〔Original〕

In Vitro Study on the Corrosion Behavior of Three Commercial Ag-Pd-Cu-Au Alloys in Ringer's and 0.1%Na₂S Solutions

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Synopsis

The corrosion resistance of three commercial Ag-Pd-Cu-Au alloys was estimated in Ringer's and 0.1% Na₂S solutions by electrochemical techniques and surface analyses.

In Ringer's solution, the three alloys showed high corrosion resistance and there was no significant difference in the anodic polarization characteristics of the three alloys.

In the 0.1% Na₂S solution, the Alloy A which had the lowest noble metal content (Au + Pd) exhibited the highest anodic reactivity with the largest amount of corrosion product on the alloy surface. It was determined that the Ag-rich phase of Ag-Pd-Cu-Au alloy was preferentially attacked to form Ag₂S corrosion product.

The polarization resistance data showed that the corrosion rate for Alloy A in 0.1% Na₂S solution was determined to be 500 times higher than that in Ringer's solution. The corrosion rate of the alloy in the freely corroded condition can be estimated quantitatively and precisely by measuring the polarization resistance.

Key words : Corrosion, Anodic potentiodynamic polarization, Polarization resistance,
Ag-Pd-Cu-Au alloy

Introduction

Ag-Pd-Cu-Au alloy has been widely used as a restorative material in dentistry. However, this alloy sometimes show discoloration due to corrosion, and the degree of corrosion and tarnish varies. Although the factors which influence the individual differences in corrosion are not fully understood, two factors are important. One is the alloy composition in relation to the

corrosion resistance, and the other is the concentration of corrosive species in the oral environment.

In this study, the corrosion resistance of three commercial Ag-Pd-Cu-Au alloys with different gold contents was investigated in Ringer's solution and 0.1% Na_2S solution at 37 °C by electrochemical techniques and surface analyses.

Materials and Methods

1. Materials

Table 1 shows the composition of the three commercial Ag-Pd-Cu-Au alloys used in this study. The amount of Au was 0, 5, and 12% in Alloy A, Alloy B, and Alloy C, respectively. The 10x30x1 mm specimens were cast according to the manufacturer's directions and polished through 1000-grit emery paper. The surface was coated with nail varnish and the surface area exposed to the electrolyte was 1 cm^2.

Table 1 Composition of the three commercial Ag-Pd-Cu-Au alloys used in this study.

Alloy	Composition
Alloy A	Ag 56, Pd 25, Cu 17
Alloy B	Ag 53, Pd 25, Cu 13, Au 5
Alloy C	Ag 51, Pd 20, Cu 14.5, Au 12

2. Electrochemical Corrosion Tests

2-1 Anodic Potentiodynamic Polarization Measurement

The polarization cell for making anodic potentiodynamic polarization measurements consisted of an Ag/AgCl reference electrode, a graphite counter electrode, and a working electrode (test specimen) as shown in Fig. 1. Ringer's solution and the 0.1% Na_2S solution were employed as corrosive solutions because

Fig. 1 Schematic diagram of the polarization cell.

of their aggressive ions. Cl⁻ is considered very destructive to dental restorations and tarnish has been considered to arise from metal sulfides. The test solutions were de-aerated by bubbling the Ar gas through the test solution for 30 min before immersing the specimen. After specimen immersion for 60 min, polarization measurements were started from the rest potential at a scan rate of 0.1 mV/sec up to an overpotential of 1200 mV. Anodic polarization curves were obtained at least twice for each solution.

2-2 Corrosion Potential and Polarization Resistance Measurement

The corrosion potential of the alloy, which shows the corrosion condition of the alloy, actively corroding or passive, was measured with a $10^9 \Omega$ input impedance electrometer. The potential in the present work are all quoted against an Ag/AgCl electrode.

The corrosion rate of the alloy was esti-
mated from the polarization resistance mea-
surement. A repetitive square wave current
which was symmetrical with respect to a zero
current was imposed on the alloy specimen,
and the corresponding potential change was
recorded as show in Fig. 2.

The polarization resistance R_{corr} is inverse-
ly proportional to the corrosion rate, and
was determined as equation (1).

$$R_{corr} = \Delta E_{p-p} / i \qquad (1)$$

where ΔE_{p-p} is the peak-to-peak value of the

Fig. 2   Square wave current and the potential
response.

potential change and i the current density imposed on the alloy specimen[1]-[3].

3 . Surface Analysis

After immersing the alloy specimen in Ringer's solution or the 0.1% Na_2S solution for 20
days, the corroded surface was examined by Scanning Electron Microscope(SEM). For
Alloy A immersed in 0.1% Na_2S solution, the corrosion products were scraped from the alloy
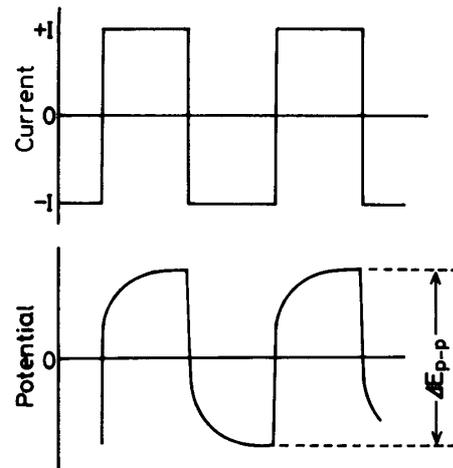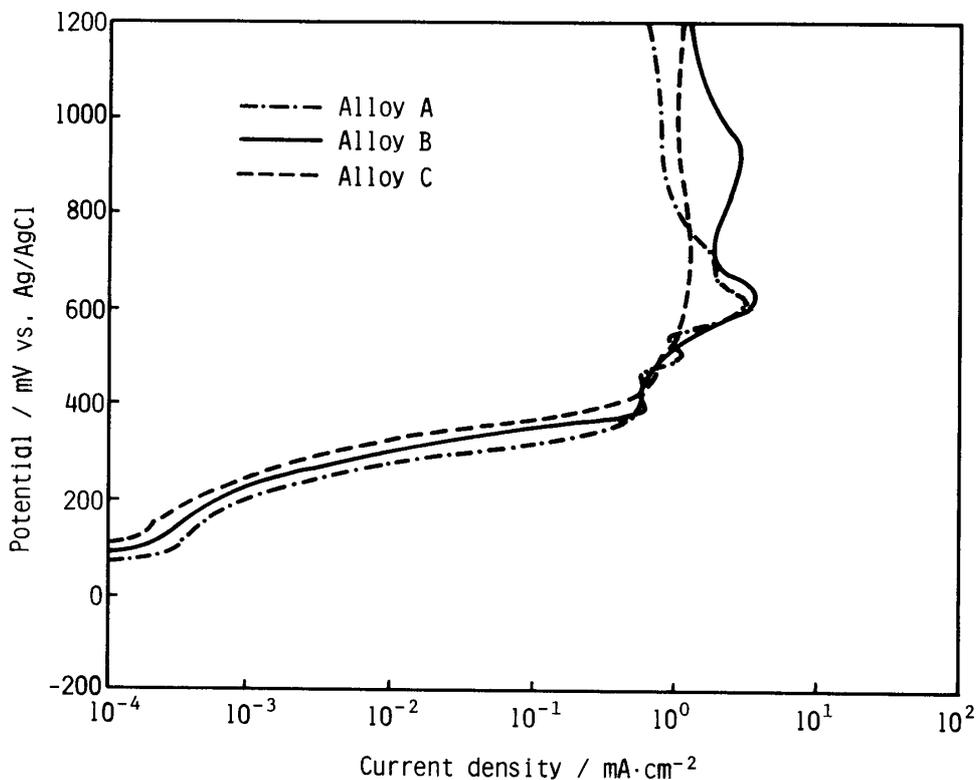surface and identified by Debye-Scherrer X-ray diffraction.

Fig. 3   Anodic polarization curves of the three Ag-Pd-Cu-Au alloys in Ringer's solution at 37°C.

Results

1. Anodic Behavior in Ringer's Solution and 0.1% Na₂S Solution

Figure 3 shows typical anodic polarization curves of the three alloys in Ringer's solution. The current densities increased slightly with polarization up to approximately 150 mV and then rose rapidly with further polarization up to 400 mV. Above this potential, the current densities remained almost constant at 1 mA/cm². No significant difference in the anodic polarization characteristics was observed among the three alloys.

Figure 4 shows typical anodic polarization curves of the three alloys in 0.1% Na₂S solution. The curves are characterized by two current density peaks around -500 mV and -375 mV. The minor peak around -500 mV is associated with the corrosion of Ag-rich phase, whereas the major peak around -375 mV is an effect of the corrosion of Cu-rich phase in Ag-Pd-Cu-Au alloy[4]. The peak current densities at both -500 mV and -375 mV were highest in Alloy A, followed by Alloy B and C. The result shows that the corrosion activity for Alloy A was the highest and that for Alloy C was the lowest.

2. Corrosion Potential and Polarization Resistance Measurement

Figure 5 shows the variations in corrosion potential E_{corr}[a] and polarization resistance R_{corr}[b] with time for Alloy A in Ringer's and 0.1% Na₂S solutions. The corrosion potential of the alloy in Ringer's solution was much more noble than that in 0.1% Na₂S solution. The polarization resistance in Ringer's solution increased gradually, indicating a slowing down of the corrosion rate. The polarization resistance in 0.1% Na₂S solution decreased and remained
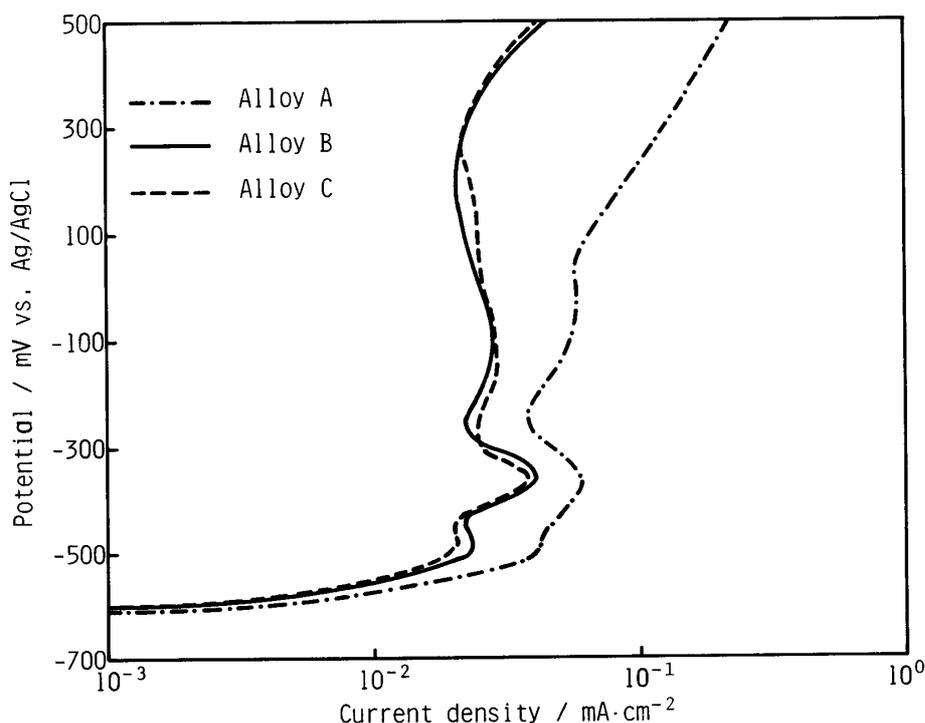

Fig. 4   Anodic polarization curves of the three Ag-Pd-Cu-Au alloys in 0.1% Na₂S solution at 37°C.
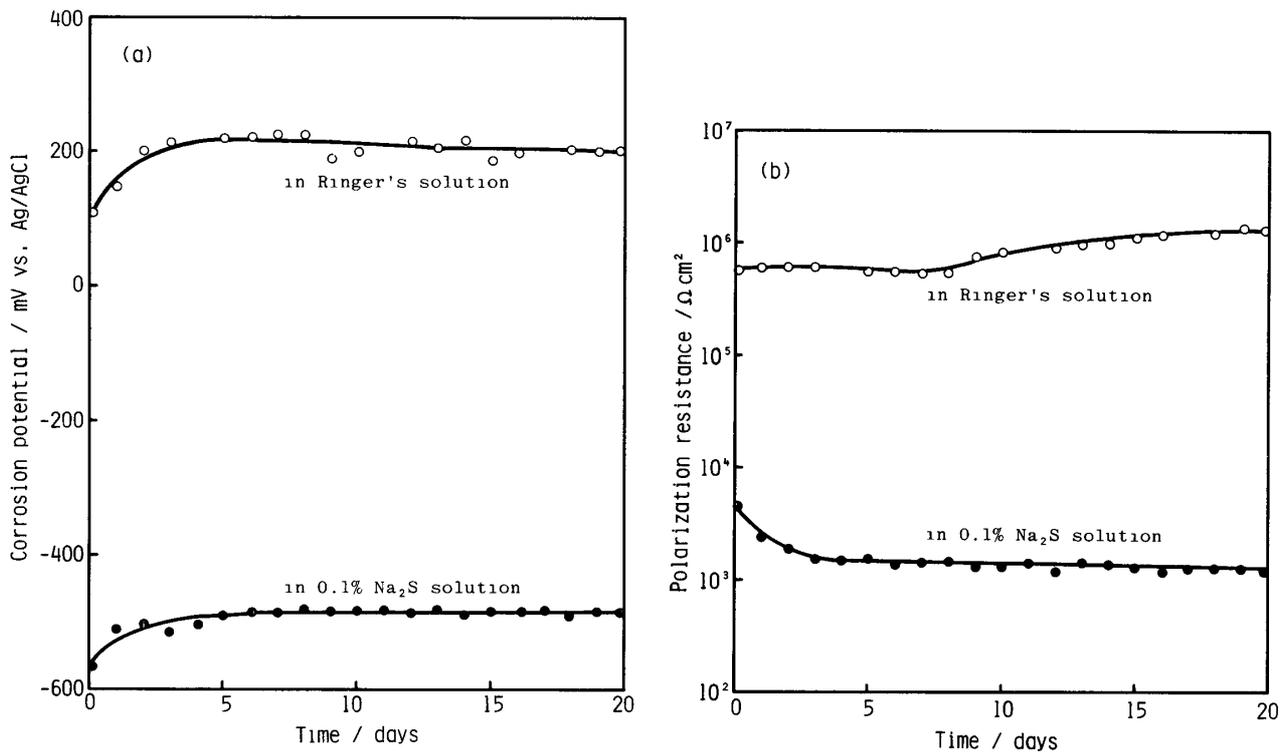
Fig. 5   Variations in corrosion potential(a) and polarization resistance(b) with time for Alloy A in Ringer's and 0.1% Na₂S solutions.
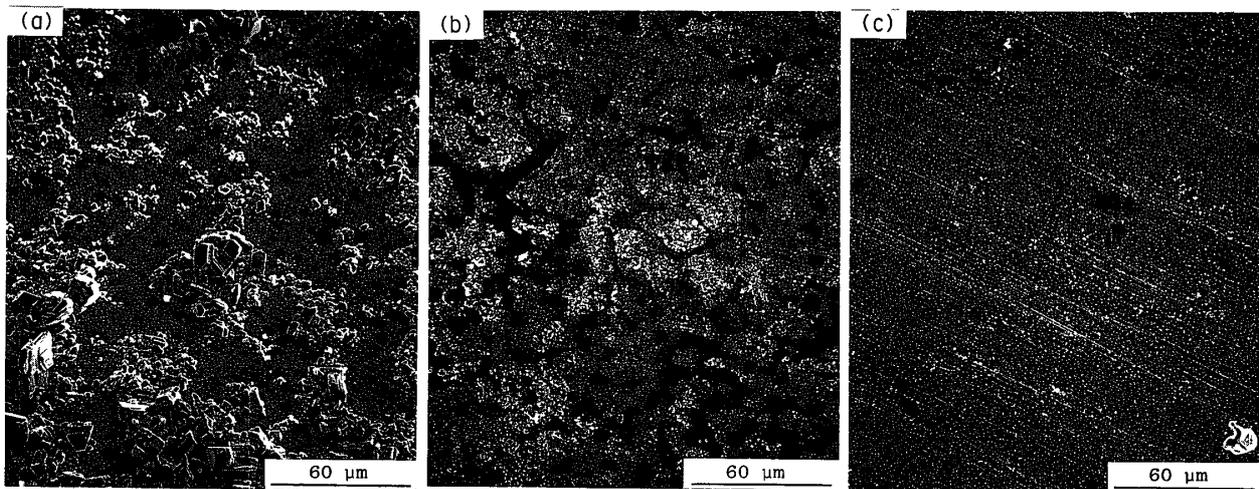

Fig. 6   SEM images of alloy surface after immersion in 0.1% Na₂S solution for 20 days. (a) Alloy A ; (b) Alloy B ; (C) Alloy C

at a steady-state value. The polarization resistance in Ringer's solution was approximately three orders of magnitude above that in the 0.1% Na₂S solution. It is apparent form these results that Alloy A corroded actively in 0.1% Na₂S solution while corrosion was negligible in Ringer's solution.

3 . Surface Analysis

Figure 6 shows the SEM images of the alloy freely corroded in 0.1% Na₂S solution for 20 days, showing the formation of corrosion products on the alloy surface. The amount of
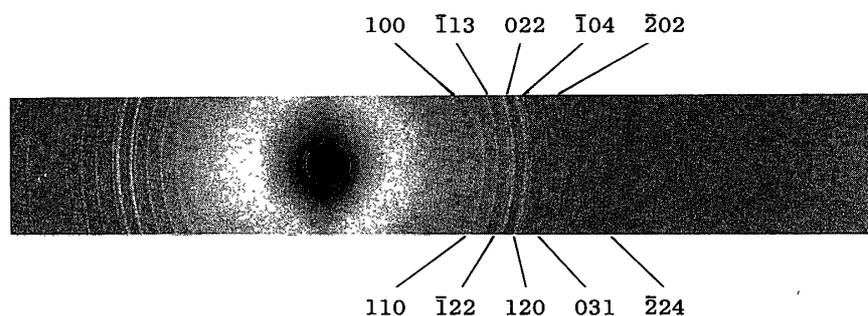
100 Ī13 022 Ī04 ẑ02

110 Ī22 120 031 ẑ24

Fig. 7   Debye-Scherrer X-ray diffraction of scrapings from Alloy A after immersion in 0.1% Na$_2$S solution for 20 days. This pattern shows that the corrosion product is Ag$_2$S.

corrosion product was the largest for Alloy A, followed by Alloy B and Alloy C, consistent with the results from the anodic polarization data shown in Fig. 4.

Figure 7 shows the diffraction pattern of scrapings from the surface of the Alloy A corroded in 0.1% Na$_2$S solution for 20 days, indicating that the main corrosion product was Ag$_2$S.

For all three alloys, the surfaces were not changed between before and after being immersed in Ringer's solution for 20 days.

Discussion

1. Anodic Reaction and Corrosion Product in Ringer's and 0.1% Na$_2$S Solutions

Based upon the equilibrium potential values, the expected anodic reaction of Ag during the potential scan in the range from 150 mV to 400 mV in Ringer's solution is,

$$Ag + Cl^- \longrightarrow AgCl + e^- \qquad E = 22.4 \text{ mV} \qquad (2)$$
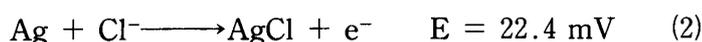
The nonprecious elements, such as Zn and Cu also corrode in this potential range. Matsuda et al.[5] demonstrated by reflection electron diffraction that AgCl existed on an Ag-Pd-Cu-Au alloy potentiostatically anodized at +400 mV.

In 0.1% Na$_2$S solution, the rest potential of the Ag-Pd-Cu-Au alloy was about 700 mV more negative than that in Ringer's solution. This may be attributed to the sulfidation reactions proceeding in the 0.1% Na$_2$S solution, where the equilibrium potentials are very negative. A possible sulfidation reaction of Ag and its equilibrium potential is,

$$Ag + S^{2-} \longrightarrow Ag_2S + 2e^- \qquad E = -891 \text{ mV} \qquad (3)$$
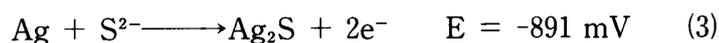
The Debye-Scherrer X-ray diffraction in Fig. 7 confirms that Ag$_2$S was formed on the surface of Alloy A corroded in 0.1% Na$_2$S solution. It has been shown by XPS analysis that the tarnish of Ag-Sn-Zn alloy and Ag-In alloy in the oral environment is not due to the formation of Ag$_2$S but due to oxides of nonprecious elements, such as Sn, Zn, and In[6),7)]. In the Ag-Pd-Cu-Au alloy system, more sensitive XPS analysis is necessary to determine whether sulfides of alloing elements other than Ag or oxides exist on the alloy surface.

2. Corrosion Resistance and Alloy Composition

The three alloys exhibited high corrosion resistance in Ringer's solution and there was no
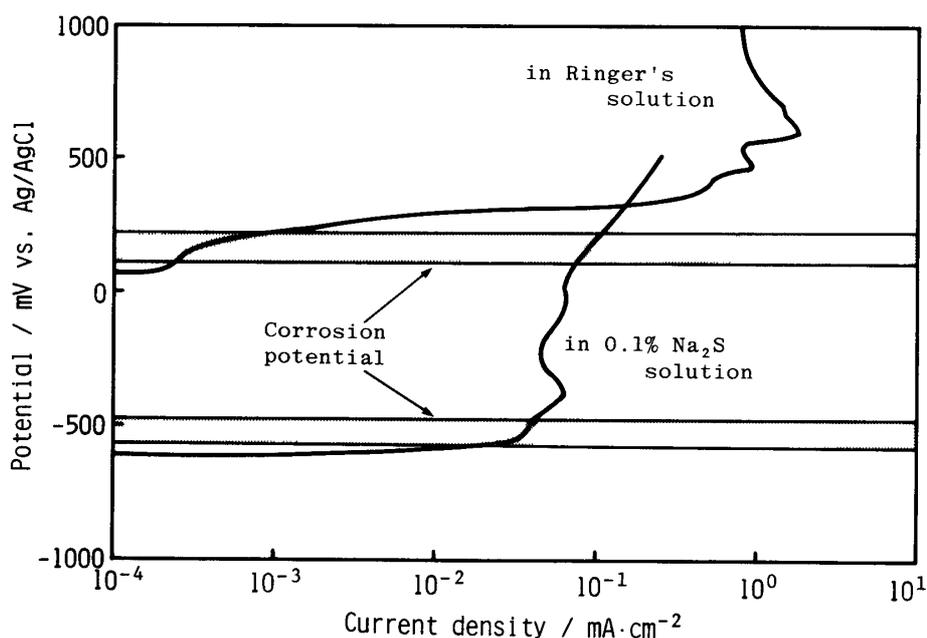
Fig. 8   Anodic polarization curves for Alloy A in Ringer's and 0.1% Na_2S solutions with the regions of the corrosion potential (shaded).

significant difference in corrosion resistance. In the 0.1% Na_2S solution, however, the alloy composition affected on the corrosion activity. In general, corrosion resistance has been found to decrease with decreasing noble metal content. Alloy A has a small amount of noble metal (Au + Pd) and a relatively large amount of Cu, and the corrosion resistance is inferior to Alloy B and C in 0.1% Na_2S solution. Alloy B and C have almost the same noble metal content in at%, but Alloy C showed slightly higher corrosion resistance than Alloy B . This may be attributed to the fact that Au existed uniformly in both Ag^-rich and Cu^-rich phases while Pd existed preferentially in the Cu^-rich phase[8]. Therefore, the (Au + Pd) concentration in the Ag^-rich phase of Alloy B was relatively small, resulting in poorer corrosion resistance than Alloy C.

The small amount of additives may also change the microstructure and influence the corrosion resistance of the alloy.

3 . Corrosion Activiy at the Corrosion Potential

Figure 8 shows the anodic polarization curves for Alloy A in Ringer's and 0.1% Na_2S solutions with the regions (shaded) where the corrosion potential varied. Here the current density at the corrosion potential in Ringer's solution was so small that corrosion would be negligible in the freely immersed condition. No corrosion product was detected by XPS analysis on the Alloy A freely immersed in Ringer's solution[9], though AgCl was detected on $Ag^-Pd^-Cu^-Au$ alloys anodized at +400mV in 0.9% NaCl solution[5].

In 0.1% Na_2S solution, the current density peaks around -500 mV and -375 mV correspond to Ag^-rich and Cu^-rich phase corrosion. Considering the corrosion potential range, the Ag^-rich phase appears to corrode preferentially with Ag_2S formation, which agrees well with the result

from the corrosion product analysis by X-ray diffraction.

The most important information about corrosion is how fast the alloys corrode in the freely corroding condition, i.e. the corrosion rate at the corrosion potential. The polarization resistance data suggest that the corrosion rate for Alloy A in 0.1% Na_2S solution was 500 times higher than that in Ringer's solution(Fig. 5). The results here show that the corrosion activity of an alloy at the corrosion potential can be thus estimated precisely and quantitatively by measuring the polarization resistance.

Acknowledgment

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〔原　著〕

市販Ag-Pd-Cu-Au合金のリンゲル液および0.1% Na₂S溶液中における腐食挙動

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　リンゲル液および0.1%Na₂S溶液中における三種の市販Ag-Pd-Cu-Au合金の腐食挙動を電気化学的手法と表面分析により評価した。

　リンゲル液中においては，いずれの合金も高い耐食性を示し，合金間に顕著な耐食性の差は認められなかった。それに対して，0.1%Na₂S溶液中では，貴金属含有量（Au＋Pd）の少ないAlloy Aが最も高いアノード反応性を示し，合金表面に最も多い腐食生成物を生成した。腐食生成物は，X線回折によりAg₂Sと同定され，合金表面のSEM観察から主にAg-rich相が選択的に腐食されることが確められた。

　分極抵抗の測定から，Alloy Aは0.1%Na₂S溶液中ではリンゲル液中に比較して，500倍の速度で腐食することが明らかとなった。分極抵抗法により，自然腐食状態にある合金の腐食速度を精度よく定量的に求めることができた。