectively. High polarization potential over 0.38 V makes easily thiourea decompose. The anodic current of gold becomes smaller at 10 mV/s than that at 100 mV/s, because of the passivation caused by longer-time polarization of gold in the alkaline thiourea solution. Subsequently, the polarization potential has significant influences on the dissolution of gold in the alkaline thiourea solution with Na_2SO_3.

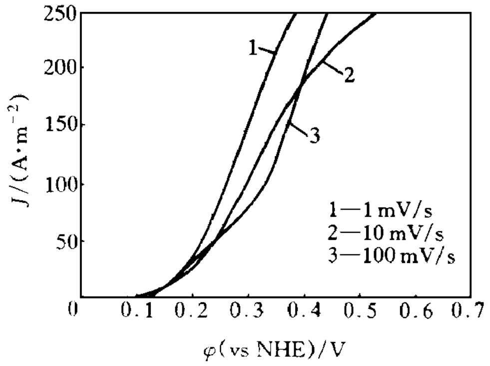

Fig.9 Effect of scanning rate on polarization of gold anode in 0.1 mol/L thiourea solution containing Na_2SO_3 at pH 12.5 and 323 K

4 CONCLUSIONS

Gold is hardly dissolved in the alkaline thiourea solution with Na_2SO_3 because of little polarization or the passivation of elemental sulfur. However, adding of Na_2SO_3 into the alkaline thiourea solution makes selective dissolution of gold conduct easily. The additive Na_2SO_3 enhances greatly anodic polarization current of gold and prevents thiourea in alkaline media from decomposing irreversibly, but does not change the passivation states of its associated elements in the alkaline thiourea solution of pH 12.5. It was concluded that the reaction of Na_2SO_3 in the dissolution of gold anode in the thiourea solution is of the first order, and the Na_2SO_3 plays the role of electrochemical reduction-catalysis under the studied conditions. And the Na_2SO_3 decreases the dissolution apparent activation energy of gold in the alkaline thiourea solution, but changes the controlling step of the process for dissolving gold in the alkaline thiourea solution from the dissolution reaction of gold anode to the solute diffusion as well. In addition, the polarization potential has significant influences on the dissolution of gold in the alkaline thiourea solution with Na_2SO_3.

The present work is a systematic study on the dissolution of gold in the alkaline thiourea solution. The current research provided a theoretical base for the selective extraction of gold efficiently and economically from the scrap by the alkaline thiourea solution.

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