Research Article

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An electrochemical method to investigate the effects of compound composition on gold dissolution in thiosulfate solution

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Abstract: The electrochemical behavior of gold dissolution in the $\text{Cu}^{2+}\text{-NH}_3\text{-S}_2\text{O}_3^{2-}\text{-EDTA}$ solution has been investigated in detail by deriving and analyzing the Tafel polarization curve, as this method is currently widely implemented for the electrode corrosion analysis. The dissolution rate of gold in $\text{Cu}^{2+}\text{-NH}_3\text{-S}_2\text{O}_3^{2-}\text{-EDTA}$ solution was determined based on the Tafel polarization curves, and the effects of various compound compositions in a $\text{Cu}^{2+}\text{-NH}_3\text{-S}_2\text{O}_3^{2-}\text{-EDTA}$ mixture on the corrosion potential and corrosion current density were analyzed. The results showed that the corrosion potential and polarization resistance decreased, whereas the corrosion current density increased for certain concentrations of $\text{S}_2\text{O}_3^{2-}\text{-NH}_3\text{-Cu}^{2+}$ and EDTA, indicating that the dissolution rate of gold had changed. The reason for promoting the dissolution of gold is also discussed.

Keywords: thiosulfate, anodic dissolution, Tafel polarization curve, electrochemical behavior

1 Introduction

Gold extraction has always been a highly polluting and toxic process due to the use of cyanide [1]. The leaching of gold in the thiosulfate solution is a promising noncyanide gold leaching method that is widely implemented [2–5]. In this method, the gold leaching rate can be optimized at room temperature when the thiosulfate, ammonia, and copper ions coexist in the

gold leaching agent [6–8]. The leaching of gold in a copper–ammonia–thiosulfate system over a prolonged period was studied in detail [9–13]. A number of studies have shown faster gold leaching kinetics with thiosulfate in the presence of ammonia and copper(II) in the form of a cupric tetraamine complex [14,15]. However, because the chemical reactions of a gold leaching process become complex when ammonia and copper ions coexist in the thiosulfate solution [16–18], the mechanism of gold leaching in the $\text{Cu}^{2+}\text{-NH}_3\text{-S}_2\text{O}_3^{2-}\text{-EDTA}$ solution has yet to be fully elucidated. The electrochemical catalytic mechanism of gold leaching in the ammoniacal thiosulfate solution has been proposed [19–21] based on the results of electrochemical studies on the anodic and cathodic reactions in the gold leaching process. The electrochemical studies revealed the dependence of the electroleaching rate in thiosulfate–ammonia solutions on different processes controlled by the anodic potential [22,23]. The cathodic and anodic processes were evaluated in a potential window where the reduction of gold and copper and the oxidation of thiosulfate and Cu(I) species occur [23]. The reaction of $\text{Cu(NH}_3)_4^{2+}$ transformation into $\text{Cu(S}_2\text{O}_3)_3^{5-}$ plays the dominant role in the cathode reaction, which is a rapid process [24–28]. Conversely, the oxidation reaction of gold is inhibited in the anodic reaction. Currently, some views show that the gold dissolution process may be interfered due to the large amount of copper present in the solutions [29,30]. Thus, the present study aims to clarify the effects of compound composition on gold dissolution in the thiosulfate solution.

The dissolution of gold is an anodic corrosion process. The electron transfer rate is proportional to the rate of gold dissolution due to the electron transfer in the process of gold dissolution; thus, the dissolution rate of gold can be described by the corrosion current density (J_{corr}). It has been reported that the anodic dissolution of gold can be controlled by an electrochemical reaction under certain conditions [31,32]. In addition, previous researchers have studied the electrochemical behavior of

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gold dissolution in the Cu^{2+} – NH_3 – $\text{S}_2\text{O}_3^{2-}$ –EDTA solution by employing the standard electrochemical method and by subsequently deriving and analyzing the steady-state polarization curves and the constant-current step curves [21–23]. However, although the Tafel polarization curve is an important tool for the analysis of electrode corrosion, there are few reports on the dissolution mechanism of gold in Cu^{2+} – NH_3 – $\text{S}_2\text{O}_3^{2-}$ –EDTA solutions.

Because the electron transfer rate is proportional to the gold dissolution rate in the oxidation–dissolution process of gold, the dissolution rate of gold can be characterized by the corrosion current density. The corrosion rate can be determined by the Tafel polarization curve [33–36]; more specifically, the corrosion potential (E_{corr}) and its corresponding corrosion current can be obtained based on the anodic polarization curve and cathodic polarization curve of the Tafel curve, which intersect at a single point. According to the Tafel polarization curves, the values of J_{corr} , E_{corr} , and polarization resistance (R_p) can be obtained by using ZSimpWin software to perform fitting.

In this study, the dissolution rate of gold in a Cu^{2+} – NH_3 – $\text{S}_2\text{O}_3^{2-}$ –EDTA mixture was determined by deriving and analyzing the Tafel polarization curves, and the effects of modifying the composition of a Cu^{2+} – NH_3 – $\text{S}_2\text{O}_3^{2-}$ –EDTA mixture on the dissolution behavior of gold were analyzed. The mechanisms for promoting gold dissolution and the main control steps of the gold leaching reaction are also discussed.

2 Experimental

This study was performed by employing a three-electrode scheme in an electrochemical system. Furthermore, the electrochemical behavior of gold dissolution in a mixture was investigated by using a CHI600E electrochemical workstation (Shanghai Huachen, China). In this study, Pt wire with a surface area of 1.0 cm^2 , Ag/AgCl (in saturated KCl), and pure gold with a surface area 1.0 cm^2 were used as the counter electrode, reference electrode, and working electrode, respectively, to form a three-electrode system [37].

The polarization curves were obtained at a scan rate of 10 mV s^{-1} . The potential range used in this study was +1500 to –1500 mV Ag/AgCl. The surface of the working electrode was mechanically polished (using alumina powder) and rinsed off with distilled water.

The reagents used were as follows: pure gold (Au, 99.99%; Luoyang, China), copper(II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$;

Panreac), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$; Tianjin, China), ammonium hydroxide ($\text{NH}_3 \cdot \text{OH}$; Guangzhou, China), sodium hydroxide (NaOH; Guangzhou, China), and EDTA ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2\text{Na}_2 \cdot 2\text{H}_2\text{O}$; Tianjin, China). The reagents used in the experiment are all analytical reagents, and the experimental temperature was maintained at 25°C by implementing water bath immersion.

According to the literature [21–23], the concentration of $\text{S}_2\text{O}_3^{2-}$ was increased from 0.01 to 0.9 mol/L in the Cu^{2+} – NH_3 – $\text{S}_2\text{O}_3^{2-}$ –EDTA solution. The concentration of NH_3 was 0–0.8 mol/L, and the concentration of Cu^{2+} was 0–0.8 mol/L. The pH of solution was determined, when the mixed solution was determined.

3 Results and discussion

3.1 Effect of $\text{S}_2\text{O}_3^{2-}$ concentration

The Tafel polarization curves for gold dissolution are shown in Figure 1 for varying $\text{S}_2\text{O}_3^{2-}$ concentrations in the absence of NH_3 and Cu^{2+} ; the corrosion rate was measured by fitting the polarization curve. Figure 2 shows that the corrosion current density of the gold dissolution process consistently increased with increasing $\text{S}_2\text{O}_3^{2-}$ concentration, indicating that the composition of $\text{S}_2\text{O}_3^{2-}$ contributes to the improvement of the corrosion rate of gold. Moreover, when the concentration of $\text{S}_2\text{O}_3^{2-}$ was increased from 0.01 to 0.1 mol/L, the corrosion current density also increased from 0.540×10^{-6} to $1.714 \times 10^{-6} \text{ A/cm}^2$. However, as the concentration of

Figure 1: Tafel plots of gold dissolution at different $\text{S}_2\text{O}_3^{2-}$ concentrations.

Figure 2: Electrochemical parameters of gold dissolution at different $S_2O_3^{2-}$ concentrations: (a) corrosion current density of gold dissolution; (b) corrosion potential of gold dissolution; and (c) polarization resistance of gold dissolution.

$S_2O_3^{2-}$ continued to increase, the amplitude of J_{corr} was observed to progressively decrease.

Increasing the $S_2O_3^{2-}$ concentration was also found to correspond to a decrease of the corrosion potential from -0.119 to 0.208 V, resulting in a reduced E_{corr} value and increased corrosion. In addition, increasing the $S_2O_3^{2-}$ concentration can reduce the corrosion potential of gold and thus facilitate dissolution. These findings indicate that the composition of $S_2O_3^{2-}$, as it enhances the ability of the solution to corrode materials and accelerates the process of gold dissolution.

The kinetics of the corrosion rate of the electrode reaction are described by the linear polarization resistance. At lower polarization resistances, gold is more likely to be dissolved when the corrosion current density is higher. Furthermore, increasing the $S_2O_3^{2-}$ concentration was found to initially decrease the linear polarization resistance before gradually increasing. Therefore, to promote the dissolution of gold in the system, the concentration of $S_2O_3^{2-}$ should be controlled at approximately 0.1 mol/L.

3.2 Effects of NH_3 concentration

Figures 3 and 4 show that the corrosion current density increased with increasing NH_3 concentration. In addition, the decreasing corrosion potential observed in the figures indicates that the composition of NH_3 can also play a role in improving the corrosion rate of gold.

As the concentration of NH_3 increased, the corrosion potential of -0.178 V decreased to -0.236 V. It was also found

Figure 3: Tafel plots of gold dissolution with different ammoniacal concentrations.

(a)

(b)

(c)

Figure 4: Electrochemical parameters of gold dissolution with different ammoniacal concentrations: (a) corrosion current density of gold dissolution; (b) corrosion potential of gold dissolution; and (c) polarization resistance of gold dissolution.

that further increasing the NH_3 concentration reduced the corrosion potential of gold, thereby facilitating the process of gold dissolution. Furthermore, as the concentration of NH_3 was increased, the linear polarization resistance decreased, making the gold more susceptible to corrosion. These results demonstrate that the corrosion resistance of the solution can be enhanced by adding NH_3 to the $\text{S}_2\text{O}_3^{2-}$ solution, which can accelerate the dissolution of gold.

3.3 Effects of Cu^{2+} concentration

In the thiosulfate solution system, the composition of NH_3 stabilized the copper ion in the solution. When the concentration of NH_3 was insufficiently low, it was too difficult to stabilize Cu^{2+} to enable the production of $\text{Cu}(\text{OH})_2$ in the solution. Therefore, it is necessary to introduce additives to stabilize Cu^{2+} in ammoniacal thiosulfate solutions with low NH_3 concentrations [20,38]. The Tafel curves for various copper concentrations are shown in Figure 5.

Figure 6 shows that the corrosion current density significantly increased with the addition of Cu^{2+} , while the corrosion potential was further reduced to -0.253 V. This indicates the significance of the role of thiosulfate solution-immersed copper in the catalytic oxidation of gold.

When the concentration of Cu^{2+} was increased from 0 to 0.2 mol/L, the polarization resistance was observed to rapidly decrease. However, further increase of the concentration of Cu^{2+} resulted in a slower polarization resistance decrease. This indicates that the Cu^{2+} in

Figure 5: Tafel plots of gold dissolution with different copper concentrations.

Figure 6: Electrochemical parameters of gold dissolution with different copper concentrations: (a) corrosion current density of gold dissolution; (b) corrosion potential of gold dissolution; and (c) polarization resistance of gold dissolution.

solutions can enhance the corrosion ability of the solution and accelerate the dissolution of gold.

3.4 Effects of EDTA concentration

The results illustrated in Figures 7 and 8 show that adding EDTA can reduce the corrosion potential and increase the gold dissolution tendency within the 0.05–0.2 g/L EDTA concentration range.

As mentioned earlier, an increase in the corrosion current density was found to correspond to the decreased linear polarization resistance, which is suggested to accelerate the gold dissolution rate. This is because it is common for the complex stability constants of Cu^{2+} and EDTA to be larger than those of Cu^{2+} and NH_3 [11], which leads to the reduced electrode potential of $\text{Cu}^{2+}/\text{Cu}^+$. In addition, it has been confirmed in this study that the addition of EDTA can reduce the corrosion potential of gold from -0.253 to -0.302 V and that the dissolution of gold would be accordingly accelerated.

When the amount of EDTA was excessive, the corrosion current density was observed to rapidly decrease, while the polarization resistance rapidly increased. During this time, the corrosion rate of gold was significantly less than that of the solution without EDTA. The reason for this is that the addition of EDTA to the Cu^{2+} – NH_3 – $\text{S}_2\text{O}_3^{2-}$ mixture would produce CuY^{2-} by complexing with Cu^{2+} . The complexes in the solution would thus significantly reduce the concentration of free Cu^{2+} [18]. Therefore, when the potential of the mixed solution is excessively low, gold cannot be easily dissolved.

Figure 7: Tafel plots of gold dissolution at different EDTA mass concentrations.

Figure 8: Electrochemical parameters of gold dissolution at different EDTA mass concentrations: (a) corrosion current density of gold dissolution; (b) corrosion potential of gold dissolution; and (c) polarization resistance of gold dissolution.

Furthermore, it was found that the amount of EDTA should be maintained within the 0.05–0.2 g/L range.

4 Conclusions

1. Under the experimental conditions of an $\text{S}_2\text{O}_3^{2-}$ concentration of 0–0.09 mol/L, NH_3 concentration of 0–0.8 mol/L, and a Cu^{2+} concentration of 0–0.8 mmol/L, the corrosion potential and polarization resistance decreased with increasing concentrations of $\text{S}_2\text{O}_3^{2-}$ and NH_3 , whereas the corrosion current density increased. In addition, the corrosion current density significantly increased with the addition of Cu^{2+} . The experimental results indicate that the presence of Cu^{2+} can strengthen the catalytic ability of gold oxidation in the thiosulfate solution.
2. Under the condition of 0.1 mol/L $\text{S}_2\text{O}_3^{2-}$, 0.4 mol/L NH_3 , 0.8 mmol/L Cu^{2+} , and 0.05–0.2 g/L EDTA, the addition of EDTA can reduce the corrosion potential and increase the corrosion current density, thereby facilitating the dissolution of gold. However, a high concentration of EDTA will decrease the corrosion current density and increase the corrosion potential, leading to a decreased gold corrosion rate.

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