An Electrochemical Study on the Dissolution of Gold and Copper from Gold/Copper Alloys

YICHANG GUAN and KENNETH N. HAN

The dissolution behavior of gold and copper from their elemental states and from gold/copper alloys in cyanide solutions has been investigated using a rotating-disc electrode. The anodic and cathodic reactions were studied separately, and the resulting polarization curves were combined to examine the overall dissolution reactions. The dissolution rate of pure gold in the aerated cyanide solutions was inhibited by the anodic passivation on the gold surface, whereas the dissolution rate of pure copper was found to be mass-transfer controlled. On the other hand, the dissolution of gold and copper from the alloys was partially controlled by electrochemical reaction and largely by mass transfer.

I. INTRODUCTION

There have been numerous studies concerning the dissolution behavior of pure gold in cyanide solutions. However, very few investigations have been conducted to study the dissolution behavior of metals from alloys. The current study is part of an ongoing investigation on the understanding of the underlying principles involved in the extraction of metals from scrap.

In the previous article, the dissolution behavior of copper and gold from their pure states and gold/copper alloys in aerated cyanide solutions was studied using rotating discs by monitoring the amount of these metals dissolved in the solution.

In general, the overall reaction for the dissolution of the alloy AuₙCuₘ in aerated cyanide solutions may be written as

\[
\text{AuₙCuₘ} + (2n + 3m)\text{CN}^- + \frac{m+n}{4} \text{O}_2 + \frac{m+n}{2} \text{H}_2\text{O} = n\text{Au(CN)₂}^- + m\text{Cu(CN)₃}²^- + (n + m)\text{OH}^- \tag{1}
\]

which can be separated into two electrochemical components representing the oxidation of AuₙCuₘ and the reduction of oxygen, respectively.

\[
\text{AuₙCuₘ} + (2n + 3m)\text{CN}^- = n\text{Au(CN)₂}^- + m\text{Cu(CN)₃}²^- + (n + m) e \tag{2}
\]

and

\[
\frac{n+m}{4} \text{O}_2 + \frac{n+m}{2} \text{H}_2\text{O} + (n + m) e = (n + m)\text{OH}^- \tag{3}
\]

Reactions [2] and [3] occur at the alloy-electrolyte interface. At the mixed potential, the oxidation of the alloy and the reduction of oxygen are taking place in the same rate, and the net current is zero.

The anodic and cathodic reactions can be studied separately. A potential difference can be imposed across the alloy-electrolyte interface with the aid of an external voltage source. The study on the anodic reaction can be conducted in oxygen-free cyanide solutions. When the potential difference across the interface is made more positive, the dissolution rate, measured as an electrical current, will keep increasing until it reaches the limiting current, provided sufficient cyanide is present and there is no change occurring in the composition of the alloy surface.

The cathodic reaction can be studied in cyanide-free oxygen solutions. When the potential difference across the interface is made more cathodic, the oxygen reduction rate, measured as a current, increases and leads to a limiting current with the decrease of potential, provided sufficient oxygen is present.

According to the mixed-potential theory, the dissolution potential and the dissolution rate (current) can be obtained by combining the anodic and cathodic current-potential curves. It is the purpose of this study to identify and discuss the electrochemical reaction mechanism by which the dissolution process of gold and copper takes place from gold/copper alloys.

II. EXPERIMENTAL

Analytical-grade chemicals were used in this study. Sodium cyanide (NaCN) was used as a lixiviant and sodium hydroxide (NaOH) was used as a pH adjustor. All anodic dissolution experiments were conducted in an air-tight nitrogen atmosphere. Potassium nitrate was used as a supporting electrolyte. The cathodic reaction was studied in mixtures of oxygen-nitrogen gases with a known oxygen partial pressure and in cyanide-free solutions. Sodium chloride was also used as a supporting electrolyte. Nitrogen and oxygen were obtained from Air Products (Rapid City, SD). All tests were carried out at 25 °C using distilled water.

The compositions of Au/Cu alloys used in this study are shown in Table I. All samples were exactly the same as in the previous study. Disc holders were made of TEFLONF and were ensured to provide extra frame to...
avoid the edge effect. The disc was mounted in the holder with the aid of Dure Super Glue.

The EG&G Princeton Applied Research Model 273A Potentiostat/Galvanostat and Model 616 Rotating-Disk Electrode (RDE) were used in this study. The EG&G Princeton Applied Research Model 352 SoftCor™ II Corrosion Measurement Software was used to control the Potentiostat/Galvanostat. The EG&G PARC Model K47 Corrosion Cell System was employed throughout the electrochemical study (EG&G, Princeton, NJ). The system includes the following:

1. a 1-L flask with a flat bottom to prevent tipping;
2. a leakproof assembly for mounting specimens to be tested;
3. twin high-density and nonpermeable graphite counter electrodes;
4. a reference-electrode bridge tube incorporating an ultra-low-leakage VYCOR® frit; and
5. a saturated calomel electrode.

Solutions were prepared from analytical-grade reagents by dissolving a known amount of reagent in distilled water. The pH was adjusted by adding sodium hydroxide. One liter of solution was placed in the testing cell, which was then purged for one hour with oxygen-free nitrogen for the anodic dissolution and an oxygen-nitrogen mixture for the cathodic reaction. The system was purged continuously during the experiment. The working electrode was abraded with fine emery paper, polished with 1-μm alumina, washed with distilled water, and then mounted on the electrode spindle. The reference-electrode bridge tube was adjusted so that the VYCOR tip was positioned within about 2 mm of the disc surface.

Polarization curves were obtained and analyzed by performing the computer operation. Unless otherwise mentioned, the general experimental conditions used were the following: temperature, 298 K; initial sodium-cyanide concentration, 0.01 mol/L; disc-rotation speed, 47.1 rad/s (450 rpm); the concentration of the electrolyte (potassium nitrate or sodium chloride), 0.5 mol/L; pH, 11.0; scan rate, 1.0 mV/s; the potential range for the anodic dissolution, -1.0 to +0.6 V vs saturated calomel electrode (SCE); and the potential range for the cathodic reaction, 0 to -1.0 V vs SCE. The current interrupt infrared radiation (IR) compensation mode was used throughout the experiments.

All potentials were reported against the SCE.

### Table I. Chemical Compositions of Au/Cu Alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>Au At. Pct</th>
<th>Cu At. Pct</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Sample 2</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>Sample 3</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Sample 4</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>Sample 5</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

### III. RESULTS AND DISCUSSION

#### A. Anodic Behavior

The anodic behavior of different samples in oxygen-free cyanide solutions was investigated. The variables investigated included concentration of cyanide, rotation speed of the disc, and pH of the solution. The typical anodic current-potential curves for different samples are shown in Figures 1 through 5.

It can be seen that the anodic dissolution behavior of Sample 1 (pure gold) is the most complex one. Within