

Computer simulations of anodic dissolution in Cu–Au–Pd ternary alloys

M. NAKAGAWA, T. SHIRAISHI, S. MATSUYA, M. OHTA

Department of Dental Materials Engineering, Faculty of Dentistry, Kyushu University, Fukuoka 812, Japan

Computer simulation experiments were performed for the anodic dissolution process of $\text{Cu}_{0.7}\text{Au}_{0.3-x}\text{Pd}_x$ ($x=0-0.3$) alloys. Dissolution probabilities of constituents which represented the dissolution rate were defined by considering the standard electrode potential of the dissolution reaction and atomic interaction between Cu and the other atoms. The simulation results qualitatively reproduced the experimental results of anodic potentiostatic polarization tests regarding the dependence of the anodic dissolution behaviour on the polarization potential and the alloy composition, and the atomic concentration depth profile of the constituents after anodic polarization. Atomic interaction among the constituents of an alloy was found to be one of the important factors which control the anodic dissolution features of the alloys.

1. Introduction

In the alloys containing noble elements, it is well known that the selective dissolution of less noble elements and surface enrichment of noble elements take place when the alloys are polarized at a lower potential than that of anodic reaction of the noble elements [1, 2]. Pickering and Wagner [3] suggested that the preferential anodic dissolution of copper was caused by solid-state diffusion of copper via a divacancy mechanism in Cu–Au binary alloys. Forty and co-workers [4, 5] showed that corrosion in Ag–Au and Cu–Au alloys proceeded by the selective dissolution of less noble elements and the formation of Au-rich islands via surface diffusion. Recently, computer simulation experiments were carried out to clarify the selective dissolution mechanism. Sieradzki *et al.* [6] applied percolation theory to the de-alloying (i.e. dissolution) of a binary alloy including noble elements. They reproduced the process of selective dissolution in the binary alloy by computer simulation. Song Qian *et al.* [7] showed, using the percolation model, that the passivation of Fe–Cr binary alloy occurred by the selective dissolution of Fe and surface covering of Cr. They introduced the dissolution probability in the selective dissolution model.

Anodic dissolution of the less noble elements in an alloy is a process in which the atoms detach from the alloy surface by cutting bonds with the surrounding atoms. The amount of dissolution is thought to be affected not only by the standard electrode potential of the dissolution reaction but also by the atomic interaction energy between a less noble atom and the surrounding atoms. The atomic interaction energy varies with the kinds of the nearest-neighbour atoms.

In this study, computer simulations of the anodic dissolution process in Cu–Au–Pd ternary alloys were

performed using the dissolution model and taking into account the effect of atomic interaction energy. To compare the simulation results with experimental results, anodic potentiostatic polarization tests were also carried out in a 1% NaCl aqueous solution at 37 °C.

2. Experimental procedure

2.1. Computer simulation model

In this simulation, a dissolution probability p was employed to represent the dissolution rate of constituents. The anodic dissolution features of an alloy will be governed mainly by the dissolution of the least noble element, i.e. Cu in a Cu–Au–Pd alloy. The dissolution probability of Cu depends on the kinds of the surrounding atoms. Atomic pairs Cu–Cu, Cu–Au and Cu–Pd exist around a copper atom in this alloy. According to the results of calculation of the Cu–Au–Pd ternary phase diagram [8] and analysis of the atom configuration of the ordered lattice in Cu–Au–Pd ternary alloys [9, 10], the atomic interaction energy of these pairs becomes larger in this order: Cu–Cu < Cu–Au < Cu–Pd. Although there were many configurations around a copper atom, only three dissolution probabilities of Cu were defined to simplify the simulation, as follows:

$p(\text{Cu–Cu})$: the dissolution probability of Cu whose nearest neighbours are all Cu atoms.

$p(\text{Cu–Au})$: the dissolution probability of Cu which possesses at least one Au atom as nearest neighbour.

$p(\text{Cu–Pd})$: the dissolution probability of Cu which possesses at least one Pd atom as nearest neighbour.

These probabilities become smaller in the following order:

$$p(\text{Cu–Cu}) > p(\text{Cu–Au}) > p(\text{Cu–Pd})$$

Simulations were carried out at 300, 500 and 700 mV versus Ag/AgCl (KCl saturated) electrode*. At all these potentials the dissolution of Au atoms does not occur, i.e. the dissolution probability of Au atoms is equal to zero ($p(\text{Au}) = 0$). At 300 mV, since the Pd atoms do not dissolve, the dissolution probability of Pd atom is also equal to zero ($p(\text{Pd}) = 0$). At 500 and 700 mV, the Pd atoms dissolve at the given dissolution probabilities which are smaller than those of Cu atoms.

Assuming that the dissolution of constituents qualitatively obeys Tafel's law, $\log(\text{current density } i)$ is proportional to the anodic polarization potential E . In that case, it is considered that $\log(\text{dissolution probability } p)$ is proportional to the anodic polarization potential E because the current density i corresponds to the amount of atoms dissolved. The dissolution probabilities of constituents used in this simulation are shown in Fig. 1.

The computer simulations were performed on a three-dimensional simple cubic lattice of 50×30 atoms \times 11 layers. Cu, Au and Pd atoms of the prescribed composition (Table I) were randomly arranged on the lattice points. A periodic boundary condition [11] was applied in this simulation. Dissolution was simulated by detaching atoms in the prescribed probabilities from the surface exposed to an electrolyte.

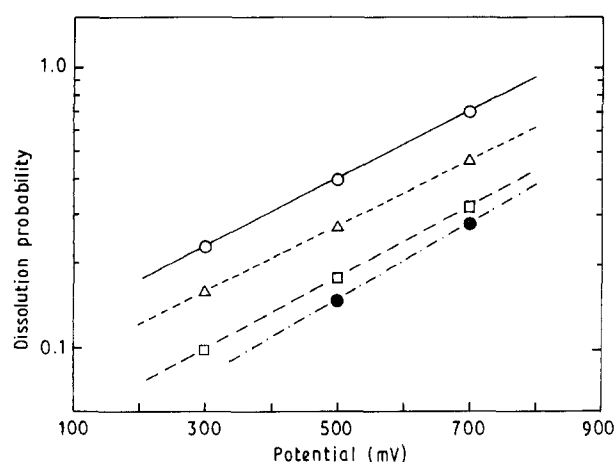


Figure 1 Relation between anodic polarization potential and dissolution probability for simulation: (○) $p(\text{Cu-Cu})$, (△) $p(\text{Cu-Au})$, (□) $p(\text{Cu-Pd})$, (●) $p(\text{Pd})$.

TABLE I Chemical compositions of alloys used

Specimen	Composition (at %)		
	Cu	Au	Pd
70Cu-30Au	70.0	30.0	—
70Cu-28Au-2Pd	70.0	28.0	2.0
70Cu-25Au-5Pd	70.0	25.0	5.0
70Cu-20Au-10Pd	70.0	20.0	10.0
70Cu-15Au-15Pd	70.0	15.0	15.0
70Cu-10Au-20Pd	70.0	10.0	20.0
70Cu-30Pd	70.0	—	30.0

* $E(\text{SCE}) = E(\text{Ag/AgCl}) - 48.4 \text{ mV}$.

In this simulation, it was assumed that diffusion of atoms and rearrangement of surface atoms did not occur during dissolution. However, only noble elements were allowed to move downward when their surrounding atoms dissolved. The amount of atoms dissolved was counted by the total number of atoms detached from the alloy for constant time steps.

2.2. Potentiostatic polarization tests

Sample alloys as shown in Table I were made from 99.99% Cu, Au and Pd in evacuated quartz ampullae using a high-frequency induction furnace. These ingots were hammered, cold-rolled and homogenized at 850°C for 2 days. These specimens were cut into a size of 5 mm \times 5 mm \times 2 mm and embedded in epoxy resin. They were polished by waterproof polishing papers and abrasive aluminium oxide powder of 0.3 μm diameter.

The dissolution behaviour of constituents from the alloy was examined by potentiostatic polarization tests. Deaerated 1% NaCl aqueous solution kept at 37°C was used as an electrolyte. A platinum counter-electrode and an Ag/AgCl (KCl saturated) reference electrode were used. Potentiostatic polarization tests were carried out at 300, 500 and 700 mV. The time-integrated current density (denoted by parameter Q) obtained from the potentiostatic polarization test corresponds to the total amount of Cu and Pd dissolved [12].

Electron spectroscopy for chemical analysis (ESCA) measurements were carried out to obtain the atomic concentration depth profiles of constituents after anodic polarization. The analysis was made using $\text{MgK}\alpha$ operating at 10 kV under 1×10^{-6} Pa. Argon ion etching was performed at 2 kV under 5×10^{-4} Pa.

3. Results and discussion

3.1. Computer-simulated pictures of anodic dissolution

Fig. 2 shows the change in the surface morphology with polarization potential (dissolution probability) in the 70Cu-10Au-20Pd alloy. Dissolution markedly occurs and the alloy surface becomes rougher as the polarization potential becomes higher. Fig. 3 shows the changes in computer-simulated pictures with alloy composition in the anodic dissolution of alloys polarized at 700 mV. It can be seen that the surface enrichment of Au occurs markedly as the Au content increases, and that surface enrichment of Pd does not occur at this potential.

3.2. Changes in the amount of dissolution with polarization potential and alloy composition

Figs 4a, 5a and 6a show changes in the amount of Cu and Pd dissolved with Pd content by simulation at 300, 500 and 700 mV, respectively. The amount of Cu and Pd dissolved is indicated by the total number of atoms detached from the alloy for ten time steps. It

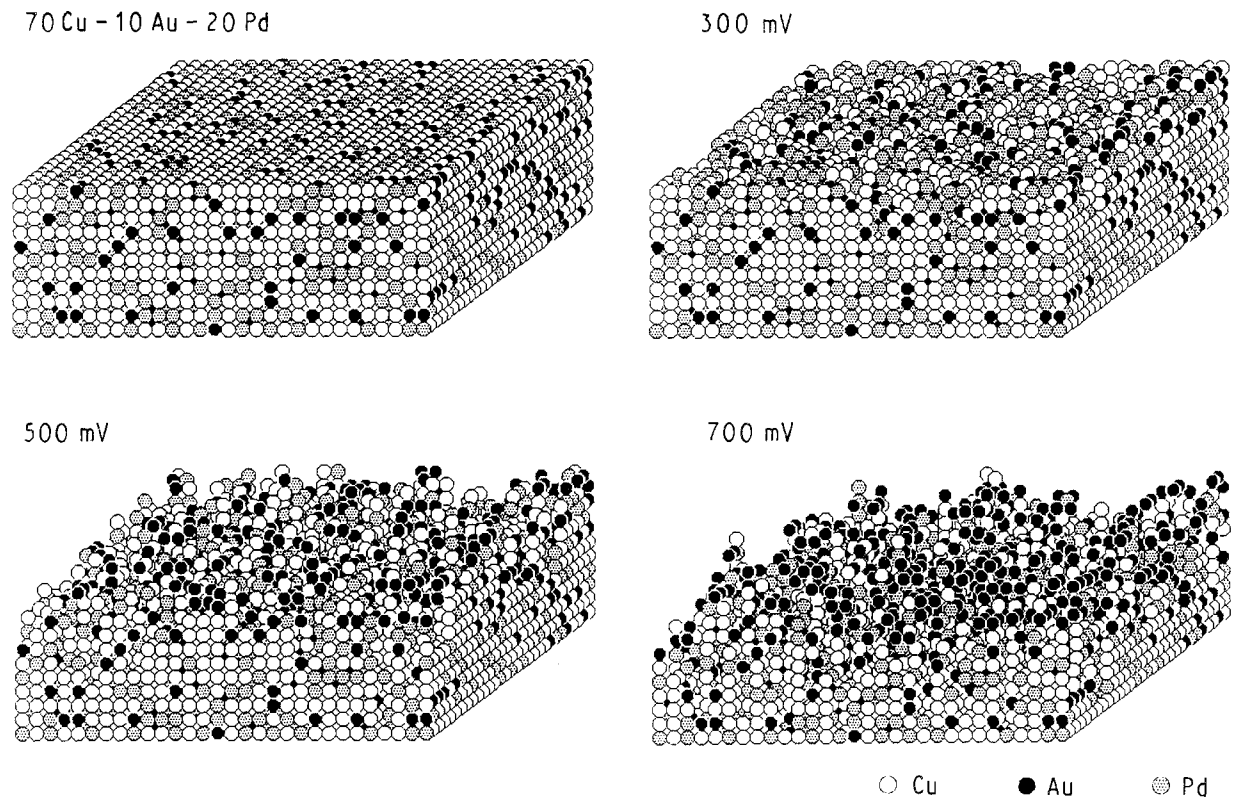


Figure 2 Computer-simulated pictures of anodic dissolution of the 70Cu-10Au-20Pd alloy polarized at various potentials.

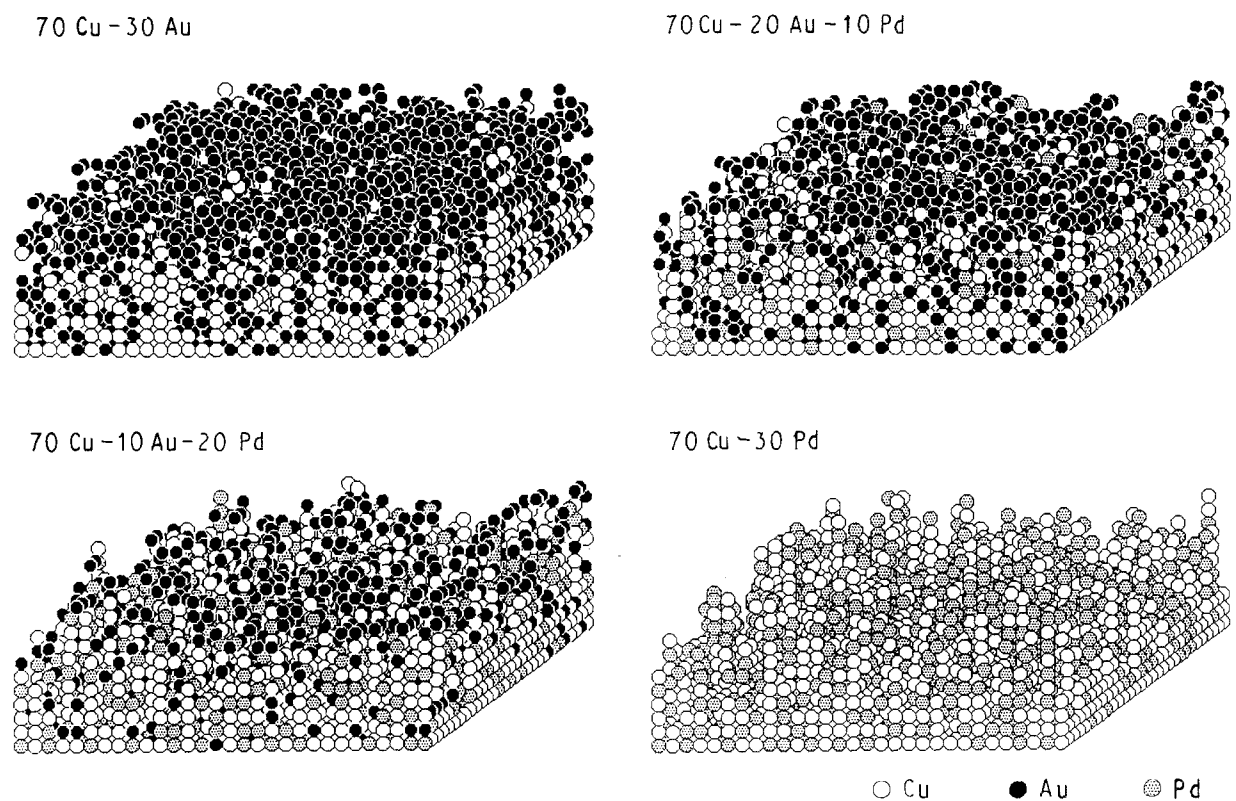


Figure 3 Computer-simulated pictures of anodic dissolution of various alloys polarized at 700 mV.

can be seen that the amount of Cu and Pd dissolved becomes larger as the polarization potentials become higher (note the difference in scale of the vertical axis in each figure).

At the polarization potential of 300 mV, the simulation result shows that the amount of Cu dissolved decreases as the Pd content increases (Fig. 4a). We can

consider two retarding effects on the dissolution of Cu. One is the atomic interaction between Cu atoms and Au or Pd atoms. The other is a surface covering by noble elements such as Au and Pd. At this potential, both Au and Pd atoms do not dissolve and they remain on the alloy surface. Therefore, the retarding effect on Cu dissolution due to covering with Au

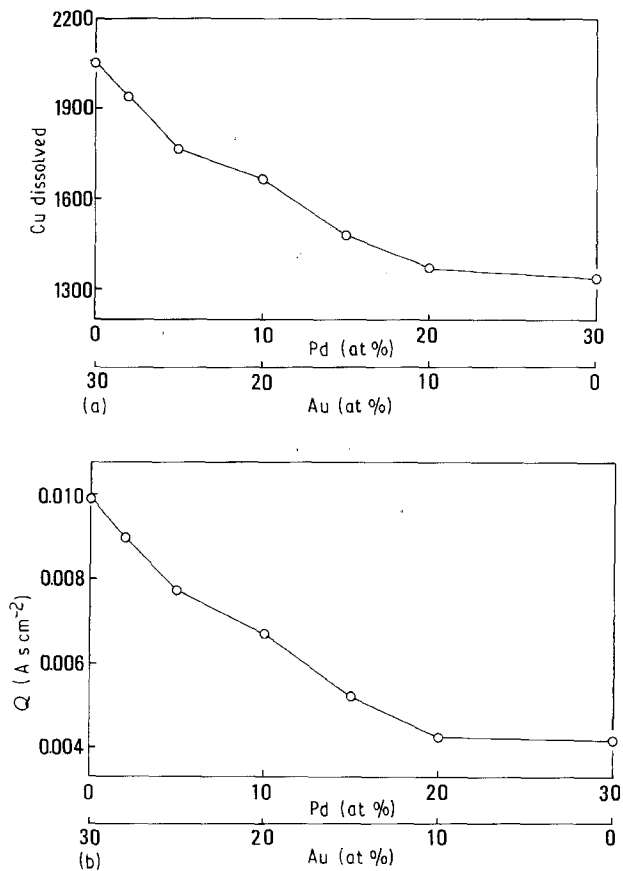


Figure 4 Changes in the amount of Cu dissolved and the Q value with Pd content. (a) Simulation of polarization at 300 mV: $p(\text{Cu-Cu}) = 0.23$, $p(\text{Cu-Au}) = 0.16$, $p(\text{Cu-Pd}) = 0.10$, $p(\text{Pd}) = 0$. (b) Potentiostatic polarization test at 300 mV for 10 min.

and Pd atoms should be constant at any composition (the total content of Au and Pd is kept constant at 30 at %). The amount of Cu dissolved was decreased by replacing Au with Pd because the atomic interaction of Pd with Cu was greater than that of Au.

At the polarization potential of 500 mV, the amount of Cu and Pd dissolved is almost unchanged up to 20 at % Pd and increases at 30 at % Pd (Fig. 5a). The retarding effect due to atomic interaction of Pd with Cu increases as the Pd content increases, as already described. At this potential, however, the retarding effect cannot be expected to be as much as at 300 mV because the Pd atoms dissolve at a prescribed dissolution probability $p(\text{Pd}) = 0.15$. The dissolution of Pd also decreases the retarding effect of covering the alloy surface with Au and Pd atoms because of the decreasing Au content. Therefore, it is suggested that the amount of Cu and Pd dissolved was kept nearly constant with increasing Pd content to 20 at % Pd as a result of an adverse effect of the decrease in surface covering and the atomic interaction of Pd with Cu. The amount of Cu and Pd dissolved increased in the 30 at % Pd alloy because this alloy did not contain the Au atom which had a retarding effect due to covering on the dissolution of Cu.

Fig. 6a shows the result of simulation at 700 mV. This result is substantially the same as the result at 500 mV except that the amount of Cu and Pd dissolved decreases in the 5 to 15 at % Pd alloys. It is

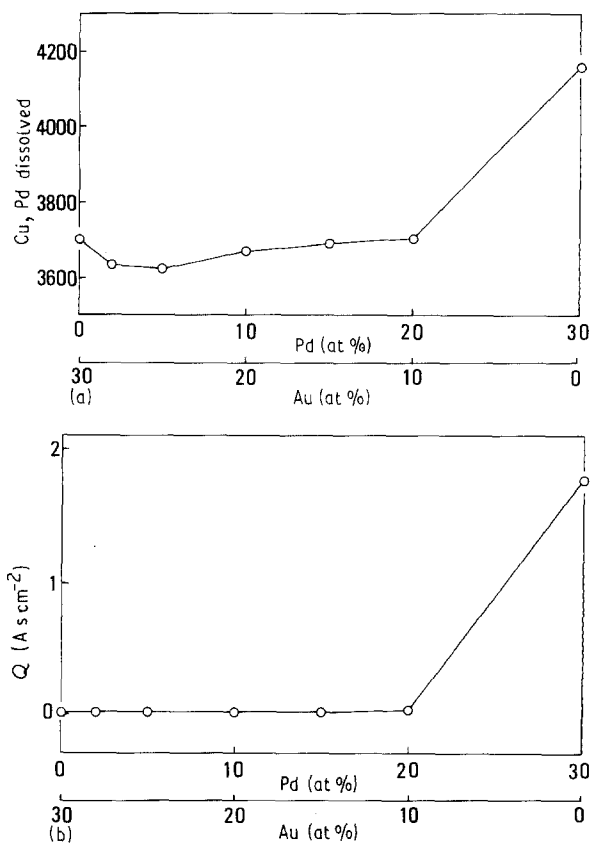


Figure 5 Changes in the amount of Cu and Pd dissolved and the Q value with Pd content. (a) Simulation of polarization at 500 mV: $p(\text{Cu-Cu}) = 0.40$, $p(\text{Cu-Au}) = 0.27$, $p(\text{Cu-Pd}) = 0.18$, $p(\text{Pd}) = 0.15$. (b) Potentiostatic polarization test at 500 mV for 10 min.

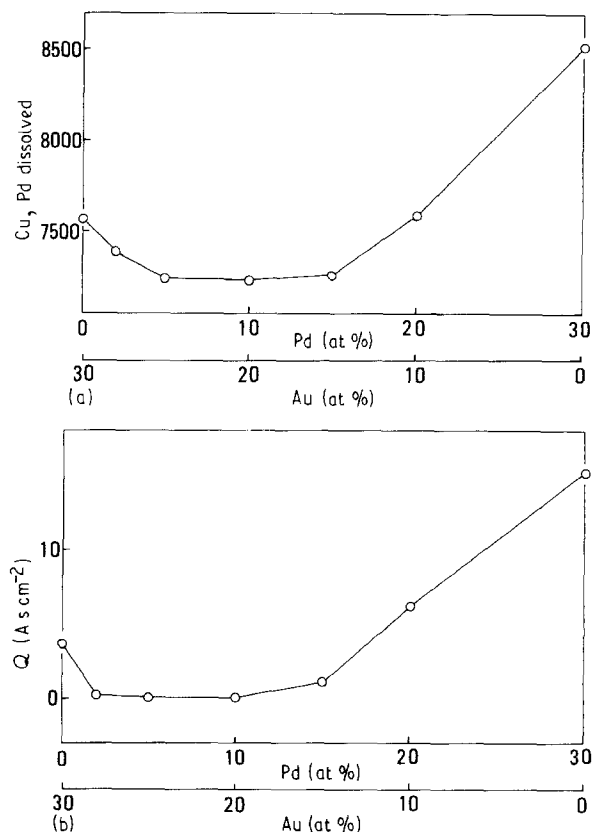


Figure 6 Changes in the amount of Cu and Pd dissolved and the Q value with Pd content. (a) Simulation of polarization at 700 mV: $p(\text{Cu-Cu}) = 0.70$, $p(\text{Cu-Au}) = 0.47$, $p(\text{Cu-Pd}) = 0.32$, $p(\text{Pd}) = 0.28$. (b) Potentiostatic polarization test at 700 mV for 10 min.

thought that the retarding effect of Pd on Cu dissolution appears notably by replacing a part of the Au with Pd, because there is a large difference between p (Cu–Cu) and p (Cu–Pd) at this potential.

Figs 4b, 5b and 6b show the variation of Q values with alloy composition obtained from anodic potentiostatic polarization tests at 300, 500 and 700 mV for 10 min, respectively. The experimental results qualitatively fitted the simulation results.

3.3. Atomic concentration depth profile of the constituents after dissolution

The atomic concentration depth profiles of the constituents after the simulation of anodic dissolution were obtained from the fractions of the number of Cu, Au and Pd atoms in each layer from 4th to 11th. The depth profile data from 1st to 3rd layers were excluded because few atoms remained in these layers after the simulation of anodic dissolution.

Figs 7a and 8a show the atomic concentration depth profiles of the constituents in 70Cu–25Au–5Pd and 70Cu–10Au–20Pd alloys, respectively, after the simulation at 700 mV. In both alloys, it can be seen that enrichment of Au and depletion of Cu take place in the vicinity of the alloy surface. The concentration of Pd was almost constant from the surface to the inside of the alloy. If the alloy is polarized at a lower potential than the potential at which Pd can be dissolved, the surface enrichment of Pd will occur [13].

Figs 7b and 8b show, respectively, the experimental results obtained by ESCA analysis in the 70Cu–25Au–5Pd alloy after polarization at 700 mV

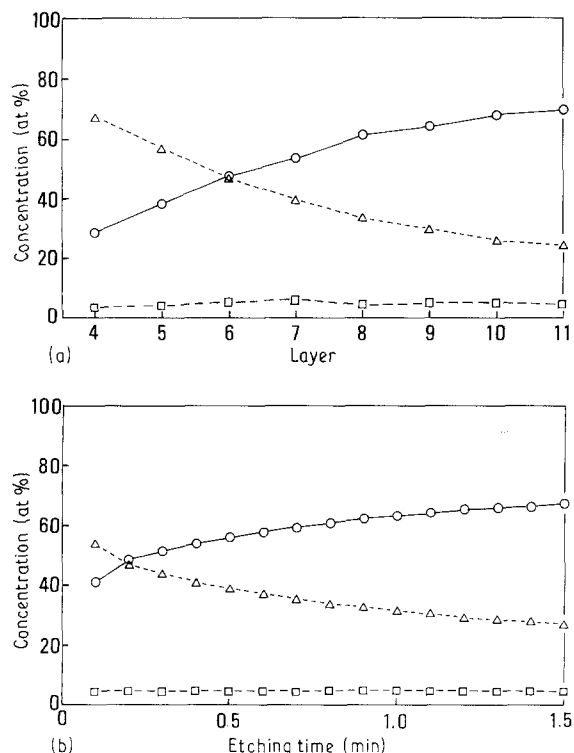


Figure 7 Atomic concentration depth profiles of constituents in the 70Cu–25Au–5Pd alloy: (○) Cu, (△) Au, (□) Pd. (a) Simulation of polarization at 700 mV: p -(Cu–Cu) = 0.70, p -(Cu–Au) = 0.47, p -(Cu–Pd) = 0.32, p -(Pd) = 0.28. (b) Potentiostatic polarization test at 700 mV for 10 min.

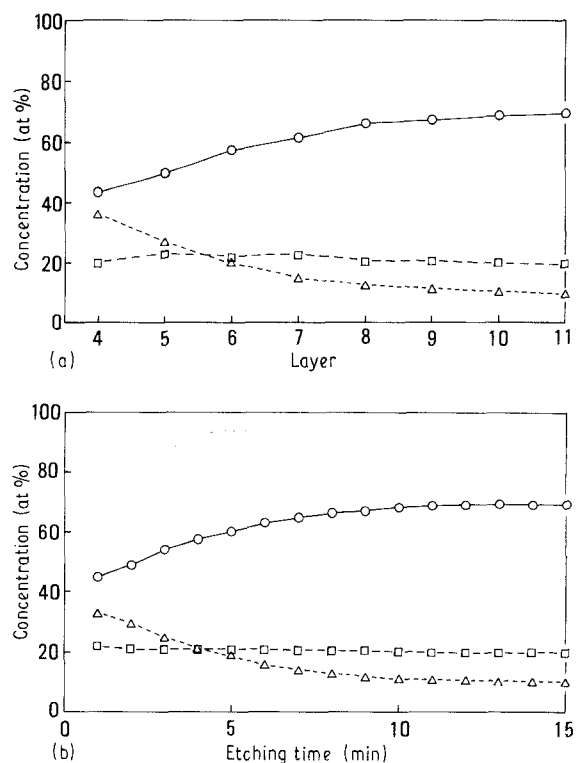


Figure 8 Atomic concentration depth profiles of constituents in the 70Cu–10Au–20Pd alloy: (○) Cu, (△) Au, (□) Pd. (a) Simulation of polarization at 700 mV: p -(Cu–Cu) = 0.70, p -(Cu–Au) = 0.47, p -(Cu–Pd) = 0.32, p -(Pd) = 0.28. (b) Potentiostatic polarization test at 700 mV for 10 s.

for 10 min and the 70Cu–10Au–20Pd alloy after polarization at 700 mV for 10 s. The atomic concentration depth profiles of the constituents after potentiostatic polarization were qualitatively in good agreement with those of the simulation of anodic dissolution.

4. Conclusion

The anodic dissolution process of the $\text{Cu}_{0.7}\text{Au}_{0.3-x}\text{Pd}_x$ ($x = 0-0.3$) alloys was studied by computer simulations, taking into account the atomic interaction energy in the alloys. The results of simulation qualitatively reproduced the experimental results of anodic potentiostatic polarization tests regarding the dependence of the anodic dissolution behaviour on the polarization potential and alloy composition, and the atomic concentration depth profile of the constituents after anodic polarization. Atomic interaction among the constituents of alloys was found to be one of the important factors which controlled the anodic dissolution features of the alloys.

References

1. G. HULTQUIST and H. HERO, *Corros. Sci.* **24** (1984) 789.
2. H. W. PICKERING, *ibid.* **23** (1983) 1107.
3. H. W. PICKERING and C. WAGNER, *J. Electrochem. Soc.* **114** (1967) 698.
4. A. J. FORTY and P. DURKIN, *Phil. Mag. A* **42** (1980) 295.
5. A. J. FORTY and G. ROWLANDS, *ibid.* **43** (1981) 171.
6. K. SIERADZKI, R. R. CORDERMAN, K. SHUKLA and R. C. NEWMAN, *ibid.* **59** (1989) 713.

7. SONG QIAN, R. C. NEWMAN, R. A. COTTIS and K. SIERADZKI, *J. Electrochem. Soc.* **137** (1990) 435.
8. K. NAKAHIGASHI and M. KOGACHI, *Jpn. J. Appl. Phys.* **18** (1979) 1915.
9. S. MATSUMURA, T. MORIMURA and K. OKI, in Proceedings of 12th International Congress on Electron Microscopy, Seattle, (1990) p. 488.
10. R. KUMAR, C. J. SPARKS, T. SHIRAISHI, E. D. SPECHT, P. ZSCHACK, G. E. ICE and K. HISATSUNE, *Mater. Res. Soc. Symp. Proc.* **213** (1991) 369.
11. K. MAEDA and S. TAKEUCHI, *Phys. Status Solidi (a)* **49** (1978) 685.
12. M. OHTA, S. MATSUYA and M. YAMANE, *J. Mater. Sci.* **21** (1989) 951.
13. J. GNIEWEK, J. PEZY, B. G. BAKER and J. O'M. BOCKRIS, *J. Electrochem. Soc.* **125** (1978) 17.

*Received 17 September 1991
and accepted 9 July 1992*