Dissolution and Precipitation of Gold and Silver in the System 6N HCl Solution - Au–Ag Alloys at 150°C Over 120 Days.

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Abstract: The experiments were carried out in the system 6N HCl aqueous solution-synthetic Au–Ag alloys with various Ag/Au ratios in order to investigate the dissolution and precipitation of gold and silver at 150°C over a period of 120 days. Pure gold precipitate was formed in run #3(Au50Ag50), #4(Au75Ag25) and #5(Au90Ag10), in which the Ag/Au atomic ratio in solution was less than 1. Gold-silver alloy (electrum) was formed in run #1(Au10Ag90) and #2(Au25Ag75), in which the Ag/Au atomic ratios in solution were about 330 and 670, respectively. Assuming that gold and silver chloro-complexes are dominant in ore fluids, Ag/Au atomic ratios in ore fluids for the Transbaykalial gold deposits and the Japanese auriferous hydrothermal vein deposits are calculated and estimated to lie in the range of 7 to 690.

Introduction

The dissolution and precipitation of gold and silver at 150°C were investigated in the system containing some strong acid solutions-synthetic Au50Ag50 alloy (atomic ratio) (Honma et al., 1990). They reported that precipitates and high concentrations of gold and silver in the solution were obtained only from the system 6N HCl solution-Au50Ag50 alloy for 120 day's run.

The present study is a continuation of the previous work (Honma et al., 1990), in which the hydrothermal dissolution and precipitation of gold and silver using synthetic Au–Ag alloys with various Ag/Au ratios as starting materials was investigated. The solution used was 6N HCl solution at 150°C, over a period of 120 days.

The present paper describes briefly solution compositions and changes of post-reacted alloys, and we consider the Ag/Au atomic ratio in solutions for electrum formation.

Experimental Procedure and Results

The synthetic Au-Ag alloys as starting materials were Au10Ag90, Au25Ag75, Au50Ag50, Au75Ag25 and Au90Ag10 (atomic ratio). The acid solution used was 6N HCl solution. In each case, approximately 30 ml of 6N HCl solution was placed into a teflon reaction tube together with about 0.1g of a synthetic Au–Ag alloy. The teflon tube was sealed in air, enclosed in a stainless steel casing, and placed in an electric furnace, the temperature of which was controlled at 150±3°C over a period of 120 days. At the end of the runs, the teflon tubes were air cooled to room temperature. Solution compositions (Table 1) were obtained by atomic absorption spectrometry (Seiko model SAS-760).

Surfaces of the pre- and post-reaction grains were studied by scanning electron microscopy. These observations are summarized below. Surfaces of pre-reaction grains are as same as a photomicrograph in previous work (Honma et al., 1990).

Au10Ag90: Surface of the grain shows honey comb-like structure. The partition wall of the structure shows petaline texture (Fig. 1a) and other parts exhibit sponge-like texture.

Au25Ag75: Surface of the grain changes little. Linear-like textures develop towards the domain boundary which may be dissolved parts (Fig. 1b) and dendritic textures which...
### Table 1
Quantitative solution compositions by atomic absorption spectrometer, weight loss of grain and dissolution rate.

<table>
<thead>
<tr>
<th>run</th>
<th>starting alloy</th>
<th>weight of alloy</th>
<th>solution composition</th>
<th>dissolution ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>start (g)</td>
<td>end (g)</td>
<td>loss (mg)</td>
</tr>
<tr>
<td>#1</td>
<td>Au_{10}Ag_{90}</td>
<td>0.0890</td>
<td>0.0762</td>
<td>14.4</td>
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<tr>
<td>#2</td>
<td>Au_{25}Ag_{75}</td>
<td>0.1526</td>
<td>0.1493</td>
<td>2.2</td>
</tr>
<tr>
<td>#3</td>
<td>Au_{40}Ag_{60}</td>
<td>0.1206</td>
<td>0.1134</td>
<td>6.0</td>
</tr>
<tr>
<td>#4</td>
<td>Au_{75}Ag_{25}</td>
<td>0.1305</td>
<td>0.0941</td>
<td>27.9</td>
</tr>
<tr>
<td>#5</td>
<td>Au_{90}Ag_{10}</td>
<td>0.1127</td>
<td>0.0868</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Fig. 1 Scanning electron micrographs of post-reacted grains.
(a) petaline texture on the partition wall of honey comb-like structure (Au_{10}Ag_{90}). (b) linear-like texture in gold crystal domains (Au_{25}Ag_{75}). (c) honey comb-like structure on the surface of the grain (Au_{40}Ag_{60}). (d) etched pints in precipitates (Au_{75}Ag_{25}). (e) bamboo ware-like texture (Au_{90}Ag_{10}). (f) dendritic precipitates (Au_{90}Ag_{10}).
may be precipitates.

Au_{50}Ag_{50}: Surface of the grain shows a distinctive honey comb-like structure (Fig. 1c). Crystalline planes which were piled up by very thin layered ones are recognized sometimes.

Au_{75}Ag_{25}: Surface of the grain shows fine honey comb-like structures which are covered by precipitates. Etched pits are recognized on some domains (Fig. 1d).

Au_{90}Ag_{10}: Surface of the grain shows fine honey comb-like structures but part of a cuboctahedra form is tore out from the surface. Precipitates show minute triangular pits and other textures (Fig. 1e). Dendritic precipitates are also developed (Fig. 1f).

In polished sections of each post-reacted grain, all of the precipitates, whether thin or thick, covered the parent grain and showed qualitatively higher reflectance values than the parent grain (Fig. 2a). Changes in gold content between parent grain and precipitates was qualitatively investigated by using an energy dispersion X-ray micro-analyzer (Au-Ma ray, Elionix model EXM-3500) because precipitates covering the parent grain tend to form very thin layers (~15 μm) in many cases. As a result, gold content of precipitates is higher than that of parent grains in all cases (for example, Fig. 2b).

Discussion

It is an interesting evidence as shown at Table 1 that the maximum and the minimum values on weight loss of parent grains (21.4% and 1.5%), Au or (Au+Ag) contents of solutions and dissolution rate (weight of Au or Ag in solution/weight of Au or Ag in grain) are shown at runs #4 and #2, respectively. The above runs appear to be the most and the least dissolvable experimental cases of gold and silver from Au-Ag alloys, respectively, under chloride dominant and strongly acid conditions.

Precipitates which formed on the grains in runs #3, #4 and #5 are estimated to be nearly Au_{100}Ag_{50} within the measurement errors, but those in runs #1 and #2 contain some Ag on the basis of qualitative analysis by energy dispersion X-ray micro-analysis. That is, pure gold or gold-silver alloy (electrum) is suggested to be preferably formed under the experimental condition by small (under 1?) or large (over 1?) atomic ratio of Ag/Au in solution.

BARANOVA et al. (1980) determined the gold and silver contents of fluid inclusions in quartz and calcite from the Transbaykalian gold-ore deposits which are hydrothermal subvolcanic ones of the gold-sulfides-tellurium association. Their analytical results indicate that Ag/Au atomic ratios of fluid inclusions in quartz and calcite lie in the range of 7 to 690. According to SHIKAZONO and SHIMIZU (1987), electrum from the Japanese auriferous vein deposits contains 10–20 atomic % Ag. On the basis of this value together with assumptions on ore fluids mentioned above under acid and high fO2 conditions, Ag/Au atomic ratios of the ore fluids for these ore deposits are calculated to
be about 150 (SHIKAZONO and SHIMIZU, 1987). Those values are roughly consistent with the range obtained in the present study for run #1 and #2 (Table 1).

**Summay**

Au$_{75}$Ag$_{25}$ and Au$_{25}$Ag$_{75}$ are the most and the least dissolvable alloys (electrum), respectively, in 6N HCl solution at 150°C.

When the Ag/Au atomic ratio in sample solutions is under or over 1(?) at 150°C, pure gold or gold-silver alloy (electrum) is formed in the systems, respectively.

Assuming that gold and silver chloro-complexes are dominant in acid ore fluids, the range of Ag/Au atomic ratios obtained from this study is roughly consistent with that in ore fluids by which the Transbaykalial gold-ore deposits and the Japanese auriferous vein deposits were formed.

**Reference**

