Effects of (NH₄)₂SO₄ and BTA on the nanostructure of copper foam prepared by electrodeposition

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ABSTRACT

Copper foam with dendritic copper nanostructure was synthesized by an electrodeposition process using hydrogen bubbles as dynamic templates. To modify the morphology of the copper nanostructure in the foam walls, (NH₄)₂SO₄ and BTA (benzotriazole) were introduced into the electrolytic bath as chemical additives, and their influences on the morphologies and the structural characteristics of copper deposits were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The mechanical strength and stiffness of the copper foam were evaluated by the compression test. The corncob-like deposits of the copper foam were changed to needle-like nanodendrites by the addition of (NH₄)₂SO₄, which significantly improved the mechanical strength and stiffness due to the self-supporting effects of the tightly interlocked needle-like nanodendrites. In contrast, the copper foam prepared from the solution with (NH₄)₂SO₄ and BTA shows high ductility but low mechanical strength due to the formation to grape-like copper deposits. Both the copper foams exhibited higher mechanical properties than the one with corncob-like deposits formed in the additive-free solution. The reaction mechanism of (NH₄)₂SO₄ and BTA on the nanostructure of the copper foam at high cathodic current density was clarified by analyzing the effects of the additives on the copper deposition reaction and hydrogen gas evolution reaction, respectively.

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1. Introduction

Metallic foams have been investigated based on their specific structure, which exhibits extremely large surface area, low density and high strength and stiffness. Recently, an interest in thin metallic foams has increased as the application of metallic forms has expanded to electrochemical devices such as energy absorbers, catalyst carriers, and electrodes for batteries. However, the conventional manufacturing processes for metallic foams, e.g., foaming with blowing agents and vapor deposition, are not appropriate for thickness and porosity control of the foams.

Shin et al. [1–3] succeeded in fabricating thin copper foams by electrodeposition using hydrogen bubbles as a dynamic template with no polymer framework. This process has several advantages compared with conventional processes: low cost, simple bath preparation, easy thickness control, and no additional process to remove the polymer template. Since the copper foams are formed rapidly by extremely high cathodic potential, they have two inherent problems to be solved for wide applications: the first one is weak bonds between the foam structure and substrate, causing the detachment of copper deposits from the substrate, and the other is the weak mechanical strength or the brittleness of copper foam due to fragile copper deposits in the foam walls [4].

The mechanical strength of the copper foam prepared by the electrodeposition is greatly influenced by the structural morphology and density of the copper deposit. The major parameters affecting the morphology of the copper deposit are the cathodic overpotential [5], the composition of the electrolytic bath [6,7], and the solution temperature [8]. However, the morphology of copper deposits controlled by these parameters is not sufficient for the formation of the copper foam with high mechanical strength.

Several research groups reported that using chemical additives is an effective way for controlling the size, shape, and density of copper deposits. When chloride ions are added into an electrolytic bath, the size of copper deposits was reduced and the density of the copper deposits was increased as a result of accelerated deposition reactions [3]. Likewise, the addition of CTAB (cetyltrimonium bromide) as surfactant causes a size reduction and an increase in the density of copper deposits in the foam walls [7]. Kim et al. also demonstrated that PEG (polyethylene glycol) and MPSA (3-mercapto–1-propane sulfonic acid sodium salt), which are commonly used as additives for copper electroplating, played a crucial role in forming 3D interconnected copper foams by changing the size, shape, and density of copper deposits [9]. Thus, it is anticipated that mechanical properties of copper foam can be improved...
by modifying the nano-structure of the copper foam using suitable chemical additives.

In this work, two chemical additives, (NH₄)₂SO₄ and BTA (benzotriazole), were used to modify the nanostructure of the copper deposits in the foam walls, and hence to improve the mechanical properties of the copper foam. Typically, (NH₄)₂SO₄ is an important agent for copper electrodeposition because ammonia increases the solubility of copper ions in an aqueous solution by forming highly stable copper ion–ammonia complexes. The diverse speciation of aqueous cuprous and cupric ions influences the copper nucleation mechanism and growth kinetics [10], such that ammonia is recognized as an essential additive to produce acicular-shaped or needle-shaped particles [11,12]. In addition, it was reported that, in the presence of ammonia in a bath, long strands or rod-shaped nanodendrites were obtained by the formation of linear complexes that induces an anisotropic crystallographic growth of deposits [13]. Therefore, the mechanical properties of copper foams would be improved by modifying the nanostructure of the copper foams with (NH₄)₂SO₄.

BTA (benzotriazole, C₆H₄N₃H) has been widely used as an effective corrosion inhibitor for copper by forming protective chemisorbed films on copper metal [14–16] and as a suppressive agent for copper electrodeposition in sulfate plating baths [17]. Accordingly, the mechanical strength of the copper foams would be enhanced by suppressing the dendritic growth of the copper deposits by BTA.

Therefore, the research objective of the work is to examine the effects of (NH₄)₂SO₄ and BTA on the nanostructure and mechanical properties of copper foams, and further to clarify the reaction mechanism of the additives in the copper electrodeposition at high cathodic current density.

2. Experimental

2.1. Reagents

Basic constituents in the electrolytic bath for the preparation of the copper foams were 0.2 M CuSO₄ (Junsei, 99.0%) and 0.7 M H₂SO₄ (Junsei, 95.0%). To examine the effects of the additives on the copper deposits, 1.2 M (NH₄)₂SO₄ and 0.4 mM BTA were added into the electrolytic bath. The compositions of the each electrolytic bath are described in Table 1: (i) bath 1, basic constituent with no additives; (ii) bath 2, basic constituent with the 1.2 M (NH₄)₂SO₄; (iii) bath 3, basic constituent with 0.4 mM BTA; and (iv) bath 4, basic constituent with 1.2 M (NH₄)₂SO₄ and 0.4 mM BTA.

2.2. Preparation of copper foam by electrodeposition

The copper electrodeposition for preparation of the foam structure was conducted by using a two-electrode cell; a nodule-type copper sheet (IIJIN Copper Foil Co., Ltd) and pure copper plate were used as cathode and anode, respectively. The distance between the cathode and the anode was 1.5 cm. The electrodeposition was executed at a constant current density of −3 A/cm² for 4 s in a solution magnetically stirred at ∼800 rpm. The temperature of all experiments was room temperature, 25 °C. The copper foams were dried in vacuum for 1 h after rinsing with distilled water and ethanol to prevent the oxidation of the copper deposits.

2.3. Characterization of the copper foam

The copper foams were observed using a scanning electron microscope (SEM) to examine the effects of (NH₄)₂SO₄ and BTA on the morphology of the copper deposits. The microstructure of the copper deposits was further investigated with transmission electron microscopy (TEM). For the TEM analysis, the dried copper deposits were raked out from the substrate with tweezers, and then dispersed in ethanol by sonication for 30 min. The crystal structure of copper deposits was identified by selected area electron diffraction (SAED) analysis.

2.4. Compression test

To evaluate the mechanical properties of the copper foams, compression tests were conducted on three different samples prepared from bath 1, bath 2 and bath 4 by using a micro-compression testing machine. The copper deposit formed in the bath 3 was excluded from the compression test because the morphology of the deposit was not a “foam structure”. The force–displacement curve describes the displacement (μm) of the compressive indenter into the foams due to an applied force (gf). Because the compressive indenter was not in contact with the whole surface of the copper foam at the beginning of the test, the initial period of the test should not be considered. In the linear part of the force–displacement curve, two parameters were obtained to evaluate the mechanical properties of the copper foams; the slope value of the force–displacement curve and the maximum compressive force value, which are equivalent to the stiffness and the mechanical strength of the foam structure, respectively. The slope value was calculated from the linear part of the force–displacement curve (that is called “region I”), and the maximum compressive force was determined at the end of the region I where an obvious inflection point is observed in the curve.

2.5. Electrochemical analysis

Galvanostatic tests were performed in the four baths listed in Table 1 at −3 A/cm² for 4 s to investigate the effects of (NH₄)₂SO₄ and BTA on the copper electrodeposition. All experiments were conducted in a conventional three-electrode cell using the nodule-type copper sheet as the working electrode and a platinum foil as the counter electrode. A saturated calomel electrode (SCE, 0.241 V vs. SHE) was used as the reference electrode.

2.6. Hydrogen gas evolution measurement

To better understand the reaction mechanism of additives on copper deposition, the effects of additives on the hydrogen evolution reaction must be taken into consideration because the hydrogen evolution occurs competitively with the copper reduction reaction at high cathodic current density. A gas flow meter was used in the measurement of hydrogen evolved during electrodeposition at a constant current density of −3 A/cm².

2.7. Local pH measurement

The local pH measurement test is an effective way to prove the temporary local alkalization in the vicinity of the cathode surface at high cathodic current density. To elucidate the reaction mechanism of (NH₄)₂SO₄ on the copper deposition, “temporary local alkalization” was assumed, which enables the reaction of ammonia
with copper ions in spite of highly acidic conditions. The pH measurement was carried out using a technique similar to that in the previous work [18] as a function of the distance from the electrode of 0, 1, 2, 3 cm, and the applied cathodic current density of 100, 500, 1000, 3000 mA/cm². The solution was stirred with a magnetic stirrer at ~800 rpm in accordance with the condition for the preparation of copper foam. The deposition time was 10 s, and the local pH values were averaged in the stable region.

3. Results and discussion

3.1. Effects of (NH₄)₂SO₄ and BTA on the morphology and the crystal structure of copper foams

Fig. 1 represents the SEM images of the copper foams prepared by electrodeposition at a constant current density of ~3 A/cm² for 4 s. The copper foams feature a porous structure for different (NH₄)₂SO₄ and BTA contents, but they show a clear distinction in the morphology of copper foam, the degree of compactness in the foam wall, the mean pore size, and the pore density.

As shown in Fig. 1a, the copper foam obtained from the additive-free solution (see bath 1) exhibits a 3D structure with highly porous foam walls that consists of corncob-like copper deposits. Although the overall morphology of this structure was similar to those reported by Shin et al. [1,2], the mean pore size (~10 μm) and wall thickness (~5 μm) of the foam were reduced because the nodular-type copper sheet was used as a substrate that splits hydrogen bubbles generated on the surface of the substrate [19]. However, the size and the shape of copper deposits in the foam walls remain unchanged in spite of the morphological changes in the foam structure.

As opposed to the copper foam with porous foam walls obtained in the additive-free bath, the structure of the copper foam prepared from the (NH₄)₂SO₄-containing bath (see bath 2) shows denser walls than those obtained without the additive, which are composed of needle-like nanodendrites with a high degree of interlocking (see Fig. 1b). It was expected that the needle-like nanodendrites would improve the mechanical strength of the foam structure because they seem to be tightly interlocked with each other.

Fig. 1c represents the morphology of the copper deposits prepared from the BTA-containing bath (see bath 3). It shows a porous structure comprised of numerous globular particles (~1 μm). However, to be more exact, this structure could not be considered as a type of “foam structure”. Given that BTA functions as an effective suppressive agent for copper electrodeposition, it appears that the specific morphology of these copper deposits resulted from the suppressed dendritic growth of copper.

The synergy effects of (NH₄)₂SO₄ and BTA on the morphology of copper foam were observed in Fig. 1d. The foam electrodeposited in the (NH₄)₂SO₄ and BTA-containing bath (see bath 4) exhibited more compact foam walls consisting of sphere-shaped nanoparticles than those obtained without the additive. In addition, this foam obviously shows a smaller mean pore size (~5 μm) and an increased pore density compared with the copper foam depicted in Fig. 1a. Consequently, these morphology changes are the result of the addition of (NH₄)₂SO₄ and BTA, which affect not only the copper deposition but also the hydrogen gas evolution kinetics; the pore size and the pore density of the copper foam are dependent
on the size and amounts of hydrogen bubble working as a dynamic template \[1,7\].

Fig. 2 shows the TEM images and corresponding selected area diffraction (SAED) patterns of the copper foams obtained from each bath. As depicted in Fig. 2a, the overall shape of the copper deposits obtained from bath 1 is a corncob-like deposit with irregularly shaped small copper crystals (30–40 nm) on its surface, in accordance with the SEM results. The SAED pattern for this sample shows the discontinuous ring-like pattern, which validates the formation of polycrystalline copper with different crystallographic orientations.

Contrary to the corncob-like copper deposit of Fig. 2a, the morphology of the copper deposit prepared from bath 2 shows needle-like nanodendrites \(\sim 250\) nm long (Fig. 2b). The corresponding SAED pattern for this deposit reveals that the crystal structure of each branch is a single crystal, which implies that \((\text{NH}_4)_2\text{SO}_4\) influences not only the morphology but also the crystal structure of the copper deposits.

Fig. 2c displays the TEM image and SAED pattern of the copper deposit obtained from bath 3. In spite of a fast copper deposition, the highly compact copper deposit is formed due to the inhibiting effects of BTA on the dendritic growth of copper. The SAED pattern represents the blurred discontinuous ring-like pattern, which indicates the formation of crystalline copper with low crystallinity.

As shown in Fig. 2d, the copper deposit prepared from bath 4 exhibits a similar shape to the corncob-like deposit rather than the needle-like or the globular one. The morphology of the deposits shows aggregated spherical nanoparticles (Fig. 1d) because the apparent morphology of the numerous small bumps (\(\sim 50\) nm) formed on the surface seems to be powdery crystals. This copper deposit would be called “grape-like deposits”. The most interesting point of the grape-like copper deposit is that the small bumps are made up of extremely fine copper crystals less than \(5\) nm in size, contrary to the aforementioned deposits. The SAED pattern of the copper deposit shows a clear ring-like pattern compared with that in Fig. 2a, which is probably due to an increase in the number of fine primary copper crystals.

The other effect of additives on copper electrodeposition is that, when \((\text{NH}_4)_2\text{SO}_4\) and/or BTA are involved in electrodeposition reactions, the \(\text{Cu}_2\text{O}\) crystals are not formed in the copper deposits. As shown in Fig. 2a, several cubic-shaped crystals over the copper deposits were observed, which were identified as \(\text{Cu}_2\text{O}\) crystals by EDS analysis and corresponding SAED patterns. Although the reason why the cubic \(\text{Cu}_2\text{O}\) crystals were formed in the copper deposits at high cathodic current density is not clear, that might be associated with the copper reduction kinetics and evolution reaction of hydrogen gas. Because the local pH near the electrode will rise due to the depletion of hydrogen ions resulting from vigorous hydrogen gas evolution, \(\text{Cu}_2\text{O}\) crystals could be formed...
on the cathode surface similar to the formation of insoluble nickel hydroxide at high cathodic current density [18]. Though not included this paper, the increase in the local pH was identified as ~pH 11 by a pH measurement test in the additive-free solution.

3.2. Effects of (NH$_4$)$_2$SO$_4$ and BTA on the mechanical properties of copper foams

Micro-compression tests were performed to evaluate the mechanical properties of copper foams electrodeposited from bath 1, bath 2, and bath 4. The copper deposit prepared in bath 3 was excluded from the compression test because the morphology of deposit was not a “foam structure” (Fig. 1c).

As shown in Fig. 3a, the entire compressive curves could be divided into three regions: region I (endurance step), region II (collapse and densification step), and region III (end step). In region I, the force–displacement curve shows a straight line because the compressive force increases linearly with displacement. The proportional relation between force and displacement remains until the foam structure begins to crumble. At the beginning of region II, a significant change in the slope of force–displacement curve occurs due to the collapse of the foam structure by the increased compressive force. In region III, a rapid increase in the compressive force is observed because the crushed copper deposits were totally densified by the compressive indenter.

In this study, the mechanical properties of electrodeposited copper foams were determined by two parameters, the slope value and the maximum compressive force value. The slope value calculated in the linear part of the force–displacement curve (region I) was assumed to indirectly reflect the stiffness of the copper foam, and the maximum compressive force value obtained in region I demonstrates the mechanical strength of the copper foam. The slope value and the maximum compressive force in region I for the copper foams are listed in Table 2.

Fig. 3b shows the force–displacement curves for copper foams prepared in bath 1, bath 2, and bath 4. The slope value of the copper foam deposited from bath 1 is ~0.247 gf/μm, and its maximum compressive force is ~1.11 gf. The copper foam prepared from bath 2 has a slope value that is six times higher (1.569 gf/μm) and a maximum compressive force value that is three times higher (~4.17 gf) than those from bath 1. The increase in the slope value and the maximum compressive force indicates the improvement in the stiffness and the mechanical strength of the copper foam. In contrast, when both (NH$_4$)$_2$SO$_4$ and BTA were involved in the bath, the slope value and the maximum compressive force of the copper foam decreased to ~0.152 gf/μm and ~2.07 gf, respectively. These changes might be attributed to the morphological change of the copper deposits from the interlocked needle-like nanodendrites to non-interlocked grape-like deposits. In fact, the mechanical properties of a network structure are quietly affected by the crystalline characteristics and the arrangement of crystals in the walls [20]. As opposed to the decrease in the mechanical strength, the force–displacement curve for the copper foam from bath 4 shows an obvious increase in the displacement of region I with a low slope value, confirming the significant increase in the ductility of the foam structure.

Based on the above results, it is evident that the mechanical properties of copper foam, such as the mechanical strength and stiffness or ductility, can be controlled by the morphology and the arrangement of the copper deposits in the foam walls. In particular, the copper foam consisting of the needle-like copper deposits showed the improved mechanical strength and stiffness of the foam structure. As shown in Fig. 1b, the needle-like copper nanodendrites in the foam walls were tightly interlocked with a higher degree of compactness than those formed in the additive-free bath. Since the randomly oriented needle-like copper nanodendrites are structurally favorable for supporting the compressive load, the enhanced mechanical strength and stiffness can be achieved by the addition of (NH$_4$)$_2$SO$_4$. On the other hand, the copper foam composed of the grape-like copper deposits exhibits the highly compact foam walls as shown in Fig. 1d, but those were not interlocked or cross-linked each other. Consequently, the copper foam consisting of the grape-like copper deposits would be weaker to the compressive load, and more easily crumbled than that composed of interlocked needle-like nanodendrites.

3.3. Effects of (NH$_4$)$_2$SO$_4$ and/or BTA on copper deposition and hydrogen evolution

To elucidate how the morphology of copper deposits is influenced by the (NH$_4$)$_2$SO$_4$ and BTA, galvanostatic potential transient tests were performed simultaneously with measuring the evolved
hydrogen gas. The galvanostatic potential transient curves in each bath are shown in Fig. 4a. The cathodic overpotential for the overall cathodic reaction was increased with the addition of \((\text{NH}_4)_2\text{SO}_4\), and also BTA due to their suppressive effects on the copper deposition [14]. When both \((\text{NH}_4)_2\text{SO}_4\) and BTA were added in the electrolytic bath, the highest cathodic overpotential among all baths was required for the electrodeposition of copper foam.

The other observation in the potential transient curves is the effects of additives on hydrogen evolution. The random fluctuations in all potential transient curves denote that the hydrogen gas evolution occurs concurrently with copper deposition. Since the hydrogen bubbles grow on the substrate, and then depart from the substrate, an increase in the fluctuation due to the addition of \((\text{NH}_4)_2\text{SO}_4\) and BTA implies that the additives affect not only the copper reduction reactions but also the hydrogen gas evolution. For this reason, the effects of additives on hydrogen evolution reaction must be taken into consideration to better understand the reaction mechanism of additives in copper deposition.

To examine the effects of additives on the hydrogen evolution, volume of hydrogen gas generated simultaneously with the copper deposition was measured by a gas flow meter during copper electrodeposition. At the deposition time of 4 s, the amounts of evolved hydrogen in the solution without additive and with BTA are 0.83338 ml and 0.84702 ml, respectively. The amounts of evolved hydrogen gas were increased about 1.64% by the addition of BTA. When \((\text{NH}_4)_2\text{SO}_4\) was added in the bath, the volume of evolved hydrogen gas was increased to 0.95595 ml (by 14.7%). Moreover, the quantities of generated hydrogen in the presence of both \((\text{NH}_4)_2\text{SO}_4\) and BTA were measured as 1.05262 ml that is increased by 26.3% than those in the additive-free solution. These results demonstrate that \((\text{NH}_4)_2\text{SO}_4\) effectively promotes the hydrogen gas evolution, but the effects of BTA on the hydrogen generation may be negligible.

Under galvanostatic conditions, an increase in the amounts of evolved hydrogen gas is closely related to an increase in the partial cathodic current for hydrogen reduction, whereas the partial cathodic current for the copper deposition decreased. Considering this mechanism, the increase in the hydrogen evolution by the addition of \((\text{NH}_4)_2\text{SO}_4\) suggests that \((\text{NH}_4)_2\text{SO}_4\) acts as an additional hydrogen bubble source and increases the partial current for hydrogen reduction, according to the following equation [21,22]:

\[
2\text{NH}_4^+ + 2e^- \rightarrow 2\text{NH}_3 + \text{H}_2
\]  

On the other hand, the little increase in the hydrogen gas evolution by the addition of BTA implies that BTA does not increase the partial current for hydrogen reduction in spite of its suppressive influence on the copper deposition.

It is well known that the pore size and wall thickness of the copper foam are determined by the size of hydrogen bubbles [1,7]. Hence, the morphological changes of foam structure by the additives, shown in Fig. 1 can be explained based on the results of hydrogen measurement test. The number and size of pore in the copper foam (Fig. 1b) formed in the bath with \((\text{NH}_4)_2\text{SO}_4\) were not changed from those obtained without any additive (Fig. 1a). This reveals that the additive \((\text{NH}_4)_2\text{SO}_4\) does not affect the size of hydrogen bubbles but only increases the amount of hydrogen evolution. On the contrary, the morphology of copper foam is significantly changed such that the pore size was reduced and the number of pores were greatly increased (Fig. 1d) when both additives were added in the bath. Since \((\text{NH}_4)_2\text{SO}_4\) does not affect the size of the hydrogen bubbles, these structural changes may be due to an influence of BTA on the hydrogen bubble size. Previous study reported that coalescence of the hydrogen bubbles is suppressed by the surfactant (CTAB), and hence leads to the formation of smaller hydrogen bubbles [7]. Likewise, BTA might reduce the hydrogen bubbles size by certain reaction mechanism, which is similar to that of CTAB, but its mechanism is not yet clear.

### 3.4. Reaction mechanism of \((\text{NH}_4)_2\text{SO}_4\) during copper deposition

As mentioned above, \((\text{NH}_4)_2\text{SO}_4\) is an effective additive to change the morphology of copper deposits and that it acts as additional hydrogen bubble source. However, it is not yet clear how \((\text{NH}_4)_2\text{SO}_4\) affects the copper deposition reaction at high cathodic current density.

According to the ammonia chemistry, \((\text{NH}_4)_2\text{SO}_4\) is considered as an important additive to increase the solubility of copper by forming highly stable cupric or cuprous ammine complexes in aqueous solutions [23]. The most common ammine complexes in alkaline aqueous solutions are given the general formula \(\text{Cu}(\text{NH}_3)_n^{2+} (n = 1, \ldots , 5)\) [24,25] because these ammine complexes are more stable than hydrolyzed ammine complexes.

Fig. 5a shows the Pourbaix diagram [23] of the copper–ammonia system, in which copper exists as \(\text{Cu}(\text{H}_2\text{O})_n^{2+} (n = 1, \ldots , 5)\) in the range of \(7 < \text{pH} < 11\), whereas copper exists as the hydrated form \(\text{Cu}(\text{H}_2\text{O})_n^{2+}\) at \(\text{pH} < 5\). It should be emphasized that cuprous and
cupric ions cannot form a copper–ammonia complex in acidic environments; that is, NH₃ does not affect the copper reduction reaction under highly acidic conditions (the pH is 0.96 in this experiment), which is consistent with the previous study on the stabilization of copper in the copper–ammonia system [26]. Thus, to explain the effects of (NH₄)₂SO₄ on the morphology of copper deposits, an alkaline environment was assumed to form temporarily in the solution due to H⁺-ion depletion. When the supply of hydrogen ions is insufficient to meet the depletion rate, the local pH would be increased more than that in the bulk electrolyte [18].

To validate the temporal occurrence of an alkaline environment during the electrodeposition of copper, a local pH measurement test was performed at cathodic current densities of 100, 500, 1000, and 3000 mA/cm². Fig. 5b shows the pH changes in bath 2 with the variation of distance from the surface of the electrode. As expected, the local pH in the vicinity of the cathode surface was much higher than the bulk pH at a high current density above 100 mA/cm². In particular, the local pH further increased with an increase in the applied current density because the hydrogen evolution rate (or the amounts of evolved hydrogen gas) is inversely proportional to the amount of hydrogen ions in the solution. This phenomenon is termed “temporary localized alkalization” because the pH near the electrode surface is restored to its initial state when the applied current is removed.

Under alkaline conditions, NH₄⁺ ions is changed to NH₃ according to reaction (1) [21,22]. As the NH₃ is accumulated in the vicinity of the electrode surface, the complexation reaction of hydrated cupric ion (Cu(H₂O)₆²⁺) to cupric ammine complexes (Cu(NH₃)₆²⁺) should occur according to reaction (2). Concurrently, one of the following reactions may occur in the vicinity of the cathode [24]: reduction of cupric ammine (Cu(NH₃)₆²⁺) to cuprous ammine complex (Cu(NH₃)₄²⁺) (reaction (3)); copper deposition through the reduction reaction of cuprous ammine (Cu(NH₃)₂²⁺) (reaction (4)), and chemical dissolution of copper from the cathode (reaction (5)).

\[
\begin{align*}
Cu(H_2O)_6^{2+} + nNH_3 &\rightarrow Cu(NH_3)_6^{2+} + nH_2O \quad (2) \\
Cu(NH_3)_6^{2+} + e^- &\rightarrow Cu(NH_3)_2^{2+} + (n-2)NH_3 \quad (3) \\
Cu(NH_3)_2^{2+} + e^- &\rightarrow Cu + 2NH_3 \quad (4) \\
Cu^{0} + Cu(NH_3)_2^{2+} &\rightarrow 2Cu(NH_3)_2^{2+} \quad (5)
\end{align*}
\]

It should be noted that the cuprous ammine and cuprous diammine complexes are exclusively formed under the temporary alkaline condition. This reaction mechanism is valid because the formation reaction for Ni(NH₃)₈²⁺ (2 ≤ n ≤ 6) should take place at a high cathodic current density [22]. Therefore, according to the proposed reaction mechanism, the concentration of cuprous diammine species increases in the solution during the electrodeposition, which induces different copper deposition kinetics from those of hydrated cuprous ions because the cuprous diammine species are linear complexes.

In the previous study [13], Kaniyankandy et al. demonstrated that the adsorption energy of linear complexes is enormously influenced by the surface energy of private crystal faces. In other words, the linear complex significantly affects the crystal growth rate along the preferred orientation. Thus, it is anticipated that the formation of needle-like copper deposits in the (NH₄)₂SO₄-containing bath is due to the interfacial anisotropy created by Cu(NH₃)₂²⁺ linear complex and copper.

3.5. Reaction mechanism of BTA on copper deposition

According to the SEM analysis and TEM analysis, BTA affects not only the morphology but also the crystal structure of copper deposits. In fact, the suppressive effects of BTA on copper deposition have been studied by numerous research groups in various ways. Although the adsorption mechanism of BTA on copper deposits during Cu²⁺ reduction has been reported [17,27,28], no one has considered the effects of BTA on the morphology and nanostructure of copper deposits at high cathodic current density. Thus, in this section, the reaction mechanism of BTA in the rapid copper deposition at high cathodic current density is suggested to elucidate the formation of globular deposits (Fig. 1c) and grape-like copper deposits (Fig. 1d).

While the significant effects of BTA on the morphology of copper deposits were observed, organic additives such as MPSA and PEG, which are commonly used as a suppressor and a leveler, show weaker inhibiting influences on the dendritic growth of copper deposits than those of BTA at high cathodic current density [30]. Thus, it is anticipated that the reaction mechanism of BTA on copper reduction would be different from that of MPSA and PEG.

Fig. 6 illustrates the schematic diagrams on the electrodeposition of copper in the presence of BTA. As the copper reduction proceeds at the high cathodic current density, small copper nuclei are created on the copper substrate. Simultaneously, BTA could be adsorbed not only on the substrate but also on the surface of the copper nuclei [17], as shown in Fig. 6a. The adsorbed BTA and the copper nuclei forms complex layers by reaction (7), and the existence of Cu(II)BTA could be identified by XPS [17], TOF-SIMS [31], and other techniques [27,29].

\[
Cu^{2+} + e^- \rightarrow Cu^{0} \quad (6)
\]
\[ \text{Cu(I)} + \text{BTA}_{\text{ads}} \rightarrow \text{Cu(I)BTA} \quad (7) \]

\[ \text{Cu(I)BTA}_{\text{ads}} + e^- \rightarrow \text{Cu} + \text{BTA}_{\text{ads}} \quad (8) \]

Since the copper deposit grows via the formation of Cu(I)BTA on the surface of the copper deposit, the cuprous ions produced by reaction (6) should be combined with the existed BTA on the copper deposit as shown in Fig. 6b (reaction (7)). Following this step, the reduction reactions of cuprous ions in Cu(I)BTA occur through reaction (8). Finally, the remaining BTA on the surface of the copper deposit repeatedly reacts with other cuprous ions [17]. Through the processes (6)–(8), BTA strongly affects the growth kinetics of copper by forming the Cu(I)BTA film layer on deposits in spite of the rapid deposition condition at high cathodic current density. Therefore, the formation of the globular copper deposits in the presence of BTA is due primarily to the uniform formation of Cu(I)BTA film layer on copper deposits, which effectively inhibits the dendritic growth of copper deposits, but lead to the isotropic 3D copper growth (Fig. 6c).

The formation of grape-like copper deposits (Fig. 1d) in the bath containing \((\text{NH}_4)_2\text{SO}_4\) and BTA is the result of the combined effects of the two additives on the growth of the deposits; the suppression effect of BTA on dendritic growth of copper deposits, and the effects of \((\text{NH}_4)_2\text{SO}_4\) on the formation of needle-like nanodendrites.

4. Conclusions

Copper foams with improved mechanical properties were successfully fabricated by an electrodeposition process with additives of \((\text{NH}_4)_2\text{SO}_4\) and BTA into the electrolytic bath. Copper foam obtained in the presence of \((\text{NH}_4)_2\text{SO}_4\) alone showed significantly improved mechanical strength and stiffness due to the self-supporting effects of tightly interlocked needle-like nanodendrites. In contrast, the copper foam deposited from the solution containing both \((\text{NH}_4)_2\text{SO}_4\) and BTA was consisted of the non-interlocked grape-like copper deposits, and hence it showed lower mechanical strength but higher ductility than those obtained with \((\text{NH}_4)_2\text{SO}_4\) alone. The results of the compressive test demonstrate that a modification of the morphology and the arrangement of copper deposits using the suitable additives is an effective way to achieve enhanced mechanical properties of copper foam.

In addition, the reaction mechanisms of \((\text{NH}_4)_2\text{SO}_4\) and BTA on copper electrodeposition at high cathodic current density were elucidated. To explain the reaction mechanism of \((\text{NH}_4)_2\text{SO}_4\) on copper deposition, the temporary local alkalinization in the vicinity of the electrode surface was suggested. In spite of the highly acidic solution, the local alkalinization enables the formation of cuprous diammine linear complexes, which causes the interfacial anisotropy. Otherwise, BTA suppressed the dendritic growth of copper deposits due to the formation of the Cu(I)BTA complex layer on the copper nuclei, thereby causing the isotropic 3D growth of deposits. The copper foam with the modified nanostructure and the enhanced mechanical properties is more suitable for practical use in such applications as lithium-ion batteries, fuel cells, sensors, and catalysts.

Acknowledgements

This work was supported by the BK21 program funded by the Korea Ministry of Knowledge Economy and the Growth Engine Technology Development Program (Project No. 10016472).

References
