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Anodic dissolution of gold in alkaline solutions containing thiourea, thiosulfate and sulfite ions①

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[Abstract] Gold dissolves electrochemically in alkaline solutions containing ligands to form complex ions with gold ion. Therefore, selective leaching of noble metals is expected without dissolution of base metals such as steels, aluminum alloys in scrap treatment. Gold electrodes were investigated using linear sweep voltammetry, EQCM method and potentiostatic electrolysis in alkaline solutions containing thiourea, Na_2SO_3 and $Na_2S_2O_3$. The solution composition, electrode potential affect gold dissolution rate and current efficiency. The gold dissolved from anode electrode forms complex ions, suspension particles as compound precipitates and deposits on cathode electrode as a metal. Anodic efficiency for gold dissolution is between 10% and 22%. This is caused by the oxidation decomposition of sulfite ions and thiourea. The stability of the alkaline solution containing these elements was also estimated by capillary electrophoresis technique.

[Key words] gold selective dissolution; sulfite; alkaline thiourea solution
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1 INTRODUCTION

The demand for the rare metals and noble metals has increased to fabricate functional materials in recent decades according to the development of industrial technology, especially the information technology. In the case of gold application in Japan, the usage ratio of demand for industry, 10%, is the third largest after demand for investment, 55%, and demand for jewelry and decoration, 24%. Industrial usage will be expected to grow larger in the future. Therefore, importance of gold recovery technology, in particular, hydrometallurgical processing is recognized in view point of metal resources recycling. Industrial recycling technique of gold is mainly leaching with aqua regia or cyanide aqueous solution in spite of their difficulty in handling and toxicity. The process using aqua regia dissolves every metal without selectivity and acid treatment and waste treatment is necessary in the current method. In cyanide process, gold dissolves selectively into the aqueous solution and recovery is easy electrochemically, except of the disadvantage of toxic solution.

Many researches[1~4] have been investigated on the alternative techniques with low environmental impact and concern and treatment cost. Thiourea was known to be an effective, selective and novel lixiviant for gold as early as 1932[5]. But it is since 1970 that thiourea has attracted attention due to the necessity of recycling gold from its secondary resource[6]. It has been reported that gold is dissolved more efficiently by thiourea in acidic solution than in alkaline solution[7~11]. For example, much attention is paid on the process, which uses alkaline solution, complexing agent; thiourea, TU ($CS(NH_2)_2$) and thiosulfate ion ($S_2O_3^{2-}$)[12, 13]. The formation reactions of complex ions with gold are represented as follows electrochemically.

$$Au+2TU=Au(TU)_2^{+}+e \quad (1)$$

$$Au+2S_2O_3^{2-}=Au(S_2O_3)_2^{3-}+e \quad (2)$$

These complex ligands are, however, instable in alkaline solutions. They are likely to be oxidized to FD ($NH_2NHCSSCNHNH_2$) and sulfate ion, respectively[14], which makes lower the current efficiency and dissolved rate of gold:

$$2TU=FD+2H^{+}+2e \quad (3)$$

$$S_2O_3^{2-}+5H_2O=2SO_4^{2-}+10H^{+}+10e \quad (4)$$

The effect of sulfite ions on the gold dissolution behavior as an oxidizing inhibitor to complex agent for gold dissolution was shown in our previous work[15]. We performed polarization measurement with electrochemical quartz crystal microbalance(EQCM) method to examine how much effective of each ion concentration against gold dissolution and current density. Constant potential electrolysis was carried out with gold pellet electrode. By examining changes of pellet mass and performing atomic absorption spectrometry, the effect of electrolysis potential and bath composition on current efficiency was investigated. Stability of ligands in the alkaline solution was estimated by

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capillary electrophoresis technique.

2 EXPERIMENTAL

2.1 Experimental procedure

The solution was prepared by dissolving recrystallized thiourea, sodium thiosulfate and sodium sulfite in distilled water. The pH of the solution was adjusted with NaOH. The volume of solution used in the experiments was 0.5 dm^3. The solution was agitated with a magnetic stirrer in order to assist the convection of ligand ions. The electrochemical measurement and potentiostatic electrolysis were performed using a typical three electrode system, consisting of a metal working electrode, a platinum counter electrode, and a saturated calomel electrode, Ag/AgCl sat. KCl, as a reference electrode through a Luggin probe with a potentiostat at room temperature. All potentials were represented versus this reference electrode. The linear sweep voltammetry in several solutions was measured with a scanning rate of 10 mV/s. Tests of metal dissolution were conducted in pH 12 solutions with various concentrations of thiourea, thiosulfate and sulfite under potentiostatic condition. Before and after the electrolysis, mass changes of gold anode and platinum cathode were measured to estimate the dissolved gold and deposited gold, respectively.

2.2 EQCM measurement

The anodic polarization curve and mass change of the gold electrode were measured in situ using EQCM equipment, Seiko EG&G Instrument QCA917. The EQCM electrode is shown in Fig. 1. The dissolution of Au electrode on quartz crystal leads to the frequency increase in QCM. Mass change, Δm, is related to the resonance frequency change, Δf, as represented in Eqn. (5) called Sauerbrey's equation. In this equipment, the increase in resonance frequency of 1 Hz corresponds to the decrease in mass of 1.07 ng.

$$\Delta f = -f_0 \Delta m / (N \rho_q A) \tag{5}$$

where $f_0 = 9$ MHz, $N = 1.67 \times 10^5$ Hz·cm, $\rho_q = 2.648$ g·cm^{-3}, $A = 0.195$ cm^2.

2.3 Electrolysis at potentiostatic condition

The gold pellet with d10 mm diameter, 5 mm thickness and over 99.9% purity was used as a specimen. The pellet was mounted by epoxy resin as a working electrode with the surface area of 0.79 cm^2. It was polished with 2 000 mesh abrasive paper and set in the cell.

2.4 Measurement of ion concentration

Concentration of gold-complex ion dissolved from gold pellet electrode was measured by atomic absorption spectrometry. Concentrations of $(NH_2)_2CS$, $S_2O_3^{2-}$ and SO_3^{2-} were measured by capillary electrophoresis before and after electrolysis. In order to examine the stability of electrolysis bath, measurement of ion concentrations were conducted after leaving solution in air as prepared or with oxygen bubbling.

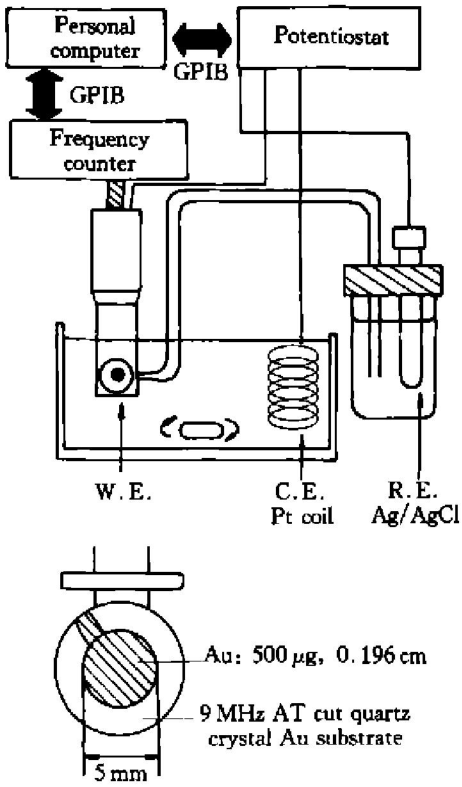

Fig. 1 Experimental apparatus for electrolysis and quartz crystal microbalance coated gold

Precipitates formed in electrolysis were filtered, dried and identified by XRD.

3 RESULTS AND DISCUSSION

3.1 Effect of reagent on anodic gold dissolution

The dissolution behavior of gold anode was examined by EQCM technique in the alkaline solution including complex ligand with gold ion such as thiourea and thiosulfate, and inhibitor against the oxidation of ligand such as sulfite. Changes in current density and mass of gold anode in various solutions are shown in Fig. 2. Gold dissolution could be hardly observed in the thiourea solution and sulfite solution. Increase of current density in the solution only containing sulfite is caused by anodic oxidation of sulfite ions. Little amount of gold dissolution was observed in thiosulfate solution and sulfite-thiosulfate solution. The largest amount of gold dissolution in these solution systems was observed in the solution containing thiourea, thiosulfate and sulfite.

Next, the effect of sulfite concentration on gold dissolution behavior was examined by EQCM in the solution of 0.1 mol/L thiourea solution. Mass of dissolved gold tended to increase after 0.6 V. It was considered that the addition of sulfite ions restricted

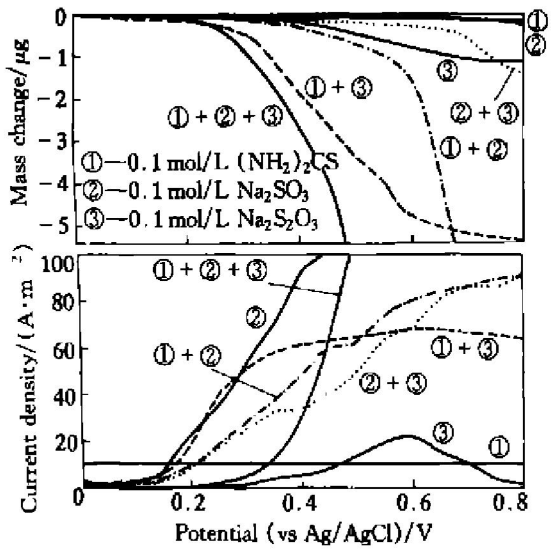

Fig. 2 Anodic polarization curves and mass change of Au electrode in alkaline solutions at pH 12

the anodic oxidation of thiourea and this resulted in the increase of gold dissolution according to Eqn. (1). Then, electrolysis was conducted at 0.6 V with gold pellet electrode in thiourea-sulfite solution. The highest current efficiency for anodic dissolution of gold was observed in 0.1 mol/L thiourea solution added 0.1 mol/L sulfite, when the total amount of dissolved gold from anode was divided into the dissolved gold ions in the solution of 3%, the deposits on cathode of 35% and precipitates in the solution of 62%.

On the other hand, the effect of thiosulfate concentration on gold dissolution behavior was examined by EQCM in 0.1 mol/L thiourea + 0.1 mol/L sulfite solution. Gold dissolution increased at 0.5 V by adding thiosulfate. It is probably because the addition of thiosulfate ion enhanced electrochemical reaction of Eqn. (2). Electrolysis was conducted at 0.6 V with gold pellet electrode in 0.1 mol/L thiourea + 0.1 mol/L sulfite solution with various concentration of thiosulfate. Mass of dissolved gold and current efficiency became maximum in the solution containing 0.1 mol/L thiosulfate, and decreased for 0.5 mol/L. These results showed that excessive addition of sodium sulfate inhibits gold dissolution.

Summarizing results above, optimum combination in our experiment for gold dissolution was 0.1 mol/L thiourea, 0.1 mol/L sulfite and 0.1 mol/L thiosulfate.

3.2 Effect of electrode potential on anodic Au dissolution

Fig. 3 is anodic polarization curves of Au and Pt electrodes in the solution with 0.1 mol/L $(NH_2)_2CS$, 0.1 mol/L Na_2SO_3 and 0.1 mol/L $Na_2S_2O_3$ at pH 12 with the scanning rate of 10 mV/s.

Platinum does not dissolve as a complex ion with ligands in the solution. Therefore, the increase in

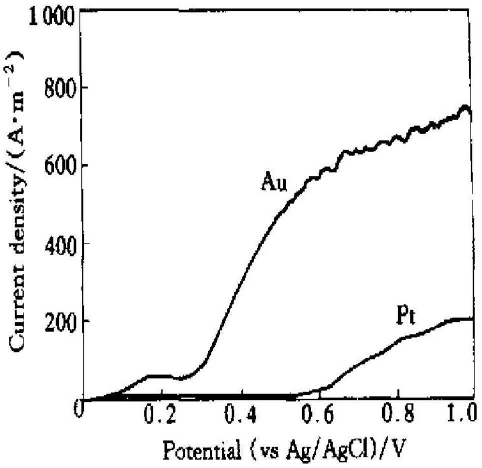

Fig. 3 Anodic polarization curves of Au and Pt electrodes in solution with 0.1 mol/L $(NH_2)_2CS$, 0.1 mol/L Na_2SO_3 and 0.1 mol/L $Na_2S_2O_3$ at pH 12 (scanning rate is 10 mV/s)

anodic current at the potential over 0.6 V corresponds to the decomposition of sulfite ions and so on. The anodic current on gold electrode increases at the potential over 0.3 V. This current mainly includes the dissolution of gold.

Electrolysis tests were carried out at the various potentials of 0.3, 0.4, 0.5 and 0.6 V in the solution containing 0.1 mol/L $(NH_2)_2CS$, 0.1 mol/L Na_2SO_3 and 0.1 mol/L $Na_2S_2O_3$ at pH 12. The mass loss of gold anode increases with the potential as shown in Fig. 4. Maximum current efficiency to the mass loss of gold anode achieved to 22% at 0.5 V in the electrolysis. The dissolution rate of gold anode is 337 $mol/(cm^2 \cdot h)$ at 0.6 V. The amount of gold dissolved as ions is very few in comparison with the precipitates over 60% in the solution and the deposits on cathode of c. a. 30%.

In comparison with the role of reagent in the

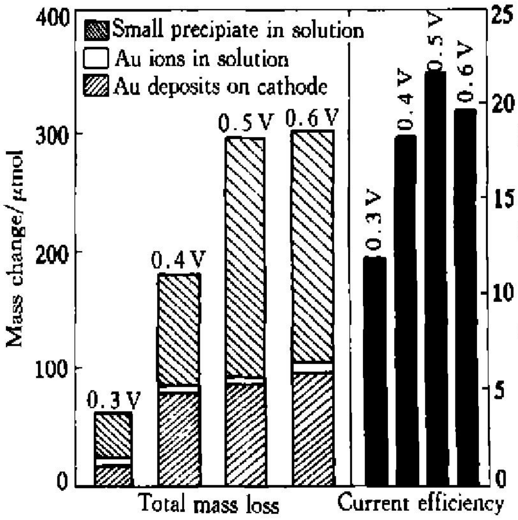

Fig. 4 Effect of Au anode potential on mass change and current efficiency in electrolysis for 1 h in solution with 0.1 mol/L $(NH_2)_2CS$, 0.1 mol/L Na_2SO_3 and 0.1 mol/L $Na_2S_2O_3$ at pH 12

solution, electrolysis was also carried out in the solution with two reagents under constant anodic potential to compare the dissolution behavior of gold in three reagents system.

Fig. 5 is results of two- and three-reagents systems. The largest amount of gold dissolution was confirmed in the solution of three-reagents system. Based on EQCM results, thiourea-sulfite combination could not enhance sufficient Au-complex formation because of their instability and easy decomposition by anodic oxidation, which caused the decrease in current efficiency compared with three-reagents solution. Sulfite was found to be effective for gold dissolution not only with thiourea but also with thiosulfate.

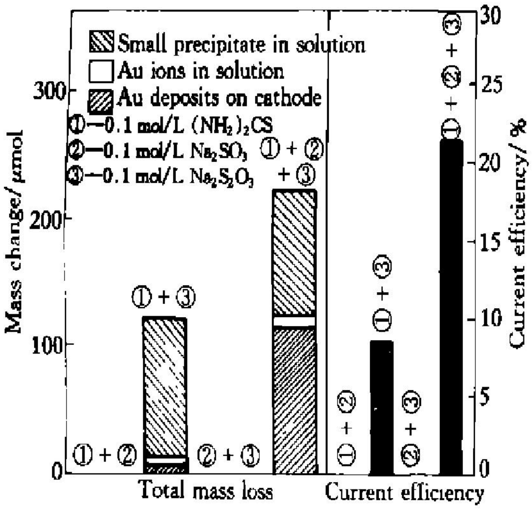

Fig. 5 Effect of solution composition on mass change and current efficiency in electrolysis at 0.6 V for 1 h at pH 12

3.3 Stability of solution

Electrolyte consists of reagents containing sulfur in complicated oxidation stage. Sulfur has several oxidation valencies, such as − 2 for $(NH_2)_2CS$, 0 for S, + 2 for $S_2O_3^{2-}$, + 4 for SO_3^{2-}, + 6 for SO_4^{2-}. Therefore, the oxidation/reduction reactions spontaneously take place in the mixed solution each other and with dissolved oxygen. Fig. 6 is the result of oxygen effect on the solution stability estimated by capillary electrophoresis technique. The solution with 0.1 mol/L $(NH_2)_2CS$, 0.1 mol/L Na_2SO_3 and 0.1 mol/L $Na_2S_2O_3$ at pH 12 changed both with and without oxygen bubbling for 12 h. In this period, precipitate is not observed in the solution. The increase in sulfate ion came from the oxidation of sulfite ion and thiourea. Thiosulfate ion is stable relatively and sulfite ion is instable in this system. Oxygen gas influences the oxidation decomposition of the chemicals, but not too strong. The gold was anodically dissolved for 1 h in each solution after the test shown in Fig. 6. Since the dissolved amount of gold was similar in each solution, the decomposition of chemicals observed in Fig. 6 is negligible for the gold electrolysis. Additionally, electrolysis was carried out using the solution after oxidation test with or without oxygen bubbling for 40 h. The gold dissolution behavior is same in these two solutions. But, the chemical species in the solution after electrolysis changed as shown in Fig. 7. It was found that sulfite ion is easy to oxidize in long time exposed in oxidation stage. Considering the mass balance between the increase in sulfate ion and the decreases in other three species, almost all of three decomposed species change to somewhat different chemicals except sulfate ion. Visible small particles were observed in the solution after electrolysis. It is supposed that these chemical species including sulfur composition were oxidized at anode, otherwise reduced at cathode in the electrolysis, and formed chemicals with different oxidation valencies of sulfur.

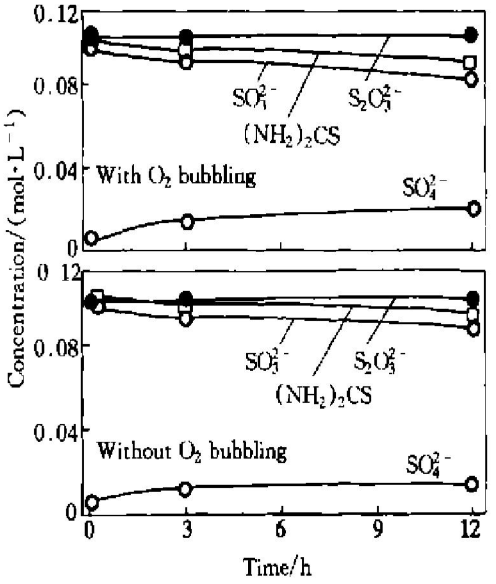

Fig. 6 Stability of alkaline solution with 0.1 mol/L $(NH_2)_2CS$, 0.1 mol/L Na_2SO_3 and 0.1 mol/L $Na_2S_2O_3$ at pH 12 under condition with or without oxygen bubbling

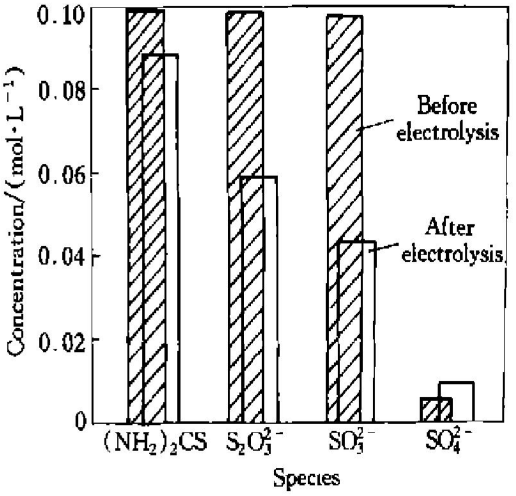

Fig. 7 Change of alkaline solution with 0.1 mol/L $(NH_2)_2CS$, 0.1 mol/L Na_2SO_3 and 0.1 mol/L $Na_2S_2O_3$ at pH 12 by electrolysis at 0.6 V for 1 h

3.4 Analysis of precipitate

The solution after electrolysis at potentiostatic condition including much amount of small particle suspension, i. e. precipitate, is observed as shown in Fig. 4 and Fig. 5. The precipitates were estimated by X-ray diffraction analysis. The precipitates consist of metallic gold and elemental sulfur. The sulfur is thought to form due to the oxidation/ reduction reactions of sulfite ion, thiosulfate ion and thiourea. Detail process of the sulfur reduction and oxidation, and the composition of other compounds with sulfur, AuS, Au_2S, could not be confirmed in this electrolysis process.

4 CONCLUSION

Anodic dissolution behavior of gold electrode was investigated in the alkaline solution at pH 12 containing thiourea, sodium thiosulfate and sodium sulfite. Linear sweep voltammetry and QCM measurement showed that the addition of Na_2SO_3 could make the anodic dissolution of gold possible in the alkaline thiourea and thiosulfate solution, although gold has been known to dissolve with great difficulty in an only alkaline thiourea solution. It is concluded that Na_2SO_3 might prevent thiourea from decomposing in successive stages and thus forming degradation products such as cyanamide and sulfur.

It was found from the potentiostatic electrolysis that gold dissolves effectively at the potential of 0.6 V vs Ag/ AgCl in the solution with three reagents of 0.1 mol/ L concentration. Though the dissolved oxygen didn't inhibit gold dissolution, the reagents, particularly sulfite ions, decomposed in the electrolysis. The reduced species and dissolved gold made small particles suspended in the solution. Gold dissolved once from the anode became suspension particles of c. a. 63%, cathode deposits of c. a. 32% and dissolved complex ions of c. a. 5%. The precipitates included sulfur decomposed from the chemicals instead of gold particles. The mechanism to form the precipitates with gold and sulfur is not clear in the electrolysis. It is clear, however, that gold dissolves at anode and electrodeposits at cathode in a cell. To improve this process, it is necessary to prevent the formation of solid precipitation containing gold and the decomposition of chemicals in the electrolysis.

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