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

——Electrochemical Study on Au-Fe Mix Anode in Alkaline Thiourea Solution Containing Na_2SO_3

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ABSTRACT Anodic polarization behavior of Au-Fe mix electrode has been examined in the thiourea solution containing Na_2SO_3. It was shown that the polarization characteristics of gold is incarnated in the alkaline thiourea solution and the polarization characteristics of iron is reflected in the acidic thiourea solution. Also iron decreases the apparent activation energy of gold dissolution and accelerates the dissolution of gold in the alkaline thiourea solution containing Na_2SO_3 because of galvanic electrode couple effect between gold and iron. The factors affecting selective dissolution of gold of Au-Fe mix anode in the thiourea solution containing Na_2SO_3 were also investigated by electrolysis, and the optimum condition was obtained. The dissolved mass of gold with the exposed area of 1.0 cm^2 reached 350 g/m^3 within 30 min, and that of iron was zero, in 0.1 mol/L thiourea solution containing 0.5 mol/L Na_2SO_3, at potential 0.34 V, pH 12.5 and temperature 323 K.

Key words alkaline thiourea sodium sulfite mix anode of gold and iron

1 INTRODUCTION

Many studies on the extraction of gold from ore or scrap with thiourea were reported[1-3], but all those were limited only in acidic media, where thiourea was consumed excessively because some associated elements of gold, e.g., silver, nickel, copper and the others, were dissolved easily, and the demand for apparatus was high in acidic media[4-5]. Thus, the extraction of gold from ore or scrap, especially from the scrap, by an alkaline thiourea solution has been attempted. Due to unstability of thiourea in alkaline media[6-7], the dissolution of gold in the alkaline thiourea solution was seldom reported. However, it was found that the addition of Na_2SO_3 into alkaline thiourea solution prevented thiourea from irreversible decomposition and accelerated the dissolution of gold in our previous work[8]. The polarization behaviors of the single anode of gold and iron in the alkaline thiourea solution containing Na_2SO_3 were introduced respectively in detail in the previous paper[9], which illustrated that only gold anode dissolved in the alkaline solution, other accompanied elements, e.g., iron and copper hardly dissolved.

In fact, the relationship of gold and its accompanied elements in the raw material is not isolate. Therefore, it is of importance for electrochemical aspects of the mix anode of gold and its associated elements, e.g., iron, to be studied in order to carry out selective dissolution of gold. Following the study on the anodic behavior of gold in the alkaline thiourea solution containing Na_2SO_3, a continuous discussion on the electrochemical behavior of the mix anode of gold

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and iron in the alkaline thiourea solution are further conducted in this paper.

2 EXPERIMENTAL

Experimental procedures, including the preparation of specimens and solutions were described in the previous paper, except that the working electrode in electrochemical polarization was linked by using gold electrode and iron electrode in a parallel manner, and the surface of each electrode was faced the Luggin probe of the SCE reference electrode. The polarization curves for the mix anode were measured in the thiourea solution with or without Na_2SO_3, at pH 1.4 or 12.5 and a the scanning rate of 10 mV/s. The electrolytic conditions were controlled in the solution of pH 12.5 with different concentrations of thiourea and Na_2SO_3, at potential 0.24 ~ 0.64 V and temperature 298 ~ 343 K.

During the electrolysis, 10^{-5} m^3 aliquots were withdrawn from the reactor and diluted in a 10^{-4} m^3 container every 5 min to analyze gold ion and iron ion concentrations by atomic absorption spectroscopy.

3 RESULTS AND DISCUSSION

3.1 Factors Affecting the Polarization of Au-Fe Mix Anode

3.1.1 pH value

The effects of pH value on polarization of Au-Fe mix anode in the thiourea solution with or without Na_2SO_3 are shown in Fig.1, Fig.2 and Fig.3, respectively.

From Fig.1 ~ Fig.3, in the thiourea solution with or without Na_2SO_3, the polarization characteristics of gold is incarnated in alkaline media, the polarization characteristics of iron is reflected in acidic media. The polarization curve of Au-Fe mix anode in 0.1 mol/L thiourea solution containing 0.5 mol/L Na_2SO_3 of pH 12.5 shifts negatively at potential, compared with that in the thiourea solution without Na_2SO_3. This illustrates that the additive Na_2SO_3 enlarges the polarization current of gold of Au-Fe mix anode in the alkaline thiourea solution, as the result in the single gold anode. Therefore, the gold of Au-Fe mix anode is dissoluble selectively in the alkaline thiourea solution containing Na_2SO_3.

3.1.2 Solution composition

The composition of the solution containing thiourea and Na_2SO_3 of pH 12.5 has a different effect on the polarization of Au-Fe mix anode,

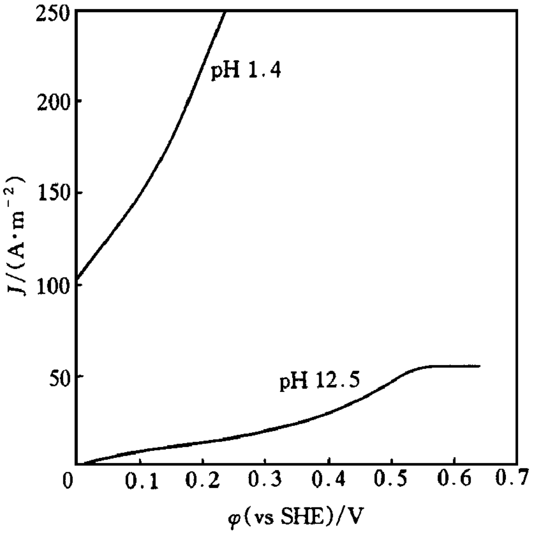

Fig.1 Effect of pH on polarization of Au-Fe mix anode in 0.1 mol/L thiourea solution at 323 K and 10 mV/s

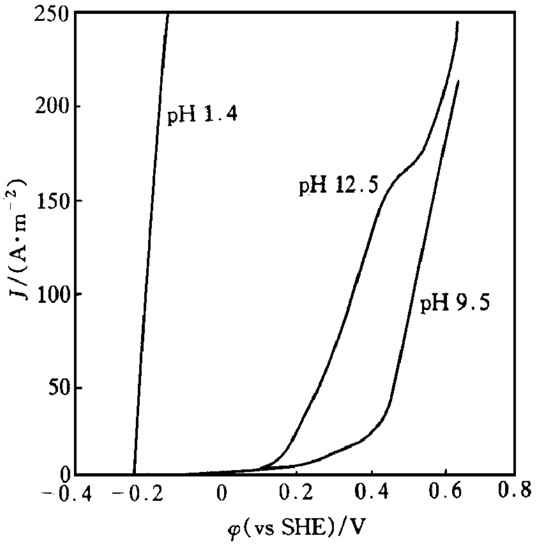

Fig.2 Effect of pH on polarization of Au-Fe mix anode in 0.1 mol/L thiourea solution containing 0.5 mol/L Na_2SO_3 at 323 K and 10 mV/s

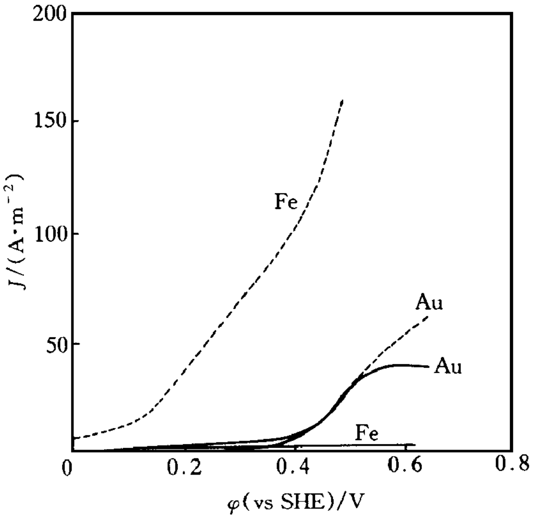

Fig.3 Anodic polarization curves of gold, iron in 0.1 mol/L thiourea solution with different pH at 323 K and 10 mV/s
Dotted line —pH 1.4; Solid line —pH 12.5

as shown in Fig.4.

The polarization current of the mix anode decreases with increasing thiourea concentration, but increases with increasing Na_2SO_3 concentration. This further shows that excessively high concentration of thiourea causes easily the mix anode to be passivated, and the Na_2SO_3 prevents efficiently the thiourea in alkaline media from irreversible decomposition. The dissolution trend of Au-Fe mix anode is larger in 0.1 mol/L thiourea solution containing 0.5 mol/L Na_2SO_3.

3.1.3 Temperature

Fig.5 shows the effect of temperature on the polarization of Au-Fe mix anode in the alkaline thiourea solution containing Na_2SO_3.

It can be seen obviously from Fig.5 that the polarization curves move negatively at potential with enhancing temperature, and the polarization current of Au-Fe mix anode increases.

According to the Arrhenius formula, $\ln J = K - \varphi/RT$, the apparent activation energy of the gold dissolution of Au-Fe mix anode in 0.1 mol/L thiourea solution containing 0.5 mol/L Na_2SO_3 of pH 12.5, at potentials of 0.24 V, 0.34 V, 0.44 V and 0.54 V, can be calculated to be 32.2 kJ/mol, 30.3 kJ/mol, 24.6 kJ/mol and 21.7 kJ/mol respectively. Namely, the increase in anodic potential results in the activation energy of gold dissolution reaction to reduce obviously, from which it is known that the process

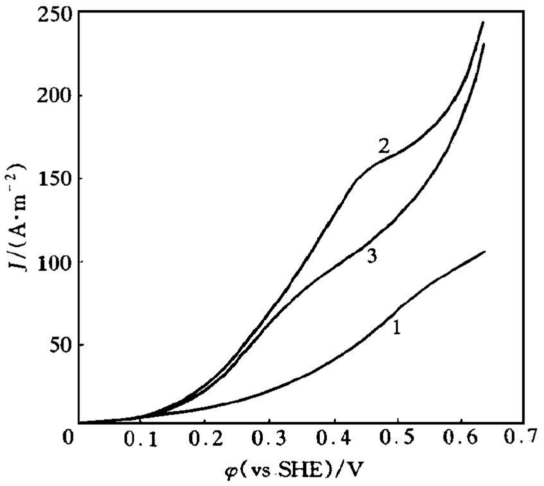

Fig.4 Polarization curves of Au-Fe mix anode in the solution containing thiourea and Na_2SO_3 at pH 12.5, 323 K and 10 mV/s
1 —0.1 mol/L thiourea and 0.25 mol/L Na_2SO_3;
2 —0.1 mol/L thiourea and 0.5 mol/L Na_2SO_3;
3 —0.25 mol/L thiourea and 0.5 mol/L Na_2SO_3

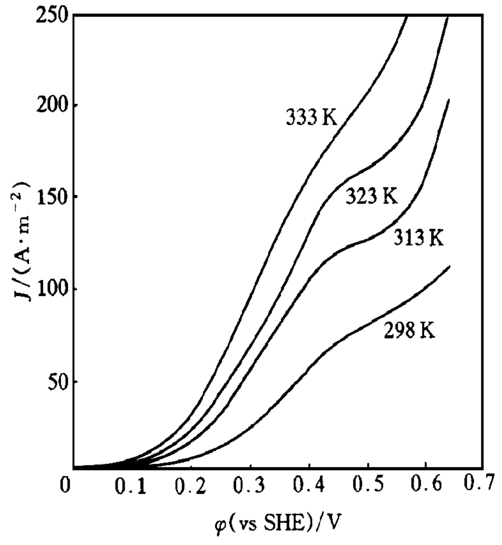

Fig.5 Effect of temperature on polarization of Au-Fe mix anode in 0.1 mol/L thiourea solution containing 0.5 mol/L Na_2SO_3 at pH 12.5 and 10 mV/s

for dissolving gold of the mix anode in the alkaline thiourea solution containing Na_2SO_3 is governed by the solute diffusion. The formation trend of formamidine disulfide increases with enhancing the potential and the solute diffusion speeds up, so the dissolution of gold of the mix anode accelerates. Thus, the apparent activation energy of gold dissolution of Au-Fe mix anode in the thiourea solution containing Na_2SO_3 at the potential of 0.24 V (32.2 kJ/mol) is smaller than that of single gold anode (40.7 kJ/mol[10]), which illustrates that the iron of Au-Fe mix anode promotes the dissolution of gold in the alkaline thiourea solution because of the galvanic electrode couple effect between gold and iron.

3.2 Dissolution of Au-Fe Mix Anode in Alkaline Thiourea Solution Containing Na_2SO_3 by Electrolysis

3.2.1 Effect of solution composition

The dissolution variation of Au-Fe mix anode in the solution containing different composition of thiourea and Na_2SO_3 is represented by Fig.6.

Fig.6 shows that the iron of Au-Fe mix anode does not dissolve in 0.1 mol/L thiourea solution containing 0.5 mol/L Na_2SO_3 of pH 12.5, where the gold of Au-Fe mix anode dissolves steadily. The dissolved mass of gold with the area 10^{-4} m^2 of Au-Fe mix anode reached 350 g/m^3 within 30 min, which is more than that of single gold anode (242.3 g/m^3)[10]. This further illustrates that iron accelerates the dissolution of gold of the Au-Fe mix anode in the alkaline thiourea solution containing Na_2SO_3 because of the galvanic electrode couple effect between gold and iron.

3.2.2 Effect of temperature

When Au-Fe mix anode was electrolyzed in 0.1 mol/L alkaline thiourea solution containing 0.5 mol/L Na_2SO_3, iron was not dissoluble, and the temperature had a remarkable effect on the dissolution of gold, as shown in Fig.7.

From Fig.7, the elevated temperature accelerates the dissolution of gold of Au-Fe mix anode in the alkaline thiourea solution. However, excessively high temperature over 333 K results in thiourea to decompose irreversibly. The prod-

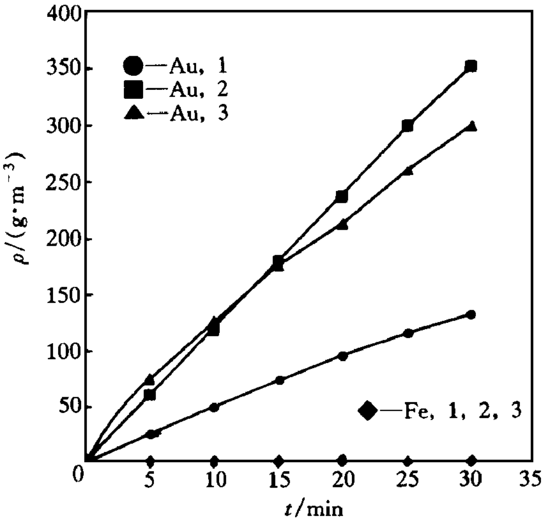

Fig.6 Variation of Au-Fe anode dissolution in the solution containing thiourea and Na_2SO_3 by electrolysis at 0.34 V, pH 12.5 and 323 K

1 —0.1 mol/L thiourea and 0.25 mol/L Na_2SO_3;
2 —0.1 mol/L thiourea and 0.5 mol/L Na_2SO_3;
3 —0.25 mol/L thiourea and 0.5 mol/L Na_2SO_3

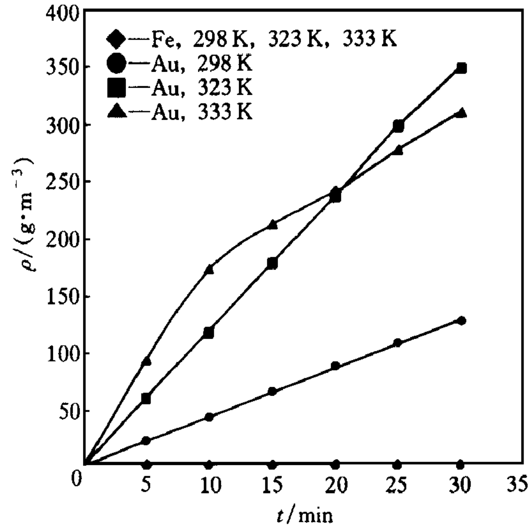

Fig.7 Variation with temperature of Au-Fe mix anode dissolution in 0.1 mol/L thiourea solution containing 0.5 mol/L Na_2SO_3 by electrolysis at 0.34 V and pH 12.5

ucts of thiourea irreversible decomposition, sulfur, cover the surface of the gold anode and prevent the dissolution of gold. This can be expained well by the polarization behavior of gold anode in the alkaline thiourea solution containing Na_2SO_3, which was reported in the previous paper. The temperature 323 K is the optimum for fast dissolution of gold of Au-Fe mix anode.

3.2.3 Effect of electrolytic potential

The effect of the electrolytic potential on the dissolution of Au-Fe mix anode in the alkaline thiourea solution containing Na_2SO_3 is depicted in Fig.8.

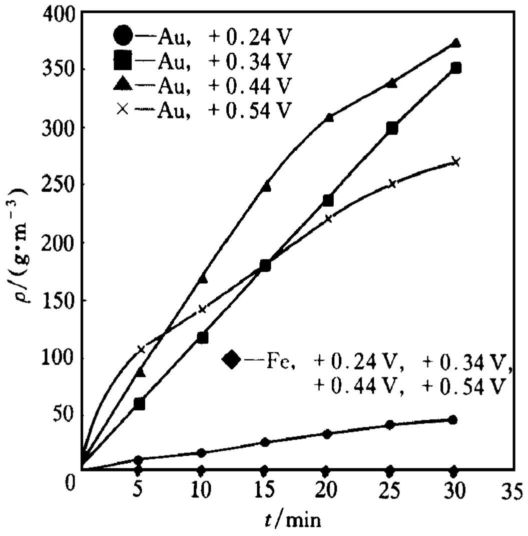

Fig.8 Variation with electrolytic potential of Au-Fe anode dissolution in 0.1 mol/L thiourea solution containing 0.5 mol/L Na_2SO_3 at 323 K and pH 12.5

In the same way, only gold of the mix anode is dissoluble in 0.1 mol/L thiouera solution containing 0.5 mol/L Na_2SO_3 of pH 12.5 at 323 K, where iron does not dissolve because of passivation. The dissolution of gold in 0.1 mol/L alkaline thiouera solution containing 0.5 mol/L Na_2SO_3 speeds up with the rise of the electrolytic potential at the beginning of electrolysis. But the potential over 0.54 V causes the dissolution rate of gold to reduce.

The current efficiencies of the gold electrolysis within 30 min were calculated at the electrolytic potentials of 0.24 V, 0.34 V, 0.44 V and 0.44 V being 49.9%, 98.0%, 84.2% and 51.1% respectively. This illustrates that the potential 0.34 V is the optimum for obtaining the fast dissolution of gold.

In addition, the dissolution of gold in the thiourea solution can be expressed simply by the following electrode reactions[11-12]:

$$[Au(CS(NH_2)_2)_2]^+ + e = Au + 2CS(NH_2)_2 \qquad \varphi^{\ominus} = 0.38\ V \qquad (1)$$

$$NH_2(NH)CSSC(NH)NH_2 + 2H^+ + 2e = 2CS(NH_2)_2 \qquad \varphi^{\ominus} = 0.42\ V \qquad (2)$$

At the low potential it is difficult to form sufficient formamidine disulfide as an oxidant for dissolving gold, and high potential over 0.42 V makes formamidine disulfide decompose to form $CNNH_2$ and elemental sulfur which passivates the surface of gold and decreases the dissolution rate of gold.

3.2.4 Effect of pH value

Fig.9 shows the effect of pH on the dissolution of Au-Fe mix anode in the alkaline thiourea solution containing Na_2SO_3. Iron dissolves steadily in the acidic thiourea solution, in which gold dissolves slowly. And iron is indissoluble in

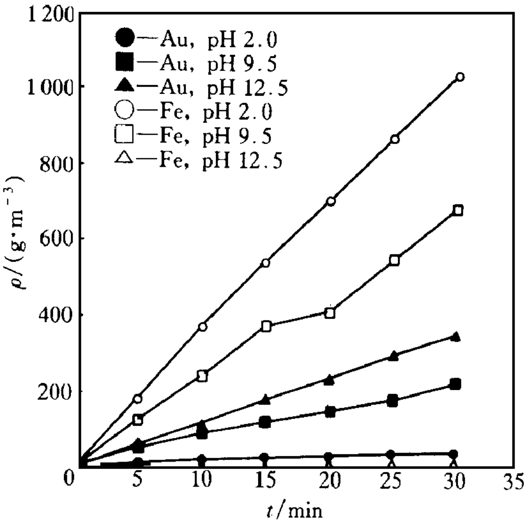

Fig.9 Variation with pH of Au-Fe mix anode dissolution in 0.1 mol/L thiourea containing 0.5 mol/L Na_2SO_3 by electrolysis at 0.34 V and 323 K

the thiourea solution of pH 9.5 or 12.5, in which the dissolution rate of gold is larger than that in the acidic solution. Also the dissolution rate of gold of Au-Fe mix anode in the thiourea solution containing Na_2SO_3 increases with enhancing pH value.

4 CONCLUSIONS

(1) The polarization characteristics of gold of Au-Fe mix anode is incarnated in the alkaline thiourea solution, the polarization characteristics of iron is reflected in the acidic solution.

(2) The apparent dissolution activation energy of gold of Au-Fe mix anode decreases with enhancing anodic potential, and iron of Au-Fe mix anode promotes the dissolution of gold in the alkaline thiourea solution containing Na_2SO_3 because of the galvanic electrode couple effect between gold and iron.

(3) Iron of Au-Fe mix anode dissolves fast and steadily in the acidic thiourea solution, is indissoluble in the solution of pH 9.5 or 12.5, in which the dissolution rate of gold of Au-Fe mix anode is larger than that in the acidic solution. Also the dissolution rate of gold in the thiourea solution containing Na_2SO_3 increases with enhancing pH value.

(4) The optimum condition for dissolving selectively gold of Au-Fe mix anode was obtained, i.e. 0.1 mol/L thiourea solution containing 0.5 mol/L Na_2SO_3 of pH 12.5, at the potential of 0.34 V and the temperature of 323 K.

(5) The present work is the continuous study on the dissolution of gold in the alkaline thiourea solution. The research results provided a theoretical base and technological parameter for the selective extraction of gold, especially from the scrap by electrolysis.

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