

# Corrosion evaluation of Au–Cu–Pd ternary alloys

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The corrosion resistivity of single-phase Au–Cu–11 at% Pd alloys was evaluated by using a parameter  $Q$  which represented the total amount of anodic reaction in a potentiostatic polarization test. The result was compared with those for binary Au–Cu, ternary Au–Cu–11 at% Ag and some commercial alloys. The validity of using  $Q$  as a corrosion parameter was confirmed by the good agreement between the analysed and calculated values of copper ion dissolved into the test solution. By replacing a part of the copper in Au–Cu alloys with palladium the corrosion resistivity can be greatly improved, but silver has no such significant effect. The value of  $Q$  decreased by both treatments of homogenization and grain refinement of the alloy. One of the advantages of the alloy having a single-phase structure is that inhomogeneity in the distribution of the constituents is small even in the as-cast state, which results in a small galvanic effect.

## 1. Introduction

Corrosion resistivity is one of the most important properties required for dental alloys which are used in the oral environment. Nobility of the alloy (the total amount of gold and platinum group metals) is a dominant factor in determining corrosion resistivity [1]. This is the reason why high gold-content alloys are widely used for dental purpose, despite their high cost.

In the oral environment, most of the corrosion proceeds through an electrochemical process and a corrosion current is produced by the galvanic couple. Consequently, the corrosion rate of the alloy is thought to be affected not only by macroscopic heterogeneity in the metallographic structure but also by the microsegregation of constituents. According to the criteria mentioned above, an alloy with a fine-grained single phase is preferred. The content of precious metals should be as low as possible in the interest of economy.

Dental gold alloys are fundamentally an Au–Cu–Ag ternary system. Previous studies on the tarnish and corrosion behaviors of these alloys indicate that silver is a corrosive element [2] and that both gold- and silver-rich phases are less noble [3]. The ternary system Au–Cu–Pd, on the other hand, has a wide compositional range of single phase with the AuCu I type ( $L1_0$ ) ordered structure [4]. Ohta *et al.* [5] have investigated the age-hardening behaviour and hardening mechanism of several Au–Cu–11 at% Pd alloys whose compositions were situated in the single-phase area. The results indicated that these alloys showed acceptable age-hardenability by the formation of the AuCu I type ordered structure, and that the hardening rate for isothermal ageing depended on the Cu/Au atomic ratio. It was also found that the addition of rhodium to this alloy system refined the grain to

about  $\frac{1}{10}$  in diameter and resulted in a homogeneous structure.

The corrosion rate of an alloy varies with the alloy system and also with the experimental method. That is the reason why techniques, except for the weight-change method, for quantitative comparison of the corrosion rate between different alloy systems are not fully developed. The weight-change method is not practical because of the very low corrosion rate of most dental alloys. Recently, Corso *et al.* [6] evaluated the corrosion resistivity of gold-based alloys by using the area under the dynamic polarization profile between  $-300$  and  $+300$  mV, which closely matched the voltage range observed in the mouth. The integrated current density ( $V A cm^{-2}$ ) is one of the quantitative measures of corrosion resistivity. In the dynamic polarization experiment, however, the anodic reaction changes and the results may fairly depend on the scanning speed. On the other hand, the time integral of current density in the potentiostatic polarization experiment ( $A h cm^{-2}$ ) is proportional to the total amount of anodic reaction and is easily converted to the weight (g) by multiplying it by the electrochemical equivalent ( $g A^{-1} h^{-1}$ ).

In this study, the corrosion resistivity of single-phase Au–Cu–11 at% Pd alloys was evaluated by using the integrated current density obtained by a potentiostatic polarization test, and was compared with those of experimental Au–Cu, Au–Cu–Ag and commercial dental gold alloys.

## 2. Materials and methods

The chemical compositions of the alloys tested are listed in Table I. Alloys I, II and III are the Au–Cu–11 at% Pd system and alloys in which 11 at% Pd is replaced by silver are denoted by –Ag. III-R is the

TABLE I Chemical compositions of alloys used

Alloy	Composition (at %)					
	Au	Cu	Pd	Ag	Rh	Pt
II	46.0	43.0	11.0	—	—	—
I	37.1	51.9	11.0	—	—	—
III	26.1	63.2	10.7	—	—	—
III-R	25.4	61.3	10.3	—	3.0	—
II-Ag	46.0	43.0	—	11.0	—	—
I-Ag	37.0	52.0	—	11.0	—	—
III-Ag	26.0	63.0	—	11.0	—	—
AuCu	50.6	49.4	—	—	—	—
AC-I	37.0	63.0	—	—	—	—
AC-III	26.0	74.0	—	—	—	—
High gold (HG)	48.9	32.5	5.2	12.8	—	0.7
Low gold (LG)	29.8	46.2	5.9	17.4	—	0.7

grain-refined alloy of Alloy III obtained by adding 3 at % Rh.

The constituents were weighed and melted in an argon atmosphere by using a high-frequency induction furnace. Hexagonal prisms with side length 3 mm and height 2 to 2.5 mm were cast. Besides as-cast specimens, homogenized ones were prepared by cold-rolling (to about a half the original thickness) and annealing (at 800°C for two hours) the as-cast specimens. After a conductor wire was spot-welded, these specimens were embedded in acrylic resin and polished by the standard metallographic technique.

The chemical stability of the alloys was evaluated by the following methods.

1. Anodic and cathodic potentiodynamic polarization curves were recorded. The potential was changed between -1000 and +1000 mV at a scanning speed of 0.1 mV sec<sup>-1</sup>. All tests were conducted in 1% NaCl solution which was de-aerated with N<sub>2</sub> gas flow. A platinum cathode and an Ag/AgCl reference electrode were used.

2. Potentiostatic polarization was performed in the above-mentioned solution. In the experiment, the total weight *w* of constituents dissolved into the solution is expressed by

$$w = \sum_i K_i I_i t \quad (1)$$

where *K<sub>i</sub>* and *I<sub>i</sub>* are the electrochemical equivalent and the fraction of current density of the element *i*, respectively, and *t* is the time for which a constant potential (+700 mV) was applied. In this study, the total amount of electrochemical reaction proceeding on the anode (specimen) surface was evaluated by the parameter *Q*, where *Q* is an integration of current density for a constant period (540 sec):

$$Q = \sum_i I_i t \quad (2)$$

In the calculation of *Q*, the additional increase in current which appeared at the initiation of polarization by the formation of an electrical double layer was corrected by extrapolating the linear relation between ln Σ<sub>*i*</sub> *I<sub>i</sub>* and time *t* back to *t* = 0.

3. Specimens were hung in 50 ml of 0.5 N H<sub>2</sub>SO<sub>4</sub> solution at 37°C and were shaken for 5 days. The amounts of constituents dissolved into the solution were determined by atomic absorption analysis.

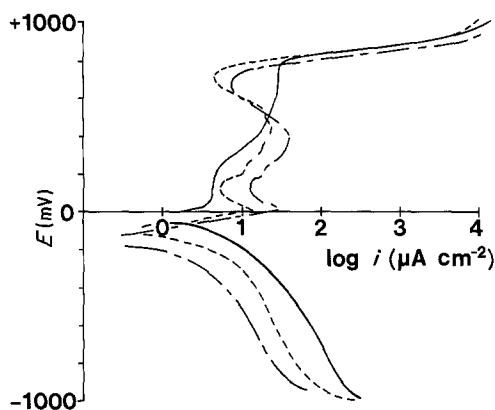
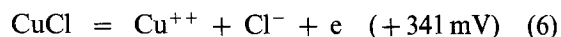
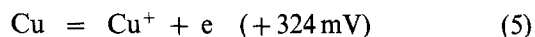
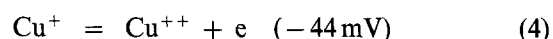
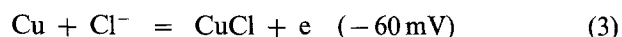


Figure 1 Anodic scanning curves of (---) Alloy I, (—) Alloy II and (-·-) Alloy III. *E* is measured against Ag/AgCl.

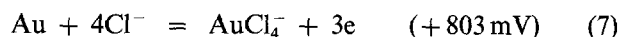
### 3. Results

#### 3.1. Potentiodynamic polarization curves

Fig. 1 shows the anodic scanning curves of Alloys I, II and III as-cast specimens. Peaks in current appeared at around 0 and +400 mV on every specimen, and were thought to correspond to one of the following electrode reactions of copper:



The abrupt increase in current at around +800 mV is due to the electrode reaction



The current density at each peak increased in the order II, I, III and the potential at which the current changed from negative to positive decreased in the same order as above, in accordance with the nobility of the alloy.

Anodic scanning curves (Fig. 2) were obtained with as-cast (III), homogenized (III-H) and grain-refined (III-R) specimens of Alloy III. Homogenization and grain refinement shift the curves to the lower current-density side of the anodic reaction range.

Fig. 3 represents (a) anodic and (b) cathodic scanning curves of as-cast Alloys II and II-Ag. Possible

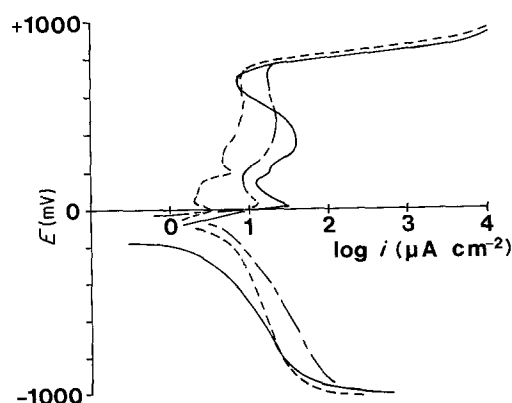


Figure 2 Anodic scanning curves of (—) Alloy III (as-cast), (-·-) Alloy III-H (homogenized) and (---) Alloy III-R (grain-refined). *E* is measured against Ag/AgCl.

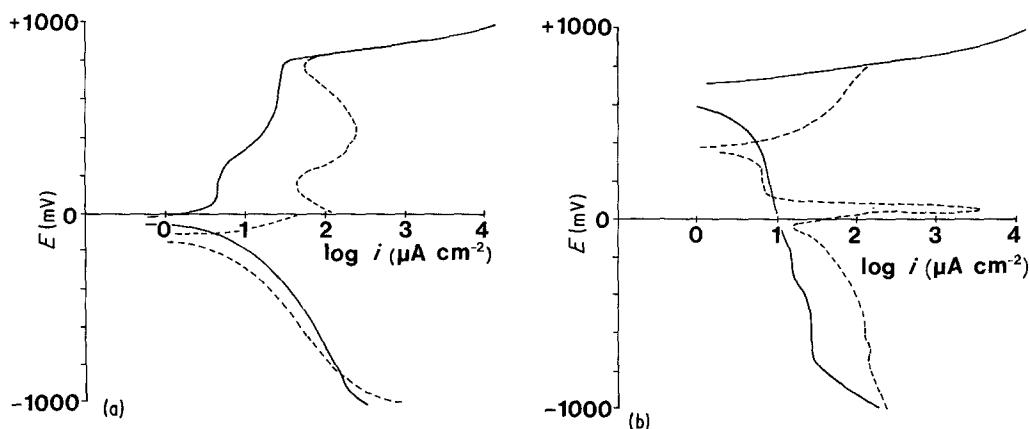
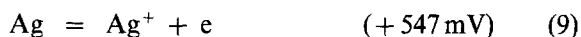
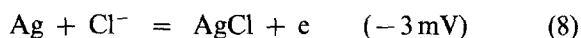


Figure 3 (a) Anodic and (b) cathodic scanning curves of (—) Alloys II and (---) Alloy II-Ag.  $E$  is measured against Ag/AgCl.

reactions for which silver is responsible are as follows:



Reaction 8 is expected to occur in solutions containing  $\text{Cl}^-$  ions. The characteristic current peaks in both anodic and cathodic scanning curves of Alloy II-Ag are thought to correspond to forward and reverse reactions of Reaction 8, respectively. To confirm this point, X-ray diffraction experiments were carried out. 33.4 at % Au–35.5 at % Cu–31.1 at % Ag alloy [7] which contains a sufficient amount of silver was subjected to potentiostatic polarization at +700 mV for 500 min and an X-ray spectrum was taken (Fig. 4a). A spectrum was taken again for the cathodically reduced surface (Fig. 4b). It is evident from the figures that AgCl is formed on the specimen surface by anodic polarization and that it is reduced to pure silver by the cathodic scan. Since AgCl is an insoluble corrosion product, it is unsafe to evaluate the corrosion properties only by chemical analysis of the solution.

The potentiodynamic polarization curves shown in Figs 1 to 3 give us some qualitative guide of corrosion resistivity but provide no quantitative data.

### 3.2. Amount of electrochemical reaction

In Fig. 5, linear relations of  $\log Q$  with copper content for the as-cast Alloys I, II and III are demonstrated. The results of an immersion test in  $\text{H}_2\text{SO}_4$  solution ( $\log W$ ) also give linear relations with copper content. These results indicate the qualitative correlation between  $Q$  and  $W$ .

The values of  $Q$  and  $W$  for Alloy III decreased by both treatments of homogenization and grain refining, indicating that the chemical stability of the alloy is affected not only by the chemical composition but also by the distribution of constituents.

The  $Q$  of Alloy III-R which contains 61.3 at % Cu corresponds to that of the alloy containing only 47 at % Cu and without grain refinement.

## 4. Discussion

### 4.1. The validity of the parameter $Q$ as a measure of corrosion rate

To ensure the validity of the parameter  $Q$  as a quantitative indication of the corrosion rate, the following experiments were performed.

Alloys III-Ag and AC-III were potentiostatically polarized at +700 mV and 5 ml of the solution was withdrawn at 5, 10, 25, 50, 100 and 200 min. These samples were submitted to atomic absorption analysis to determine the amount of copper ion dissolved. In addition,  $Q$  values for the above-mentioned times were measured and the amount of copper ion reacted on the anode surface ( $w$ ) was calculated using the equation

$$w = K_{\text{Cu}} Q_t f_{\text{Cu}} \quad (9)$$

where  $K_{\text{Cu}}$  is the electrochemical equivalent of  $\text{Cu}^+$  ( $2.371 \text{ g A}^{-1} \text{ h}^{-1}$ ) or  $\text{Cu}^{2+}$  ( $1.185 \text{ g A}^{-1} \text{ h}^{-1}$ ), and  $f_{\text{Cu}}$  is the contribution of copper to the  $Q$  value. Since both silver and copper contribute to the  $Q$  in the +700 mV polarization of Alloy III-Ag,  $f_{\text{Cu}}$  is expressed by the equation

$$f_{\text{Cu}} = C_{\text{Cu}} / (C_{\text{Cu}} + C_{\text{Ag}}) \quad (10)$$

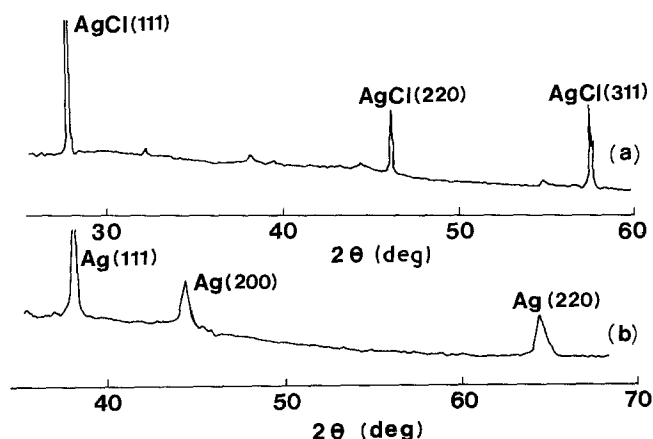


Figure 4 X-ray diffraction patterns of 33.4 at % Au–35.5 at % Cu–31.1 at % Ag alloy. (a) After potentiostatic polarization at +700 mV for 500 min. (b) After cathodic scanning from +200 to –300 mV at a scanning speed of  $0.1 \text{ mV sec}^{-1}$ .

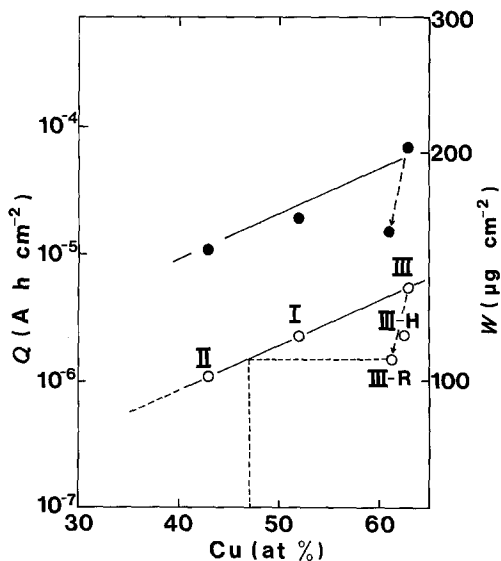


Figure 5 Relation between copper content of Alloys I, II, III and (○)  $Q$  (potentiostatic polarization test in NaCl solution) and (●)  $W$  (immersion test in  $H_2SO_4$  solution).

where  $C_{Cu}$  and  $C_{Ag}$  are copper and silver concentration, respectively.

In the case of Alloy AC-III, only the dissolution of copper is expected to contribute to the  $Q$ -value. Fig. 6a is an X-ray diffraction spectrum of Alloy AC-III taken before the anodic polarization. The lattice constant of Alloy AC-III was calculated to be 0.375 nm. After a constant potential (+700 mV) was applied for 100 min, the lattice constant changed to 0.4075 nm (Fig. 6b), which is very close to that of pure gold (0.4078 nm). This fact suggests that preferential dissolution of copper from the specimen surface takes place. In low-gold Cu-Au alloys, a copper-depleted zone has been observed at the specimen surface, and a mechanism of interdiffusion of the component in the alloy has been proposed [8]. It is apparent, therefore, that  $f_{Cu}$  for Alloy AC-III is unity.

The results in Fig. 7 show linear relations between the amount of copper dissolved and the potentiostatic polarization time. Good agreement between the analysed and calculated data is also shown in the figure. The results also indicate that copper atoms dissolve from Alloy III-Ag in the form of  $Cu^+$  ions by the Reactions 3 and/or 5, and that a part of the copper dissolves, in the case of Alloy AC-III, in the form of  $Cu^{2+}$  by the Reactions 4 and/or 6.

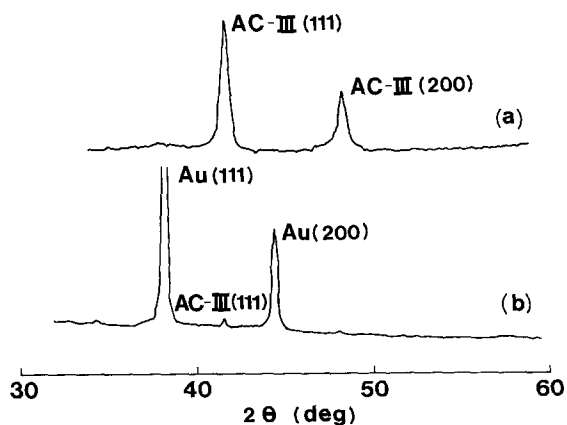


Figure 6 X-ray diffraction spectra of Alloy AC-III. (a) Before test. (b) After being anodically polarized at +700 mV for 100 min.

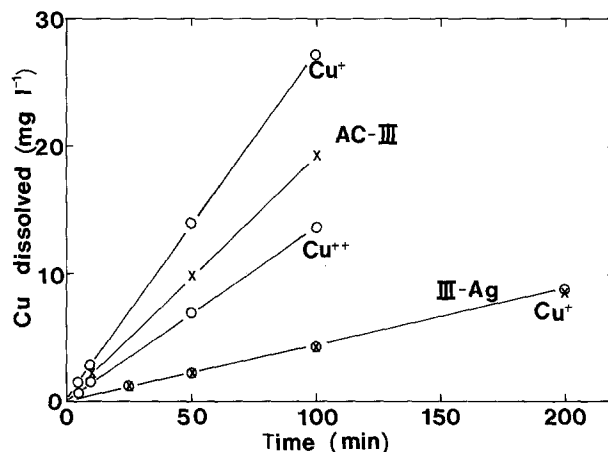


Figure 7 Relation between the amount of copper dissolved and potentiostatic polarization time for Alloys III-Ag and AC-III: (○) calculated, (x) analysed.

The validity of using  $Q$  as a corrosion parameter was confirmed by the above-mentioned result, together with the fact that a correlation between the results of the polarization test in NaCl solution and the immersion test in  $H_2SO_4$  solution was also shown (Fig. 5).

#### 4.2. Variation of $Q$ with alloy system and composition

Fig. 8 shows the relation between  $Q$  and gold content for alloys of binary Au-Cu, ternary Au-Cu-11 at % Pd and Au-Cu-11 at % Ag. In the Au-Cu-Pd system, a linear relation holds between  $\log Q$  and gold content above 26 at % Au, and the extrapolated value of  $Q$  to 100% Au is consistent with that of pure gold. In the Au-Cu and Au-Cu-Ag alloys, an abrupt increase in  $Q$  appears at around 40% Au, and  $Q$  seems to saturate to its upper limit at gold contents less than 25%. The above-mentioned results suggest that, for alloys containing gold less than 50%, the corrosion resistivity can be greatly improved by the replacement of a part of the copper by palladium, but silver has no such significant effect.

Both palladium and silver occupy higher positions than copper in the electrochemical series. Therefore, the replacement of copper with palladium or silver is expected to provide an improvement in corrosion resistivity. Palladium addition to the AuCu alloy does not change the phase structure (single phase of the AuCu I type superlattice). But silver addition causes phase separation of solid solution to copper-rich  $\alpha_1$  and silver-rich  $\alpha_2$ . Therefore, it is reasonable to speculate

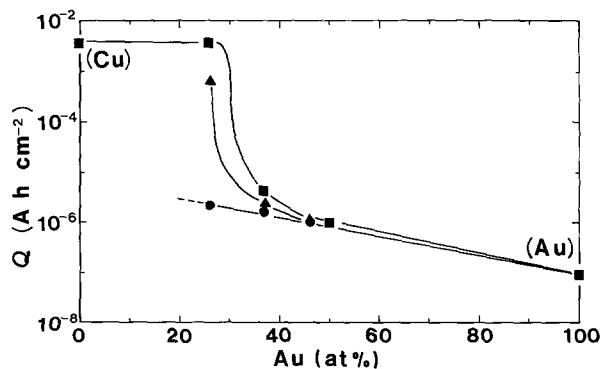


Figure 8 Relation between  $Q$  and gold content of (■) Au-Cu, (●) Au-Cu-11 at % Pd and (▲) Au-Cu-11 at % Ag systems.

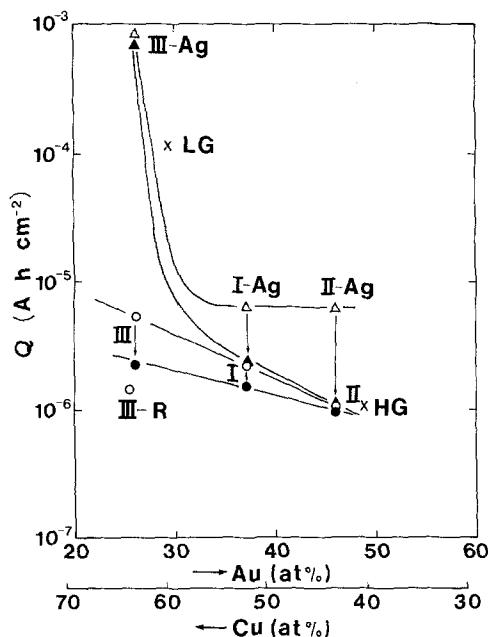


Figure 9 Variation of  $Q$  with gold (or copper) content of (O,  $\Delta$ ) as-cast and ( $\bullet$ ,  $\blacktriangle$ ) homogenized alloys for Au-Cu-11 at % Pd and Au-Cu-11 at % Ag systems. Results for two commercial dental gold alloys are also indicated.

that copper is thermodynamically less stable in the supersaturated solid solution of the Au-Cu-Ag alloys than in the solid solution of the Au-Cu-Pd alloys.

#### 4.3. The effect of microstructure

The variation of  $Q$  with gold (or copper) content is shown in Fig. 9 for both as-cast and homogenized alloys of Au-Cu-Pd and Au-Cu-Ag systems. Since the homogenized and solution-treated specimens have the single-phase structure of a disordered solid solution, results for them simply indicate the effect of chemical composition on the  $Q$  value. Accordingly, the difference in  $Q$  between as-cast and homogenized specimens indicates the effect of inhomogeneity in the microstructure of as-cast specimens.

As-cast alloys of the Au-Cu-Ag system showed a constant  $Q$  value above 35 at % Au, i.e.  $Q$  is independent of chemical composition, but composition dependency appears after homogenization. This fact clearly shows that the controlling factor of the corrosion resistance for these as-cast alloys is not chemical composition but microstructure.

In the case of the Au-Cu-Pd system alloys, on the other hand, both as-cast and homogenized specimens showed composition dependency of the  $Q$  value. The difference in  $Q$  between as-cast and homogenized specimens is not so large in comparison with the Au-Cu-Ag system. These differences in the composition dependency can be attributed to the difference between the stable phase structures of these alloy systems.

Under normal (i.e. non-equilibrium) solidification conditions, as-cast specimen exhibits a variation in composition. Since the equilibrium phase of the Au-Cu-Pd alloy is an ordered single phase, in contrast to the two-phase coexistence of the Au-Cu-Ag alloy, inhomogeneity in the distribution of constituents is smaller in the Au-Cu-Pd alloy than in the Au-Cu-Ag alloy, which results in a smaller galvanic effect. This is one of the advantages of a single-phase alloy.

In Fig. 9, the results of high-gold (HG) and low-gold (LG) commercial alloys (both homogenized specimens) are shown. It is apparent that the corrosion resistivity of the grain-refined Alloy III containing only 25 at % Au corresponds to that of high-class (Type IV of ADA Sp. No 5\*) commercial alloy.

#### 5. Conclusions

The corrosion resistivity of single-phase Au-Cu-11 at % Pd alloys was evaluated by means of a potentiostatic polarization test and chemical analysis of the test solution. A parameter  $Q$  was used which was obtained by integrating current density for a constant period. From the results obtained, the following conclusions can be drawn.

1. The chemically analysed value of the amount of copper ion dissolved into NaCl solution was consistent with that calculated from  $Q$ . A correlation between the results of the polarization test in NaCl solution and the immersion test in  $H_2SO_4$  solution was also shown. The validity of using  $Q$  as a corrosion parameter was confirmed by the above-mentioned results.

2. X-ray diffraction studies revealed the formation of a copper-depleted layer at the specimen surface, suggesting the preferential dissolution of copper from the surface by the mechanism of interdiffusion of the components in the alloy.

3. For Au-Cu alloys with gold less than 50 at %, the corrosion resistivity can be greatly improved by replacing part of the copper with palladium, but replacement with silver had no such significant effect.

4. Both treatments of homogenization and grain refinement decreased the  $Q$  value, which suggested an effect of inhomogeneity in the microstructure of as-cast specimens on the corrosion properties.

5. The equilibrium structure of the tested Au-Cu-Pd alloys was a single phase of ordered or disordered solid solution at temperatures below the solidus line. This leads to a small extent of inhomogeneity in the distribution of components and, as a result, to a small galvanic effect.

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