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Textural evolution in electrodeposits under the influence of adsorbed foreign species

Part II *A simulation study on effects of potassium chloride on textural evolution in copper electrodeposits*

D. Y. LI, K. OSSEO-ASARE
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

The texture of copper deposits produced in the bath containing potassium chloride changes with the content of the potassium chloride. This change in texture was usually explained to be caused by chloride adsorption on the cathode. This paper reports simulation studies on textural evolution in copper electrodeposits under the influence of potassium chloride, using a Monte Carlo simulation approach. The study was conducted based on the assumption that the textural development results from the minimization of the system free energy in which the surface-energy anisotropy plays the most important role. The simulation demonstrates that adsorbed potassium ions may change the surface-energy anisotropy of copper, and therefore, they also affect texture variation in copper deposits in addition to the chloride effect. It was observed the potassium effect on textural variation in copper deposits is even stronger than that of the Cl^- adsorption.

1. Introduction

Electrolytes used for copper electrodeposition often contain alkaline metal and chloride ions, such as K^+ and Cl^- dissolved from KCl. It was observed that the texture of copper electrodeposits varied with the concentration of KCl [1]. This phenomenon was usually explained to be caused by adsorbed chloride ions which may change the overpotential for copper deposition [1–3]; the adsorption of CuCl reduces the active surface area and therefore increases the local current density, thus increasing the overpotential and leading to the variation in texture type of copper deposits. However, possible influences of potassium adsorption on the textural variation were ignored. In fact, positively charged K^+ ions are attracted by the cathode more strongly than Cl^- ions. Without giving solid evidence, there is no reason to neglect potassium atoms and their possible effects on texture development. In order to understand better the effect of KCl on textural evolution in copper deposits, it is necessary to investigate the respective effects of potassium adsorption and chloride adsorption on textural evolution in copper deposits.

As discussed in Part I [4], the texture of a deposit may depend on the surface-energy anisotropy of the deposit. This gives us a "clue" to investigate the effects of potassium ions on copper texture by evaluating the effect of K^+ ions on the surface-energy anisotropy of copper. The present paper reports on our studies, using a Monte Carlo simulation approach [4], on the effect of potassium adsorption on copper surface-energy anisotropy and its consequent influence on textural evolution during copper electrodeposition in a bath containing KCl. For a comparison, the effect of chloride on the texture of copper deposits was also studied.

2. Surface-energy anisotropy of copper

As mentioned in Part I [4], the surface-energy anisotropy modifies the "surface bond", and thus leads to selective grain growth. Therefore, the key step towards the understanding of texture formation in copper deposits is to evaluate the anisotropy of surface energy of copper. When foreign species are adsorbed by the cathode, the interaction between the deposit and the adsorbed foreign species may change the surface-energy anisotropy of the deposit, and this could result in changes in texture. In order to investigate the textural evolution in copper deposits and its variation under the influences of potassium and chloride ions, the surface-energy anisotropy of copper and its variation with potassium and chloride adsorption were evaluated.

2.1. Surface-energy anisotropy of copper

Surface-energy anisotropy of copper free from the adsorption of foreign species was first studied. The surface energy of copper has been calculated by a number of researchers using different approaches [5–10]. In general, low-index planes have lower surface energies than high-index planes. However, for low-index planes of copper such as (1 0 0), (1 1 0) and

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(1 1 1) planes, surface energies of these planes evaluated by different researchers are diverse. Caglioti *et al.* [5,6] calculated surface energies of copper using phonon frequencies to deduce interplanar force constants acting between first- and higher-order neighbour plane. Their results show that (1 1 0) plane of copper at 0 K has the lowest surface energy, followed by (1 0 0) and (1 1 1). However, results obtained, respectively, by Tyson [7] and Sun *et al.* [8] show that the (1 0 0) has the lowest surface energy, followed by (1 1 0) and (1 1 1), or by (1 1 1) and (1 1 0). Smith and Banerjea [9] applied the perturbation theory to estimate the surface energy of copper, and demonstrated that the (1 1 1) plane of copper has the lowest surface energy, followed by (1 1 0) and (100). The calculation made by Wolf [10] also shows that the (1 1 1) plane has the lowest surface energy, but followed by (1 0 0) and then (1 1 0) planes. These calculations, however, were made for copper only at 0 K, and therefore the results may not be suitable for evaluating the surface-energy anisotropy of copper at the deposition temperature which is usually about 333 K (i.e. 60 °C).

In view of the diversity in calculation of copper surface-energy anisotropy, and the lack of the information about copper surface energy at the bath temperature for copper deposition (about 60 °C), we evaluated surface energies of a number of crystallographic planes of copper at 60 °C, using the following approach with the Lennard–Jones potential [11]:

$$\varphi(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{1}$$

where r is the distance between atoms i and j, and $\varphi(r_{ij})$ represents the interaction potential energy of the atoms i and j. The parameter ε represents the depth of the potential at the minimum, and σ is the closest distance at which $\varphi(r_{ij})$ is equal to zero. ε/k_B (K) and σ (nm) of copper are 4750 and 0.2338, respectively [11]. The surface energy of a crystallographic plane $(h\,k\,l)$ is defined as the difference in free energy between the surface and middle layers of the crystal, which are parallel to the $(h\,k\,l)$ plane. Because the electrodeposition is usually performed at about 60 °C, the free energy is approximated by counting only the configuration energy, neglecting the entropy contribution which may not be neglected at elevated temperatures. To evaluate the surface energy, a cubic cell having a dimension of $3.0 \times 3.0 \times 1.5$ nm^3 and containing about 1150 copper atoms was constructed. The surface layer of the cell was then relaxed at $T = 333$ K. The surface relaxation is necessary, because when a crystal is split into two parts and forms two fresh surfaces, the atoms on the surfaces do not stay in their original positions and must shift to new positions, otherwise the surfaces will not have a thermal-equilibrium configuration. During the relaxation process, each atom in the surface region was allowed to move randomly by a short distance. If the initial configuration energy is defined as E_1 and the new configuration energy after the shift is defined as E_2, each move is accepted with the probability

$$\begin{cases} P = 1 & \text{if } E_2 < E_1 \\ P = \exp[-(E_2 - E_1)/k_B T] & \text{if } E_2 > E_1 \end{cases} \tag{2}$$

where k_B is the Boltzmann constant and T the temperature. After the relaxation, the energy of a surface layer (0.4 nm thick) and that of a non-relaxed central layer with the same thickness, were calculated. The difference between these two energies gives the surface energy of the plane under study. The layer of 0.4 nm thick for the surface energy calculation was chosen, because the interaction between a pair of atoms declines with an increase in the distance between the two atoms. In addition, the interaction between nearest neighbour atoms may contribute about 90% of the system's energy. Because the chosen layers of 0.4 nm thick contain the nearest and the second nearest neighbour atoms, they should be good enough to be used for evaluating the surface energy. Fig. 1 illustrates the result of the calculation, from which it can be seen that the (1 1 0) plane has the lowest surface energy.

2.2. Effects of K$^+$ and Cl$^-$ adsorption on the surface-energy anisotropy of copper

When K$^+$ and Cl$^-$ ions are adsorbed by a copper surface, the energy of the surface could be changed. Because different crystallographic planes could have different adsorption abilities, this difference may result in changes in the surface-energy anisotropy. In order to study effects of KCl on texture of copper deposits, surface energies of copper crystallographic planes under the influence of K$^+$ as well as Cl$^-$ adsorption were evaluated using an approach similar to that used to calculate the surface energy of copper free from the adsorption of foreign species. In order to study the adsorption of K$^+$ and Cl$^-$ on a copper surface, potentials for Cu–K$^+$ and Cu–Cl$^-$ interactions are needed. In this work, these potentials are assumed, as an approximation, to have the same form as the Lennard–Jones 12-6 effective pair potential. The interaction between different species was approximated using the Lorentz–Berthelot mixing rule [12]

$$\sigma_{A-B} = \tfrac{1}{2}(\sigma_{A-A} + \sigma_{B-B})$$

$$\varepsilon_{A-B} = [(\varepsilon_{A-A}\,\varepsilon_{B-B}]^{1/2} \tag{3}$$

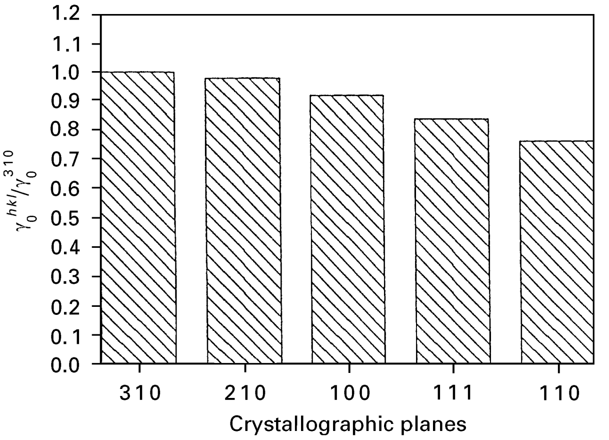

Figure 1 The surface-energy anisotropy of copper. γ_0^{hkl} represents the surface energy of a surface free from the adsorption of foreign species.

However, ε and σ parameters for potassium and chlorine available in the literature are only for potassium and chlorine atoms rather than ions, it is therefore necessary to modify the values of these parameters and make them suitable for K^+ and Cl^- ions. These parameters may be modified by considering the interaction between a pair of K^+ and Cl^- ions. Allowing for the mutual attraction caused by a pair of negative and positive electrons, respectively, from Cl^- and K^+, the ε and σ parameters, respectively, for potassium and chlorine atoms were modified by adding correction terms such as:

$$\sigma_K^+ \text{ is substituted by } \sigma_K + \Delta\sigma/2$$

$$\varepsilon_K^+ \text{ is substituted by } \varepsilon_K + \Delta\varepsilon/2$$

$$\sigma_{Cl^-} \text{ is substituted by } \sigma_{Cl} + \Delta\sigma/2$$

$$\varepsilon_{Cl^-} \text{ is substituted by } \varepsilon_{Cl^-} + \Delta\varepsilon/2$$

In order to estimate $\Delta\sigma$ and $\Delta\varepsilon$, the above-modified σ and ε parameters were used to construct the LJ potential $\varphi_{Cl^- - K^+}$ for a pair of Cl^- and K^+ ions, using the Lorentz–Berthelot mixing rule. The potential was then used to calculate the inter-atomic distance of KCl in equilibrium by letting the derivative of $\varphi_{Cl^- - K^+}$ equal to zero, that is

$$\frac{\partial \varphi_{Cl^- - K^+}}{\partial r} = 4\varepsilon_{Cl^- - K^+} \left[12 \left(\frac{\sigma_{Cl^- - K^+}}{r} \right)^{11} \left(-\frac{1}{r^2} \right) - 6 \left(\frac{\sigma_{Cl^- - K^+}}{r} \right)^{5} \left(-\frac{1}{r^2} \right) \right] \sigma_{Cl^- - K^+} = 0 \quad (4)$$

The following relationship is then obtained

$$\sigma_{Cl^- - K^+} = \frac{1}{2} (\sigma_{Cl-Cl} + \sigma_{K-K} + \Delta\sigma) = \left(\frac{1}{2} \right)^{1/6} r_0 \quad (5)$$

where r_0 is the equilibrium distance between a pair of Cl^- and K^+ ions. The correction term $\Delta\sigma$ was thus obtained by substituting available data of r_0 [13], σ_{Cl-Cl} and ε_{Cl-Cl} [12], and σ_{K-K} and ε_{K-K} [11] into Equation 5. The value of $\Delta\varepsilon$ was estimated by comparing the configuration energy of the KCl lattice calculated using the potential $\varphi_{Cl^- - K^+}(r)$ with available data of the lattice energy of KCl obtained using other methods [14]. In such a way, values of the modified σ and ε parameters, respectively, for Cl^- and K^+ ions were obtained. Combining these parameters with ε_{Cu} and σ_{Cu} [11] by using the Lorentz–Berthelot mixing rule, we finally obtained the estimated ε and σ values for the LJ potentials of Cu–K^+ and Cu–Cl^-, respectively. They are ε_{Cu-K^+}/k_B (K) $= 1.60 \times 10^4$, $\sigma_{Cu-K^+} =$ 0.2805 (nm), $\varepsilon_{Cu-Cl^-}/k_B$ (K) $= 1.57 \times 10^4$, and $\sigma_{Cu-Cl^-} = 0.2337$ (nm).

Once the ε and σ parameters were determined, the effect of K^+ as well as Cl^- on surface energy of copper can be evaluated. In the case of K^+ adsorption, a certain number of potassium ions were randomly placed into the vicinity of the copper cell surface which was under investigation. The potassium ions and copper atoms in the surface region were then relaxed. After the relaxation, the energy of the surface layer (0.4 nm thick) was calculated. The difference in configuration energy between the relaxed surface layer and a non-relaxed central layer of equal thickness represents the surface energy under the influence of adsorbed potassium ions. Fig. 2 illustrates the effect of potassium adsorption on surface energies of several low-index copper crystallographic planes. It is demonstrated that surface energies of copper decrease with an increase in the concentration of potassium ions. The slope of the curve of the surface energy versus K^+ concentration is different for different crystallographic planes, thus leading to a variation in the surface-energy anisotropy. In particular, the plane having the lowest surface energy changes from {1 1 0} to {1 1 1} plane as the K^+ concentration is increased.

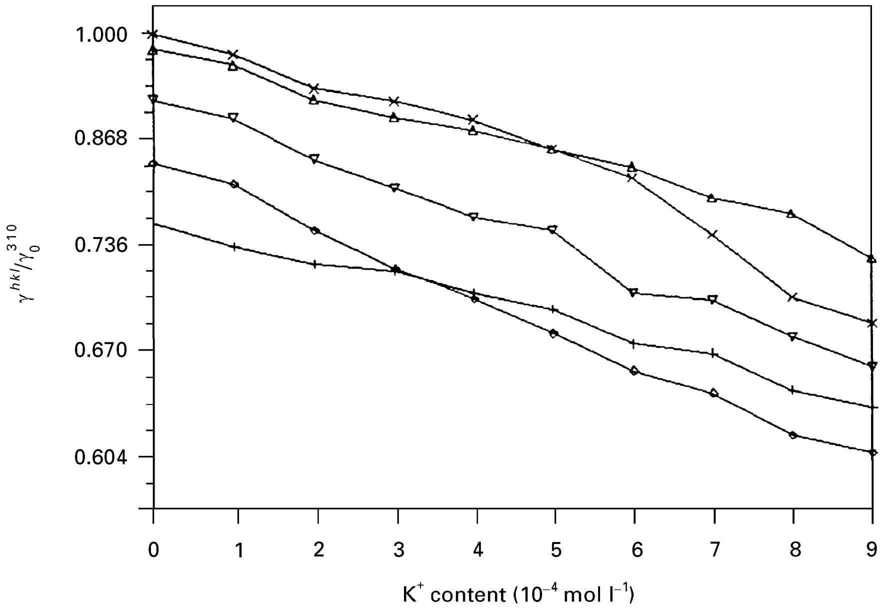

Figure 2 Variations in the surface energy of copper and its anisotropy with an increase in K^+ content. (+) (1 1 0), (◇) (1 1 1), (▽) (0 0 1), (△) (2 1 0), (×) (3 1 0).

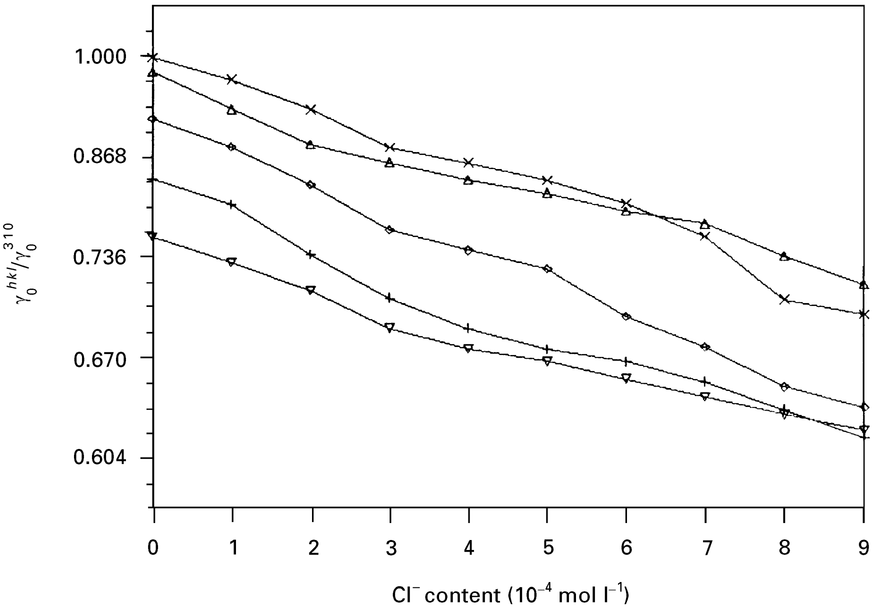

Figure 3 Variations in the surface energy of copper and its anisotropy with an increase in $\mathrm{Cl^-}$ content. (▽) (1 1 0), (+) (1 1 1), (◇) (0 0 1), (△) (2 1 0), (×) (3 1 0).

In a similar way, the effects of chloride ions on copper surface energy and its anisotropy were evaluated. Fig. 3 illustrates results of the calculation. The figure illustrates that the copper surface energy is also influenced by chloride adsorption. Under the influence of chloride ions, copper surface energy decreases and the variation in surface-energy anisotropy is similar to that caused by potassium ions. Compared with the potassium adsorption, the chloride effect is slightly weaker and it can be seen from Fig. 3 that the critical $\mathrm{Cl^-}$ concentration is higher than the $\mathrm{K^+}$ concentration at which the plane having the lowest surface energy changes from $\{1\,1\,0\}$ to $\{1\,1\,1\}$. This implies that more $\mathrm{Cl^-}$ ions are needed than $\mathrm{K^+}$ ions to cause the change in index of the plane with the lowest surface energy.

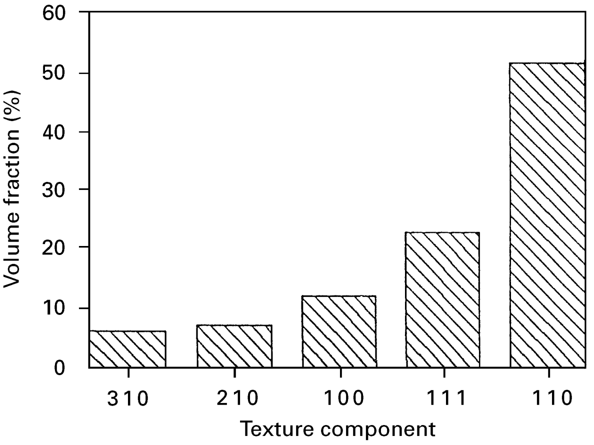

Figure 4 Volume fractions of various texture components of copper electrodeposit.

3. Simulation results of textural evolution during copper electrodeposition

Five surface energies of copper were chosen to simulate the development of five fibre texture components in copper electrodeposits. The percentage of the number of differently oriented sites was counted to represent intensities of various texture components. The simulation result of texture formation free from ion adsorption is illustrated in Fig. 4. It is demonstrated that grains having lower surface energies have higher counts (or higher volume fractions). The $\langle 1\,1\,0\rangle$ fibre texture component, which corresponds to the lowest surface energy in the free-adsorption condition, is the strongest. From the simulation, one may expect that the predominant texture component in copper is the $\langle 1\,1\,0\rangle$ fibre texture.

The influence of potassium ions on texture evolution in copper deposits was simulated as a consequence of the changes in surface-energy anisotropy of copper caused by adsorbed potassium ions. Fig. 5 presents the simulation result and illustrates that the predominant texture component changes from $\langle 1\,1\,0\rangle$ to $\langle 1\,1\,1\rangle$ with an increase in the concentration of potassium ions. Compared with the surface-energy anisotropy illustrated in Fig. 2, one may see the coincidence between the deposit texture and the index of the crystallographic plane having the lowest surface energy. The effects of chloride ions on copper deposit texture were also studied. It is shown by Fig. 6 that the effect of chloride adsorption on copper deposit texture is similar to that of potassium adsorption. However, the critical concentration of $\mathrm{Cl^-}$ at which the predominant texture component changes from $\langle 1\,1\,0\rangle$ to $\langle 1\,1\,1\rangle$ is relatively higher than that of $\mathrm{K^+}$ ions. This difference in the critical concentration is consistent with the changes in surface-energy anisotropy (i.e. the changes of the lowest-energy plane), respectively, caused by $\mathrm{Cl^-}$ and $\mathrm{K^+}$ ions.

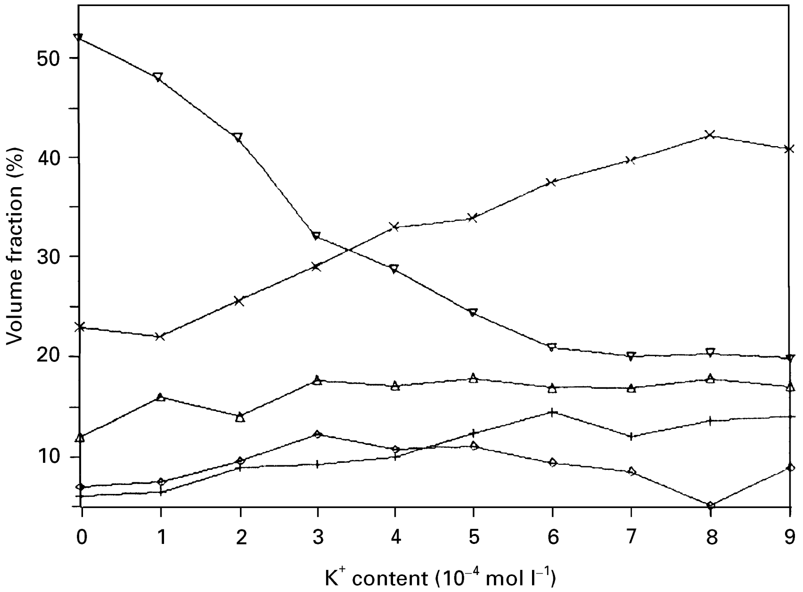

Figure 5 The axis of the predominant fibre texture component of copper deposit changes from ⟨1 1 0⟩ to ⟨1 1 1⟩ with an increase in the content of potassium ions. (▽) (1 1 0), (×) (1 1 1), (△) (0 0 1), (◇) (2 1 0), (+) (3 1 0).

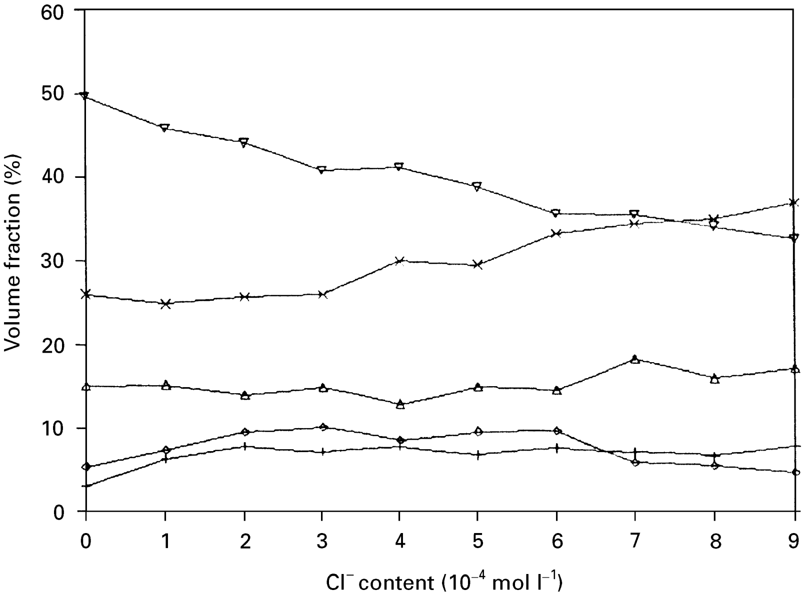

Figure 6 The axis of the predominant ⟨1 1 0⟩ fibre texture component of copper deposit changes to ⟨1 1 1⟩ with an increase in the content of chloride ions. (▽) (1 1 0), (×) (1 1 1), (△) (0 0 1), (◇) (2 1 0), (+) (3 1 0).

The simulation prediction is consistent with experimental observation. O'Keefe and Hurst [1] investigated the textural evolution in copper electrodeposits and its variation with additive potassium chloride, using the X-ray diffraction technique. They demonstrated that a ⟨1 1 0⟩ texture is the predominant texture component in copper electrodeposits without potassium chloride in the electrolyte. By adding potassium chloride into the bath, they observed that the copper deposit texture changed from ⟨1 1 0⟩ to ⟨1 1 1⟩ with increasing concentration of KCl. Their experimental observation agrees with the present simulation prediction, although their explanation of the texture variation due to the potassium chloride is different from that the simulation suggests. A similar phenomenon was also observed by Lakshmanan *et al.* [3] in copper electrodeposits obtained using a bath containing NaCl. They observed that without adding NaCl into the bath and at low current densities (in this case, the discharge or adsorption of other inhibitors may be less active), copper deposits were ⟨1 1 0⟩ textured. The copper texture, however, changed from ⟨1 1 0⟩ to ⟨1 1 1⟩ with increasing concentration of NaCl. Because K^+ and Na^+ ions behaviour similarly, a trend of the texture variation with NaCl similar to that with KCl is expected.

4. Discussion

4.1. Coincidence between the axis of texture and the surface-energy anisotropy

The simulation of copper deposition demonstrates that the copper deposit is ⟨1 1 0⟩ textured when there is no surface adsorption of foreign species; this prediction is consistent with experimental observation [1]. According to the simulation, the formation of $\langle 1\,1\,0 \rangle$ texture is attributable to the surface-energy anisotropy in which the $\{1\,1\,0\}$ plane has the lowest surface energy. This coincidence between the axis of texture and the crystallographic face could be explained. Electrodeposition is a process in which mass transfer is accompanied by charge transfer. When an ion arrives at the cathode surface, it loses its charge and diffuses until it reaches a low-energy location. The low-energy location is the site where the accommodation of the ad-atom results in the minimum increase in the free energy of the system. Therefore, the deposit growth may proceed in the "path" which leads to the minimum increase in the free energy of the system. A major part of the free energy is the surface energy which is crystallographically anisotropic, and hence it may play an important role in texture formation. For example, when arriving at a junction of two grains, an ad-atom tends to be accommodated by one of the grains bounded by the crystallographic plane which has a lower surface energy, thus leading to a decrease in the overall surface energy. As the deposition proceeds, this junction would move towards the grain that has a higher surface energy, and the other grain would therefore grow preferentially.

Reviewing available data, this coincidence between the axis of the texture and the metal face which has the lowest surface energy may also exist in other metal deposition systems. For example, $\langle 1\,1\,0 \rangle$ texture is the predominant texture of iron electrodeposits. As demonstrated Part I [4], the $\{1\,1\,0\}$ crystallographic plane of iron has the lowest surface energy. Another example is given by nickel electrodeposits. $\langle 1\,0\,0 \rangle$ and $\langle 1\,1\,0 \rangle$ fibre textures are two frequently observed textures in nickel electro-deposits [15, 19]. The present authors have also estimated the surface-energy anisotropy of nickel and observed that the $\{1\,0\,0\}$ plane of nickel has the lowest surface energy, followed by the $\{1\,1\,0\}$ plane. The coincidence between texture and surface-energy anisotropy is further favoured by some indirect experiments. In previous studies [17, 18], it was suggested that the $\langle 1\,0\,0 \rangle$ fibre texture of nickel deposits may correspond to the free mode of growth (e.g. the metallic surface is dynamically released from hydrogen adsorption) [15]. The hypothesis was suggested based on the observation that $\langle 1\,0\,0 \rangle$ textured nickel deposits exhibit the highest ductility [17] and the lowest internal stress and hardness [18], which may be attributable to less adsorption of hydrogen. These experimental results are consistent with the surface-energy anisotropy, with which one may expect that $\langle 1\,0\,0 \rangle$ fibre texture would develop preferentially in the free mode of growth due to the lowest surface energy of Ni (1 0 0) plane.

However, electrocrystallization is a complex and "wet" process. Chemical species such as chloride, metallic cations, hydrogen, hydroxides, and additives may be adsorbed by the cathode. This could modify a deposit's surface-energy anisotropy, and in turn, affect the textural evolution. For example, in iron deposits, the $\langle 1\,1\,0 \rangle$ fibre texture is replaced by $\langle 1\,1\,1 \rangle$ and $\langle 3\,1\,1 \rangle$ fibre textures at high current densities, low bath pH or at low bath temperatures. In nickel deposits, other textures such as $\langle 2\,1\,0 \rangle$ and $\langle 2\,1\,1 \rangle$ fibre textures were also observed at high pH, or at high current densities, or in different baths [15]. In copper deposits, experiments conducted by different researchers are not always consistent. For example, different from our expectation, Kang *et al.* [16] observed that at low current densities, the predominant texture of copper deposits produced using a sulphate bath is a $\langle 1\,0\,0 \rangle$ texture rather than a $\langle 1\,1\,0 \rangle$ texture. This difference might be attributable to possible co-deposition of other inhibitors. In order further to understand the effect of surface-energy anisotropy on texture formation, more accurate information of the surface adsorption and its effect on the surface-energy anisotropy is necessary.

4.2. Texture variation with K$^+$ and Cl$^-$ adsorption

The main purpose of this research is to understand the textural variation in copper electrodeposits on adding potassium chloride to the electrolyte. It was usually explained that the textural variation with additive KCl in the bath is attributable to chloride adsorption, because the formed CuCl at the deposit surface may result in an increase in overpotential. However, the present simulation studies demonstrate that potassium ions also affect copper deposit texture, and its effect is even stronger than Cl$^-$. This may be seen from the lower critical concentration of K$^+$, compared to that of Cl$^-$ at which the texture changes its fibre axis. Therefore, at low concentrations of potassium chloride, it seems that the textural variation in copper deposits is caused mainly by K$^+$ ions, and Cl$^-$ ions share the role in the textural variation at higher concentrations of KCl. This texture variation corresponds to changes in surface-energy anisotropy caused by K$^+$ and Cl$^-$ ions. Because the K$^+$ adsorption has a relatively stronger influence on copper surface-energy anisotropy, K$^+$ adsorption could be more important to copper deposit texture than Cl$^-$ adsorption, especially at low ion concentration.

This mechanism of texture variation in copper deposits demonstrated by the present simulation is different from the previous explanation which only takes into account the chloride adsorption. To understand the simulation result, it may be helpful to compare the interaction potential between Cu and Cl$^-$ with that between Cu and K$^+$. As estimated, $\varepsilon_{\mathrm{Cu-K^+}}/k_{\mathrm{B}}$ (K) $= 1.60 \times 10^4$, $\sigma_{\mathrm{Cu-K^+}} = 0.2805$ (nm), $\delta_{\mathrm{Cu-Cl^-}}/k_{\mathrm{B}}$ (K) $= 1.57 \times 10^4$, and $\sigma_{\mathrm{Cu-Cl^-}} = 0.2337$ (nm). As defined, ε and σ in the L–J potential expression represent the depth of the potential at the minimum and the closest distance at which $\varphi(r_{ij})$ is equal to zero. It is seen that values of $\varepsilon_{\mathrm{Cu-K^+}}/k_{\mathrm{B}}$ and $\varepsilon_{\mathrm{Cu-Cl^-}}/k_{\mathrm{B}}$ are on the same order of magnitude, and the former is slightly larger than the latter, i.e. the potential well of the K$^+$–Cu interaction is slightly deeper than that of the Cl$^-$–Cu interaction. This implies that the interaction between K$^+$ and Cu is relatively stronger than that between Cl$^-$ and Cu. As a result, the effect of potassium adsorption on the surface energy of copper is somewhat greater than the effect of chloride adsorption. It is, therefore, understandable that K^+ adsorption has a relatively stronger effect than Cl^- on the textural variation of copper deposits. In fact, the situation for chloride adsorption is quite complicated. The reaction between Cu^{2+} and Cl^- may form complexes such as $CuCl^+$, $CuCl_2$, etc., and this makes the case of chloride adsorption complicated. Thus, the simulation results for chloride may not well describe the chloride effect. Nevertheless, it is expected that K^+ should play an important role in the textural variation during copper deposition because the positively charged K^+ ions are attracted by the cathode, while the negatively charged Cl^- are repulsed from the cathode and this could make the Cl^- concentration much lower in the vicinity of the cathode surface than the K^+ concentration.

It should be indicated, however, that the Lennard–Jones potential used to evaluate the interaction between Cu and K^+ and that between Cu and Cl^- is only a rough approximation, because the Lennard–Jones potential may not well describe the interaction involving electrical interaction. However, before finding more suitable potential functions, we used the LJ approximation and obtained qualitative information which is consistent with experimental observation. In order to obtain more precise results, the potentials which better describe the interaction between Cu and K^+ and that between Cu and Cl^- are absolutely necessary.

In addition, it should be pointed out that the deposit texture is also influenced by some structural factors such as the surface morphology and crystallographic defects, because differently textured deposits might correspond to different morphologies and defects. It is noted that "mountainous" morphology with some facets and irregular pyramids is the surface structural feature of differently textured copper electrodeposits [1–3, 16]. The variation in deposit texture may be related to some changes in surface morphology, e.g. the index of facets or pyramid faces and their angles to the deposit surface. This is possible because the facets and pyramid surface should be the low-energy faces in order to minimize the total surface energy of the deposit. Under different deposition conditions, the faces having the lowest surface energy may change, e.g. by the adsorption of hydrogen or foreign species which change the surface-energy anisotropy. This change in facets and pyramid faces may occur, along with changes in deposit texture. In addition, texture evolution may also be associated with some crystallographic defects such as twins. The stacking fault energy is relatively low for copper and the formation of twin faults is favoured during copper deposit growth. $\{1\,1\,1\}$ twin faults have been observed in differently textured copper deposits [16]. The angle between the $\{1\,1\,1\}$ twin boundaries and the deposit growth direction changes, together with the change in deposit texture. This variation of twin-boundary orientation could be associated with changes in index of surface facets and pyramid faces caused by the variation of surface-energy anisotropy under different deposition conditions. In this case, the twin-boundary orientation is adjusted to cope with changes of surface facets/pyramid faces and thus the arrangment of these faces for a minimum total surface energy. Along with the change in twin-boundary orientation, deposit texture may also change. Kang *et al.* [16] have discussed the possible geometric relation between the orientation of $\{1\,1\,1\}$ twin boundaries, surface morphology, and the deposit texture. However, because these two structural factors, surface morphology and twinning, are somehow related to the surface-energy minimization, it seems that deposit texture may result from the surface-energy anisotropy rather than the surface morphology and twin faults which could also be "products" of the surface-energy minimization. In order to verify this hypothesis, a further investigation of the correlation between the surface-energy minimization and the twin-boundary orientation and thus the surface morphology, is necessary. Allowing for the fact that electrodeposits do not often exhibit clear facets and pyramid faces, it is therefore still questionable as to how the surface morphology and twin faults correlate with textural evolution. Nevertheless, a study on the surface morphology and twin formation would be helpful for developing a more accurate free-energy function to predict textural evolution. In order further to understand textural variation in copper deposits under the influence of KCl additives in electrolyte, studies of the effects of potassium and chloride ions on the twin-fault formation and surface morphology may be helpful.

5. Conclusion

Texture development during copper electrodeposition was studied using a Monte Carlo simulation approach. In particular, the respective effects of potassium adsorption and chloride adsorption on textural variation were investigated. The study demonstrates that in the case of free-adsorption, $\langle 1\,1\,0 \rangle$ texture is predominant in copper electrodeposits; if K^+ and Cl^- are added to the bath, the predominant $\langle 1\,1\,0 \rangle$ texture is replaced by $\langle 1\,1\,1 \rangle$ texture with an increase in the concentration of potassium chloride. The present study demonstrates that both the potassium and chloride ions may cause the textural variation. It appears that the potassium adsorption plays a relatively important role in textural variation, particularly at low KCl concentrations. However, in view of the complexity of chloride adsorption on copper, further studies on chloride effects are necessary. Nevertheless, the simulation demonstrates that, different from the previous explanation, the chloride adsorption is not the only fact responsible for the textural variation in copper electrodeposits produced in the bath containing KCl.

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