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Decahedral and icosahedral Cu-Au alloy particles grown under a controlled-potential region in acid solutions

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Decahedral and icosahedral Cu-Au alloy particles have been formed by electrochemical deposition of Cu and Au in perchloric acid and sulfuric acid solutions at electrode potentials where formation of decahedron and icosahedron Au particles has not been previously observed. This observation is thought to occur due to a contraction of the Au overlayer, induced by the presence of an incompletely discharged Cu^+ ion deposited on the Au overlayer of the alloy particles in the underpotential deposition region of Cu. This phenomenon is therefore analogous to the alkali-metal-induced reconstruction of Au surfaces. However, decahedral and icosahedral Cu-Au alloy particles were not observed in the Cu-Au alloy particles when the Cu content of the alloy exceeded 30%. It is known that the topmost layer of the reconstructed Au(111) surface is contracted by about 4% and that the lattice spacing of the Cu-Au alloy containing 30% Cu is shortened by about 3% with respect to the Au bulk lattice. Therefore, the lattice mismatch between the Au overlayer and the substrate of Cu-Au alloy particles containing more than 30% Cu is small enough so that no decahedral and icosahedral particles are formed. [S0163-1829(97)03520-0]

INTRODUCTION

Decahedral and icosahedral fine Au particles produced by evaporation and deposition in ultrahigh vacuum were first observed by Mihama and Yasuda.[1] The particles were then analyzed by Ino[2] and Ino and Ogawa[3] who designated them ‘‘multiply twinned particles’’ (MTP’s). Since then, many other fcc metals such as Ag, Ni, Cu, and Pd have also been found to form fine particles with decahedral or icosahedral geometry under similar conditions.[4–9] In another study, we found similar particle geometry for Au,[10–12] Pt,[13] and Ag (Ref. 14) prepared by electrodeposition in solution. However, we are not aware of any paper describing decahedral and icosahedral particles of bimetal alloys. In the present work, we report the formation of decahedral and icosahedral particles of Cu-Au alloy by means of codeposition of Au and Cu on an amorphous carbon electrode in the underpotential deposition region of Cu^{2+} in acid solutions.

It is well known that each of the three low-index surfaces of Au undergoes reconstruction in a vacuum,[15] where Au atoms are arranged in higher-packing density than the corresponding (1×1) surface. It is supposed[16–18] that the higher the sp electron density between the surface atoms, the stronger the in-plane sp bonding, which favors the more densely packed reconstructed state. In fact, it was found[19–23] that the adsorption of alkali metal at coverage lower than 0.3 induces a surface reconstruction of Au single crystal. Here, the electrons are thought to be donated from alkali-metal adatoms to the Au surface, so that the surface sp electron density is increased, inducing the reconstruction to a higher-packing density. The reconstruction of Au(100), Au(110), and Au(111) surfaces also occurs in solution when the Au surfaces are polarized by applying a negative electrode potential.[24–27] As the electrode potential is increased, the in-plane sp bonding is weakened by a decrease in the electron density,[18] lifting the reconstruction.

In our experiment, decahedral and icosahedral Cu-Au alloy particles were formed when Cu and Au were simultaneously electrodeposited and when the Cu content in Cu-Au alloy particles was lower than 30%. It has been reported[28–33] that the Cu^{2+} ion deposited in the underpotential deposition region of Cu^{2+} is incompletely discharged and takes an intermediate Cu^+_{int} state on the pure Au surface:

$$Cu^{2+}+e^-\rightarrow Cu^+_{\text{int}}. \tag{1}$$

Deposition of Cu^+ on the pure Au surface is similar to the deposition of alkali metal on an Au surface where the alkali-metal induced reconstruction occurs. While Cu^+ ion stays on the surface of Au particles by the underpotential deposition of Cu^{2+}, the Au outer layer will prefer to take a hexagonal arrangement. That is, the deposition of Cu^+ induces a contraction of the Au interatomic distance, resulting in the formation of the decahedral and icosahedral particles of Cu-Au alloy.

EXPERIMENT

The Cu-Au alloy particles were electrodeposited on an amorphous carbon film at controlled potentials in the underpotential deposition region of Cu^{2+}. A three-compartment electrochemical cell was employed at room temperature with Pt wire counter electrode. The carbon film was evaporated on a collodion film supported by an Au mesh as required for viewing in a transmission electron microscope (TEM). All electrode potentials were measured by a saturated calomel electrode (SCE). Electrolytes were prepared from $HClO_4$ (60% solution), H_2SO_4 (97% solution) (Wako), HCl (36% solution), $HAuCl_4$ (99%) (Kanto), $Cu(ClO_4)_2$ (98%), $CuSO_2\cdot 5H_2O$ (99.999%), Cu_2Cl (99%) (Aldrich), and triply distilled water. The Cu-Au alloy particles grown were observed by a Hitachi-9000 high-resolution TEM. The composition of the Cu-Au alloy particles was determined by com-

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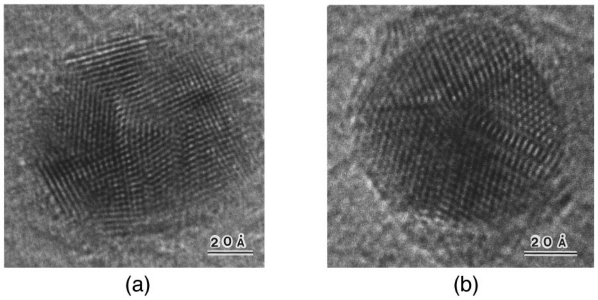

FIG. 1. Typical images of (a) an icosahedral Cu-Au alloy particle consisting of Au 80% formed in $0.1M$ $HClO_4$ $+10^{-3}M$ $HAuCl_4+10^{-3}M$ $Cu(ClO_4)_2$ solution at 0.1 V vs SCE. (b) A decahedral Au-Cu alloy particle consisting of Au 70% formed in $0.1M$ $HClO_4+10^{-3}M$ $HAuCl_4+50\times10^{-3}M$ $Cu(ClO_4)_2$ solution at 0.1 V vs SCE.

parison of data reported by Person[34] with the lattice constants of the Cu-Au alloy particles obtained by measuring the Debye-Scherrer rings of Cu-Au alloy measured with a Hitachi-700 TEM.

RESULTS AND DISCUSSION

In our previous paper[10] it was found that octahedral fcc single-crystal particles of Au are formed by the electrochemical deposition of Au ion at about 0.3 V vs SCE, decahedral Au particles are predominantly formed below 0.05 V vs SCE, and icosahedral Au particles are formed on the electrode below -0.3 V vs SCE in $10^{-3}M$ $HAuCl_4$ containing perchloric acid solution. In this paper, we found the formation of decahedral Cu-Au alloy particles [Fig. 1(b)] by electrochemical codeposition of Cu and Au between 0.3 V and 0.1 V vs SCE, and icosahedral Cu-Au alloy particles [Fig. 1(a)] at 0.2 V and 0.1 V vs SCE. The alloying of the particles is demonstrated in Fig. 2, where Debye-Scherrer rings of the Cu-Au alloy particles prepared in $HAuCl_4$ and $Cu(ClO_4)_2$ containing perchloric acid solution are compared with those for Au particles prepared in Cu^{2+} free solution. It should be noted that neither decahedral nor icosahedral particles of pure Au form at these electrode potentials [see Fig. 3(a)]. Due to Cu-Au alloying during the deposition, the contours of Cu-Au alloy particles [Fig. 3(b)] are different with those of Au particles [Fig. 3(a)]. These alloy particles are MTP's. The applied electrode potentials and the concentrations of Cu^{2+} employed are listed in Table I. The lattice constant of Cu-Au alloy particles grown in solution with different concentration of Cu^{2+} at different electrode potential can be calculated by measuring the Debye-Scherrer rings of the Cu-Au alloy particles. The compositions of these alloy particles were obtained by comparing the calculated lattice constants with standard data for the Cu-Au alloy.[34] For convenience, these data are included in Table I. The lattice constant of Cu-Au alloy particles varies with the composition of Cu-Au alloy particles such that the lattice distance is diminished as the Cu content increases in the Cu-Au alloy particles.

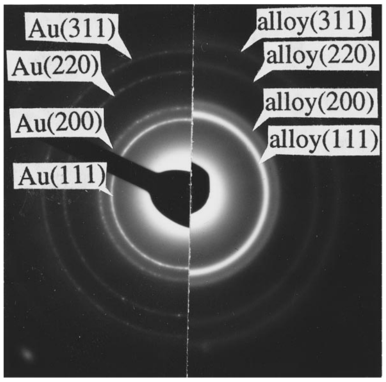

FIG. 2. A typical example of the comparison of electron diffraction Debye-Scherrer rings of Au particles grown in $0.1M$ $HClO_4+10^{-3}M$ $HAuCl_4$ solution at -0.5 V vs SCE (left) and the Cu-Au-alloy particles consisting of Cu 30% formed in $0.1M$ $HClO_4+10^{-3}M$ $HAuCl_4+50\times10^{-3}M$ $Cu(ClO_4)_2$ solution at 0.1 V vs SCE (right).

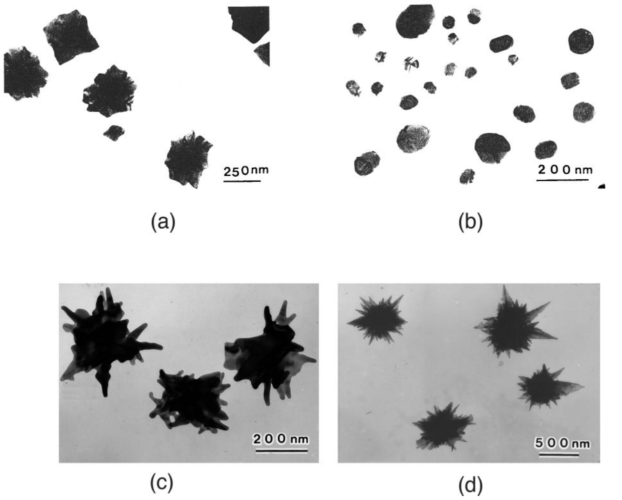

FIG. 3. TEM images of (a) Au particles formed in $0.1M$ $HClO_4+10^{-3}M$ $HAuCl_4$ solution at 0.3 V vs SCE for 60 sec, (b) multiply twinned Cu-Au alloy particles formed in $0.1M$ $HClO_4+10^{-3}M$ $HAuCl_4+0.1M$ $Cu(ClO_4)_2$ solution at 0.3 V vs SCE for 300 sec, where the fraction of Cu in the alloy particles is about 15%, (c) Cu-Au alloy particles formed in $0.05M$ $H_2SO_4+10^{-3}M$ $HAuCl_4+0.1M$ $CuSO_4$ solution at 0.32 V vs SCE for 60 sec, and (d) Cu-Au alloy particles formed in $0.01M$ $HCl+10^{-3}M$ $HAuCl_4+5\times10^{-3}M$ $CuCl_2$ at 0.3 V vs SCE for 60 sec. It is clear that due to the Cu-Au alloying during the deposition, the contours of Cu-Au alloy particles (b) is different from that of Au particles (a) and the influence of coadsorbed $SO_4{}^{2-}$ ion or Cl^- ion makes the habit of the alloy particles [(c) and (d)] different from the alloy particles in (b) and the Au particles in (a).

Decahedron and icosahedron particle surfaces consist of 10 and 20 close-packed (111) faces, respectively. We define L and L^* as the distance between adjacent atomic rows of a fcc (111) face (see Fig. 4). As listed in Table I, L is the calculated value of the grown Cu-Au alloy particles and L^* is the directly measured length from the TEM images of the Cu-Au alloy particles. It can be clearly seen from Table I that the experimental L^* is in good agreement with the calculated L, demonstrating that the particles are indeed alloyed.

We observed decahedral and icosahedral Cu-Au alloy particles only when they contained lower than 30% Cu. By

TABLE I. A list of experiment data and calculation for Au-Cu alloy. $X\times10^{-3}M$ is the concentration of Cu^{2+} in solution. E is the deposition electrode potential vs SCE. a is the lattice constant of Au-Cu alloy particles, calculated by the Debye-Scherrer rings of Au-Cu alloy particles. C_{Au} (%) is the fraction of Au in Au-Cu alloy particles, calculated by the lattice constant a comparing with the diagram by Person (Ref. 34). a^0 is 4.078 6 Å, the lattice constant of Au. L^0 is 2.4976 Å for Au. L is calculated from the formula $[(a/a^0)\times L^0]$ for Au-Cu alloy. L^* is measured from the TEM images of the Au-Cu alloy particles. The illustration of L^0, L, and L^* is shown in Fig. 4.

$0.1M$ $HClO_4+10^{-3}M$ $HAuCl_4+X\times10^{-3}M$ $Cu(ClO_4)_2$							
X	E/V (SCE)	a (Å)	C_{Au} (%)	a/a^0	L (Å)	L^* (Å)	$\lvert L\text{-}L^*\rvert/L$
100	0.3	4.021	84.8	0.986	2.463	2.462	0.04%
	0.2	4.001	80.4	0.981	−2.450	2.449	0.04%
	0.1	3.966	70.3	0.972	2.428	2.424	0.16%
50	0.2	4.005	81.3	0.982	2.453	2.449	0.16%
	0.1	3.970	71.2	0.973	2.430	2.432	0.08%
10	0.1	3.985	76.3	0.977	2.440	2.439	0.04%
5	0.1	3.992	76.7	0.979	2.445	2.439	0.24%
1	0.1	4.000	80.0	0.981	2.450	2.449	0.04%

comparing the lattice constant a of the Cu-Au-alloy particles and the lattice constant a^0 of Au (shown in Table I), one concludes that the lattice distance of the Cu-Au alloy containing Cu 30% is contracted by about 3%.

Decahedral and icosahedral Cu-Au alloy particles formed in sulfuric acid solution were also observed. However, the composition of Cu in the Cu-Au alloy particles grown in this case was lower than that in perchloric acid solution at the same electrode potential. This can be explained by postulating a steric effect due to coadsorbed $SO_4{}^{2-}$ ion, which will be discussed in more detail in another paper.[35]

We also investigated the formation of Cu-Au alloy particles in $0.01M$ $HCl+10^{-3}M$ $HAuCl_4$ solution containing $CuCl_2$, which ranged from $10^{-3}M$ to $0.1M$. However, formation of decahedral or icosahedral alloy particles was not observed under these conditions, and the fraction of Cu in the Cu-Au alloy particles formed in the hydrochloric acid solution was less than 5%. It was pointed out that the adsorption of chloride anions on the growing alloy particles hinders the codeposition of Cu ions.[36] As shown in Figs. 3(c) and 3(d), it can be seen that the effect of coadsorbed $SO_4{}^{2-}$ ion or Cl^- ion with Cu ion on the formation of the alloy particles is remarkable, resulting in a thornylike habit for the alloy particles. In contrast to this result, in a previous paper[12] we showed that there is little influence of $SO_4{}^{2-}$ ion or Cl^- ion on the formation of Au particles at 0.3 V vs SCE. The habit of alloy particles [Fig. 3(b)] formed in perchloric acid solution is different from that of those particles grown both in sulfuric acid and hydrochloric acid solutions. This suggests that chloride contamination, the maximum amount of chloride and chlorate is 10 ppm, in the perchloric acid solution gives no influence on the crystal habit of the alloy particles.

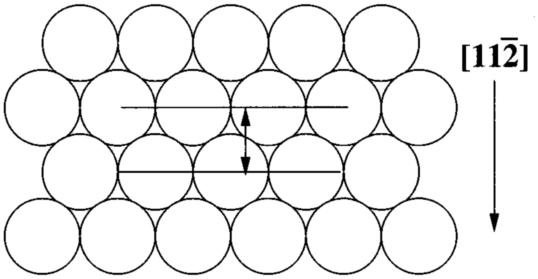

FIG. 4. The two-way arrow indicates the distance between adjacent rows of atoms at a fcc (111) surface along the [112] direction. This distance corresponds to L^0, L, and L^*, respectively (see text and Table I).

It is interesting to ask why the decahedral and icosahedral Cu-Au alloy particles can appear at electrode potentials higher than the critical potentials for the growth of either the decahedral or the icosahedral Au particles, as only fcc Au single crystal particles are typically formed at these high potentials. A possible explanation for this phenomenon is as follows: alloy particle growth is likely to be initiated by the formation of Au nuclei, because in the underpotential deposition region of Cu^{2+} the Cu^{2+} ion cannot be reduced first. The Au nuclei would likely take (111) stacking to minimize the surface free energy. Then, underpotential deposition of the Cu^{2+} ion may occur on the surface of the Au nuclei. The Cu^{2+} ion deposited on the Au layer is not completely discharged to Cu^0, but to the Cu^+ state in the underpotential deposition region as described in Eq. (1). The resulting Cu^+-covered Au surface is analogous to that covered with alkali-metal ion, and the electron density of the Au surface is increased. With increasing electron density at the surface, the surface atoms prefer to take a more densely packed arrangement as discussed in the Introduction, resulting in a shorter interatomic distance for the Au atom overlayer formed on the alloy.

It is known that the outermost layer of a reconstructed Au(111) surface is contracted by about 4% with respect to the bulk, which is responsible for the reconstruction of the low-index Au surfaces. Therefore, only when the lattice constant of the Cu-Au alloy is longer than that of the contracted Au overlayer formed on it can the decahedral or icosahedral alloy particles be formed. In other words, if the contraction of the substrate alloy particles is less than 3%, the Au overlayer formed on it prefers to take a hexagonal arrangement to lower the surface free energy, resulting in the formation of decahedral or icosahedral alloy particles. When the Cu content of Cu-Au alloy particles exceeds 30%, however, the interatomic distance of the substrate alloy shortens more than

3%, which corresponds to an Au overlayer contracted by about 4%. Hence, with only a 1% mismatch between the substrate alloy lattice and the Au overlayer, the Au overlayer simply deposits in the (1×1) stacking of the substrate. Cu-Au alloy particles grow under these conditions result in a normal structure, and decahedral and icosahedral particles of Cu-Au alloy are not formed.

CONCLUSION

We have investigated the formation of decahedral and icosahedral particles of Cu-Au alloy grown in both perchloric acid and sulfuric acid solutions in the underpotential region of Cu. At these electrode potentials, neither the decahedral Au particles nor the icosahedral Au particles appear but only the octahedral fcc structure single-crystal Au particles can form. It is postulated that this phenomenon is induced by an incompletely discharged Cu$^+$ ion deposited on the surface of Au nuclei, which leads to the contraction of surface atoms of Au nuclei. When the composition of Cu in Cu-Au alloy particles exceeded 30%, the decahedral and icosahedral Cu-Au alloy particles were not observed. This may be explained by a negligible contraction of the Au overlayer deposited on the surface of Cu-Au alloy particles, in which case there is no driving force for the formation of the icosahedral and/or decahedral particles.

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