Synergistic effects of coumarin and cis-2-butene-1,4-diol on high speed electrodeposition of nickel

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The individual and synergistic effects of coumarin and cis-2-butene-1,4-diol on the surface morphology and the crystal structure of Ni electrodeposits at a high cathodic current density were investigated using SEM, XRD, SIM and electrochemical analyses. While the rough Ni layer composed of spiral-type deposits was deposited from an additive-free bath, the electrodeposits with a smooth and bright surface were prepared from the coumarin-containing bath. XRD analysis and the cross-sectional observation suggested that coumarin promotes the large columnar growth of Ni crystallites along [200] directions, resulting in the production of a highly leveled electrodeposition layer. In contrast, cis-2-butene-1,4-diol showed strong grain refining effects on the Ni electrodeposition by the suppressive effects on the every mode of the crystal growth except [220] orientation, resulting in a significant promotion of the Ni crystal nucleation. When both coumarin and cis-2-butene-1,4-diol were contained in the bath, highly smoothed Ni electrodeposits were deposited by the synergistic effects of the additives.

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1. Introduction

Electrodeposition has been widely used as a multi-purpose surface finishing process in various decorative, engineering and electroforming applications due to the facile control of the appearance and properties of the deposited layer over broad ranges. Among electrodeposited metals, Ni is one of the materials most often employed to obtain a high luster finish, as well as improved corrosion and wear resistance of the underlying substrate. The physical and mechanical characteristics of Ni electrodeposits (such as brightness, grain size, corrosion resistance and pitting) are significantly dependent on the crystallographic and morphological properties of the electrodeposits, and therefore the electrolysis factors, the composition of the electroplating bath and the deposition technique must be selected carefully to meet the specific requirements of the application.

Brightness of electrodeposits is largely determined by the degree to which structural components of the surface are in the same plane [1]. It has been found that brightness is mainly due to the free surface of the grains being flat and parallel to the general surface direction of the specimen [2]. In addition, a production of small grains is another important matter to obtain high brightness because the grain boundaries between large grains appear as deep crevices. Despite a fine grain size, however, some electrodeposits showed low brightness [1], and thus it is generally accepted that a small grain size is a necessary but not a sufficient condition for achieving high brightness [1,3]. Accordingly, in modern decorative Ni electroplating, combinations of different additives which can act as leveling and brightening agents are considered indispensable for a high level of brightness [4]. The presence of such additives, with even small quantities in the bath, can strongly affect the surface diffusion of metal adions or adatoms to stable lattice sites or change the deposition rate at the peaks and valleys on the substrate by the preferential adsorption on surfaces, making the nucleation and growth kinetics of the Ni crystals highly variable.

The two representative additives in the Watts-type bath [5] for bright Ni electroplating are coumarin and 2-butyne-1,4-diol (CH₂=CH=C=CH₂). Coumarin is well known as an excellent leveling agent that produces fine-grained deposits and flat crystals. Under a cathodic potential, coumarin is reduced by two electrons transferred from an electrode on which Ni is depositing. The main by-product produced from coumarin differs according to the pH value of the electrolyte: pH 1.5 favors the production of o-hydroxyphenylpropanol and o-propylphenol [7], while mellilitic acid is mainly generated at pH 3–4 [6–10]. Whereas the mellilitic acid exhibits a remarkable inhibiting influence on Ni electrodeposition by strong adsorption on the Ni surface, formal compounds have little or no effect on the reduction kinetics of Ni because of the weak absorption [9]. The appropriate reduction parameters, such as the pH of the electrolyte, the proper concentration of additives and the applied potential, are required for coumarin to function as an effective leveling agent [8].
The compound 2-butyne-1,4-diol has also been widely employed as a leveling and grain-refining agent for bright Ni deposits [11–14] due to its strong inhibitory effect on the reduction of Ni [8,13]. During the deposition process, 2-butyne-1,4-diol molecules adsorb on the site of the Ni electroplating by reacting with adsorbed atomic hydrogen, thereby producing cis-butyne-1,4-diol (CH₃C≡CH – CH₂ – CH – CH₂·–HO- and 1,4-butanediol (CH₃CH₂OH, HO – CH₂ – CH₂ – CH₂ – CH₂·–OH). This catalytic hydrogenation of the unsaturated bonds of 2-butyne-1,4-diol increases the interfacial pH, and hence results in the precipitation of Ni(OH)₂ [14]. Since the growth of Ni crystals is strongly suppressed by not only cis-2-butyne-1,4-diol generated but also precipitated Ni(OH)₂, Ni electrodeposits composed of refined grains are consequently formed [14–16].

In a recent communication, Pavlatou et al. investigated the direct influence of the reduced compound of 2-butyne-1,4-diol (i.e., cis-2-butyne-1,4-diol) on Ni electrodeposition [17]. They demonstrated that an increasing concentration of cis-2-butyne-1,4-diol in the baths results in a reduction in the grain size of the deposits, the preferred growth of Ni crystals along [100] and an increase in the cathodic overpotential. The results indicate that cis-2-butyne-1,4-diol also behaves like a slow reacting brightener by the electroosorption of the –C≡C– bond at the electrode interface [17].

Nevertheless, the effects of cis-2-butyne-1,4-diol on the crystallographic characteristics and leveling of Ni electrodeposits formed at a high current density in bath with sufficiently high concentrations have been rarely examined whereas those of 2-butyne-1,4-diol were extensively investigated over the past few decades [8–16]. In particular, to our knowledge, the synergistic effects of cis-2-butyne-1,4-diol and coumarin on the surface morphology and the crystal structure of Ni for high-speed electroplating have not yet been studied.

The research objective of the present work is therefore to examine the individual and synergistic effects of coumarin and cis-2-butyne-diol on the surface morphology of the electrodeposits. The crystal structure of the Ni electrodeposits was investigated using X-ray diffraction (XRD). For the cross-sectional observation of Ni electrodeposits, scanning ion microscopy (SIM) specimens were prepared using a focused ion beam (FIB) which makes use of Ga ions to etch the material. From the diffraction intensities of the (hkl) plane, the relative texture coefficient RTC(hkl) was calculated to estimate the preferred orientation of the Ni crystallites quantitatively [14].

\[
\text{RTC}(hkl) = \frac{\sum_{hkl} \frac{I_{hkl}}{I_{0hkl}} \times 100\%}{\text{where } I_{hkl} \text{ is the diffraction intensity of (hkl), and } I_{0hkl} \text{ is the corresponding intensity of a pure Ni plate with a randomly oriented crystal structure (Fig. 3(a)). The four major peaks in the diffraction pattern, i.e., (111), (200), (220) and (311), were used as the total value in the denominator.}}
\]

Brightness of the electrodeposits was evaluated by measuring their reflectance spectra by microspectrophotometer (VSS–400, Nippon Denshoku Industries Co., Ltd.) in the wavelength range between 400 and 700 nm against the BaSO₄ white standard plate as a reference (100%).

The current efficiency of the Ni electrodeposition was determined as the ratio between the actual amounts of deposited Ni to the ideal mass calculated from Faraday’s law. The actual mass was measured from the difference of mass before and after the Ni electrodeposition.

3. Results and discussion

3.1. Effects of coumarin and cis-2-butyne-1,4-diol on the surface morphology of Ni electrodeposits

As described in the Experimental section, a nodular Cu foil was used as a substrate instead of a typical smooth Cu foil to clearly demonstrate the leveling and brightening effects of additives despite a relatively thin thickness of the Ni electrodeposited layer (~8 μm). Fig. S1 shows the surface morphology of a nodular Cu foil substrate consisting of globular deposits with a 1 μm size. Fig. 1 represents the effects of coumarin and cis-2-butyne-1,4-diol on the surface morphology of the Ni electrodeposits. The samples show a clear distinction in the morphology, the size of crystallites and the degree of the roughness of the deposits. As shown in Fig. 1(a), when Ni was electrodeposited from an additive-free bath (Bath 1) at a constant current density of ~200 mA/cm² for 120 s, the deposited Ni layer exhibits a bumpy morphology with a high roughness which is consistent with the Ni crystallites with spiral-type deposits [14,17–19]. In contrast, the electrodeposits from coumarin-containing baths have a smooth and bright morphology. As the concentration of coumarin was increased from 0.68 to 2.73 mmol/L in the bath, crevices (grain boundary) of the deposits became smaller and shallower, and the electrodeposits were therefore smoother with shallower crevices (Fig. S2). In particular, as presented in Fig. 1(b), at a coumarin concentration of 2.73 mmol/L, the crevices were hardly observed, and the smoothest electrodeposited was produced. Unlike coumarin-containing baths, the Ni electrodeposits from the cis-2-butyne-1,4-diol-containing bath exhibit a finer and more regular grain size. By increasing the concentration of cis-2-butyne-1,4-diol in the bath from 5.67 to 22.70 mmol/L, not only did the crystal size of

<table>
<thead>
<tr>
<th>Bath no</th>
<th>Coumarin (mmol/L)</th>
<th>Cis-2-butyne-1,4-diol (mmol/L)</th>
<th>Current efficiency</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>–</td>
<td>–</td>
<td>97.96%</td>
</tr>
<tr>
<td>2</td>
<td>0.68</td>
<td>–</td>
<td>97.14%</td>
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<tr>
<td>3</td>
<td>1.37</td>
<td>–</td>
<td>96.87%</td>
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<tr>
<td>4</td>
<td>2.05</td>
<td>–</td>
<td>96.05%</td>
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<tr>
<td>5</td>
<td>2.73</td>
<td>–</td>
<td>95.49%</td>
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<tr>
<td>6</td>
<td>–</td>
<td>5.67</td>
<td>97.83%</td>
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<td>–</td>
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<td>8</td>
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<td>94.13%</td>
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<td>–</td>
<td>22.70</td>
<td>91.80%</td>
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<tr>
<td>10</td>
<td>2.73</td>
<td>22.70</td>
<td>91.39%</td>
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the electrodeposits become smaller but the crystal density also increased (Fig. S3). At a cis-2-butene-1,4-diol concentration of 22.70 mmol/L, the finest grains were obtained as shown in Fig. 1(c). Interestingly, the presence of both coumarin and cis-2-butene-1,4-diol in the bath had synergistic effects on the surface smoothing of the Ni electrodeposition. As shown in Fig. 1(d), when the bath contained 2.73 mmol/L coumarin and 22.70 mmol/L cis-2-butene-1,4-diol (Bath 10), much more smooth Ni electrodeposits were produced. In particular, the highly magnified SEM images in Fig. 1(d) clearly demonstrate this improvement.

![SEM images](image)

**Fig. 1.** SEM images of Ni electrodeposits prepared at a constant current density of $-200 \text{ mA/cm}^2$ for 120 s from the modified Watts-type bath composed of 120 g/L NiSO$_4$, 30 g/L NiCl$_2$ and 45 g/L H$_3$BO$_3$ (a) without additives (Bath 1), (b) with 2.73 mmol/L coumarin (Bath 5), (c) with 22.70 mmol/L cis-2-butene-1,4-diol (Bath 9) and (d) with both 2.73 mmol/L coumarin and 22.70 mmol/L cis-2-butene-1,4-diol (Bath 10). All the SEM images were obtained for the tilt angles of 52°.

![Reflectance spectra](image)

**Fig. 2.** Reflectance spectra of Ni electrodeposits prepared at a constant current density of $-200 \text{ mA/cm}^2$ for 120 s from the electrolytic bath containing various concentrations of coumarin and cis-2-butene-1,4-diol (BUD).
image (inset, Fig. 1(d)) revealed that the spiral-type crystallites and the shallow crevices on the surface totally disappeared.

To quantitatively evaluate the degree of leveling and brightening of the electrodeposits, the total reflectance of the samples was measured as a function of wavelength using a microspectrophotometer in the range of visible light between 400 and 700 nm against the BaSO4 white standard plate as a reference (100%). Because the degree of brightening is directly associated with the surface roughness of the deposit, the higher reflectance value indicates a smoother and flatter surface. As shown in Fig. 2, with an addition of 0.68 mmol/L of coumarin into the bath, the surface reflectance of the electrodeposits increased approximately to 330% at the 400 nm wavelength, and the reflectance gradually increased over wavelengths between 400 and 800 nm. Further increases in the concentration of coumarin from 0.68 to 2.73 mmol/L result in the increase in the total reflectance of electrodeposits to 503.96%. The reflectivity data have a good correlation with the surface morphology observed by SEM in Fig. S2 where the surface of electrodeposits gets smoother with the higher concentration of coumarin.

The addition of cis-2-butene-1,4-diol to the bath did not show a significant increase in the surface reflectance of the electrodeposits like coumarin at the wavelength of 400 nm, but the reflectance value became higher with an increase in the wavelength. As the concentration of cis-2-butene-1,4-diol increased from 5.67 to 22.70 mmol/L, the reflectance value was obviously increased. Nevertheless, the increased reflectance values of Bath 9 were smaller than those of Bath 2, indicating that brightness of the electrodeposits is more dependent on the degree of the flatness than the grain size of the deposit. As expected, the surface reflectance of electrodeposits prepared from the bath containing both additives (Bath 10) had the highest value in this study. In the presence of 2.73 mmol/L coumarin and 22.70 mmol/L cis-2-butene-1,4-diol, the surface reflectance of the deposits dramatically increased to approximately 478.06% at the wavelength of 400 nm, which is 5.57 times higher than the surface reflectance of the additive-free bath (Bath 1). In particular, the reflectivity was further increased from 478.06 to 631.93% over the wavelengths between 400 and 700 nm. These results demonstrate that coumarin and cis-2-butene-1,4-diol have synergistic influences on the smoothing and the brightening of the Ni electrodeposition even at a high current density.

3.2. Effects of coumarin and cis-2-butene-1,4-diol on the crystal structure of Ni electrodeposits

The XRD patterns for a Ni standard plate with random orientation and the Ni electrodeposits prepared from an additive-free bath (Bath 1) are presented in Fig. 3. The crystal structures of the electrodeposited were characterized by five main diffraction peaks, (111), (200), (220), (311) and (222) in the range between 40 and 100°. As shown in Fig. 3(a), the main XRD peak positions of the Ni plate were well matched with those of the reference Ni phase (JCPDS card No. 00-087-0712). Based on the previous studies [11,15], it can be predicted that the Ni electrodeposits prepared from a typical Watts-type bath without additives have the preferred orientation of the (200) plane in the XRD analysis and [100] texture at high current density values with a pH higher than 2.5. However, the XRD pattern for the Ni electrodeposits formed in Bath 1 shows a mixed preferred crystalline orientation of [111] and [220]. The difference in the crystal structure between the two electrodeposits is due presumably to the difference in the deposition conditions which significantly affect the growth kinetics of the Ni electrodeposits: a low concentration of NiSO4 in the bath (variation in the chemical composition of the electrolyte) and a current density of − 200 mA/cm2 (the applied high cathodic overpotential).

As shown in Fig. 4, the crystal structure and the texture of the Ni electrodeposits are significantly influenced by the addition of coumarin to the bath. With the addition of coumarin into the bath, a mixed [111] and [110] orientation was gradually changed to the preferred [200] orientation. Specifically, the peak intensity of (200) obviously increased by more than 38 times with 2.73 mmol/L coumarin, whereas other peaks decreased with the addition of coumarin. To quantitatively evaluate the degree of the preferred orientation of the Ni deposits to the [200] direction, the relative texture coefficient (RTC) was calculated and is displayed in Fig. 4(b). In bath without coumarin, the electrodeposited had an RTC(200) value of only 21.75%, but at a coumarin concentration of 2.05 and 2.73 mmol/L, the RTC(200) values abruptly increased to 91.71% and 93.88%, respectively. These results imply that the formation of a highly smooth surface of Ni electrodeposits by the addition of coumarin is closely related to the preferred growth of Ni electrodeposits along the [200] direction.

Fig. 5 shows the influences of cis-2-butene-1,4-diol on the crystal growth and the texture of the Ni electrodeposits. With the addition of cis-2-butene-1,4-diol to the bath, the peak intensity of (111) and (200) planes were gradually decreased and broadened, but the peak of (220) was steadily increased. As shown in Fig. 5(b), it is evident that the addition of cis-2-butene-1,4-diol in the bath results in the increase in the RTC(220). According to the previous results [17,20], the [110] preferred orientation is accompanied with the finer grain size in comparison with the grain size of the deposits which have [211] or [100] orientation. Therefore, the drastic grain refinement in Fig. 1(c) is a result of the effects of cis-2-butene-1,4-diol on the crystal growth of the Ni electrodeposited.

Fig. 6 represents the individual and combined effects of coumarin and cis-2-butene-1,4-diol on the crystal structure of the Ni electrodeposits. As discussed above, coumarin and cis-2-butene-1,4-diol have thoroughly different influences on the growth of crystallites: coumarin promotes the preferred growth of Ni electrodeposits along the [200] direction, and cis-2-butene-1,4-diol provokes the imposition of [220] preferred orientation with the suppressive effects on the every mode of growth. Due to the competitive inhibition of the additives on the crystal growth, the peak of (200) was reduced compared to the coumarin-containing solution (Bath 5), and its intensity increased compared to the cis-2-butene-1,4-diol-containing solution (Bath 9). It should be emphasized that the peak of (220) was significantly enhanced by the synergistic effects of coumarin and cis-2-butene-1,4-diol. Considering the fact that the predominance of a [110] texture is correlated to a drastic grain refinement [17], the smallest grain size is expected in the presence of both additives (bath 10).

To verify the effects of the additives on crystallographic properties and the crystal size of the Ni electrodeposits, cross-sectional morphologies were observed using SIM. Because the SIM images were obtained at tilted angles of 52°, the images in Fig. 7 were expanded vertically by
1/cos(52°) to reproduce the actual dimension of the cross-section. As depicted in Fig. 7, for all electrodeposits, grains were small at the interface between Ni electrodeposits and Cu substrate, but their size increased with the deposit growth. This is because the crystal size and the orientation of the electrodeposits were affected by the Cu substrate within the deposit thickness of 2–3 μm [21]. Such influences gradually disappeared with increasing thickness of the deposits, and hence it can be thought that the crystal size and the orientation of the Ni electrodeposits in this study (approximately 7–9 μm in thickness) could be characterized by the effects of coumarin and cis-2-butene-1,4-diol. When Ni was electrodeposited from an additive-free bath (Bath 1), the deposit is composed of thin and long columns inclined to the various directions, but most columns incline between 45 and 90° against the surface plane (Fig. 7(a)). Since the XRD pattern for this electrodeposi-
and continuously repeated during the whole electrodeposition. The electrosorption of additives began with the initial Ni electrodeposition because the observation angles were 52°.

22.70 mmol/L cis-2-butene-1,4-diol (Bath 10).

22.70 mmol/L cis-2-butene-1,4-diol (Bath 9) and both 2.73 mmol/L coumarin and columns could be anticipated to grow in [100] orientation. Fig. 7(c) rin promoted the preferred growth of Ni along the [200] direction, these larly to the substrate plane. Since the XRD analysis revealed that couma-

trodeposits prepared from bath containing 2.73 mmol/L coumarin were composed of wide and extremely large columns oriented perpendicu-

larly without the formation of column-like crystallites de-

Fig. 6. XRD patterns of Ni electrodeposits prepared at a constant current density of −200 mA/cm² for 120 s in baths containing 2.73 mmol/L coumarin (Bath 5), 22.70 mmol/L cis-2-butene-1,4-diol (Bath 9) and both 2.73 mmol/L coumarin and 22.70 mmol/L cis-2-butene-1,4-diol (Bath 10).

and [110] directions. On the other hand, as shown in Fig. 7(b), the electrodeposits prepared from bath containing 2.73 mmol/L coumarin were composed of wide and extremely large columns oriented perpendicu-

larly to the substrate plane. Since the XRD analysis revealed that couma-

rin promoted the preferred growth of Ni along the [200] direction, these columns could be anticipated to grow in [100] orientation. Fig. 7(c) clearly shows the drastic grain refinement by the addition of cis-2-butene-1,4-diol, which is in accordance with the SEM observation in Fig. 1(c). The electrodeposits were composed of fine crystallites and very thin columns which were much smaller and narrower than those from Bath 1 and Bath 5. Although the growth orientation of those small crystals and thin columns was not ascertained in this study, we believed that most of these columns may grow in [110] and [111] orientations. As expected from the result of the XRD analysis, when the bath contains both additives (Bath 10), the electrodeposits show the smallest grain size (Fig. 7(d)). In particular, the crystal size of the deposit was consistently small without the formation of column-like crystallites despite the film growth. This phenomenon suggests that the electrosorption of additives began with the initial Ni electrodeposition and continuously repeated during the whole electrodeposition. The cross-sectional observation verifies the totally different influences of coumarin and cis-2-butene-1,4-diol on the growth of crystallites, and their synergistic effects on the crystallographic characteristics (particularly on the significant reduction in the crystal size).

3.3. Effects of coumarin and cis-2-butene-1,4-diol on the electrodeposition of Ni

To investigate the effects of coumarin and cis-2-butene-1,4-diol on the Ni electrodeposition, the potential transient curves for the Ni electrodeposition were measured as a function of the concentration of the additives at a constant current density of −200 mA/cm² for 120 s. As shown in Fig. 8, in the absence of additives, the cathodic potential was approximately −2.27 V_SCE, but with the addition of 0.68 mmol/L couma-

rin, the potential was shifted to a more negative value of approximately −2.3 V_SCE (Fig. S5). Further increases in the addition of coumarin from 0.68 to 2.73 mmol/L resulted in a higher cathodic overpotential. Such an increase in the cathodic overpotential with additives is generally interpreted as the adsorption of additive that blocks the active sites for the overall cathodic reactions. To understand the inhibiting effects of coumarin on Ni electrodeposition better, the cathodic current efficiency of the Ni electrodeposition should be considered because the hydrogen evolution (the reduction of H⁺) occurs competitively with the Ni electrodeposition (the reduction of Ni²⁺) under the constant current condition. Table 1 shows the current efficiency of the Ni electrodeposi-

Fig. 7. Cross-sectional SEM images of Ni electrodeposits prepared from the modified Watts-type bath (a) without additives (Bath 1), (b) with 2.73 mmol/L coumarin (Bath 5), (c) with 22.70 mmol/L cis-2-butene-1,4-diol (Bath 9) and (d) with 2.73 mmol/L coumarin and 22.70 mmol/L cis-2-butene-1,4-diol (Bath 10). All the SEM images were expanded vertically by 1/cos(52°) because the observation angles were 52°.
relatively small quantity of coumarin results in the decrease in the RTC_{111} and the RTC_{311}, with an increase in the RTC_{200}, as shown in Fig. 4(b).

As shown in Fig. S6, with the addition of cis-2-butene-1,4-diol, the potential was also shifted to the more negative value of approximately $-2.35$ V_{SCE}. Further increases in the addition of cis-2-butene-1,4-diol from 5.67 to 22.70 mmol/L resulted in a significant increase in the cathodic overpotential, indicating the enhanced inhibiting effects of cis-2-butene-1,4-diol on the overall cathodic reactions. As shown in Table 1, with an addition of 5.67 mmol/L of cis-2-butene-1,4-diol into the bath, the current efficiency was slightly decreased from 97.96% to 97.83%. However, a further increase in the addition of cis-2-butene-1,4-diol from 5.67 to 22.70 mmol/L results in a steep reduction in the current efficiency to 91.80%. The results of the increased cathodic overpotential and the reduced current efficiency demonstrated that cis-2-butene-1,4-diol inhibits the electrocrystallization of Ni, and the reduction of Ni is suppressed more by cis-2-butene-1,4-diol than by coumarin.

The ability of cis-2-butene-1,4-diol to refine the grain size can be accounted for two possible reasons: one is the formation of Ni(OH)$_2$, and the other is the adsorption/desorption of H$_{ads}$ on the Ni active sites. As reported in a previous work, very rapid adsorption and desorption of the acetylenic alcohol[$^{10}$] cause an increase in local pH near the cathode and promote the formation of Ni(OH)$_2$, which is accompanied with an enhanced [211] preferred orientation [$^{11,14}$]. In this study, however, the [211] texture was not enhanced by the addition of cis-2-butene-1,4-diol as depicted in Fig. 5, and therefore the precipitation of Ni(OH)$_2$ is not the cause of the grain refining effects of cis-2-butene-1,4-diol. Rather, the grain refinement is expected to be the result of the enhancement of [110] texture by the adsorption/desorption of H$_{ads}$ on the Ni active sites with a weak catalytic hydrogenation of cis-2-butene-1,4-diol.

When both additives were added to the electrolytic bath, the highest cathodic overpotential among all baths was observed, indicating that coumarin and cis-2-butene-1,4-diol have synergistic inhibiting effects on the overall cathodic reactions. Specifically, the current efficiency for Bath 10 (the bath containing both additives) was the lowest value (91.39%), indicating that inhibiting effects on the electrocrystallization and the growth of the Ni deposits were particularly enhanced. Fig. 8(b) shows the cathodic polarization curves for the Ni electrodeposition with additives. With the cathodic polarization, Ni electrodeposition began at potentials below approximately $-0.6$ V_{SCE}. The notable feature in cathodic polarization curves is that below cathodic potentials near $-0.6$ V, the cathodic current density of Bath 10 always has the lowest value among all of the baths, representing that the electroadsorption of additives began with the Ni electrodeposition.

4. Conclusions

In this work, the individual and synergistic effects of coumarin and cis-2-butene-diol on the surface morphology and the crystal structure of Ni electrodeposits at high cathodic current density were investigated using SEM, XRD, SIM and electrochemical analyses. While the rough and bumpy Ni layer composed of spiral-type deposits was deposited from the additive-free bath, the electrodeposits prepared from the coumarin-containing bath showed a smooth and bright surface. Cross-sectional observation revealed that coumarin enhanced the columnar growth of the deposits with the [200] preferred orientation. On the other hand, cis-2-butene-1,4-diol showed the strong grain-refining effects of the Ni electrodeposits. Cis-2-butene-1,4-diol suppresses almost every mode of the crystal growth that causes the inhibition of the surface diffusion of adatoms and the acceleration of the nucleation rate. When both coumarin and cis-2-butene-1,4-diol were contained in the bath, highly smooth Ni electrodeposits were produced by the synergistic effects of the additives. Because the production of flat surfaces composed of fine-grained deposits is essential to obtaining high brightness of the electrodeposits, the results presented here demonstrate that the proper combination of coumarin and cis-2-butene-1,4-diol is an effective way to obtain mirror-like brightened Ni at a high cathodic current density.

Conflict of interest statement

There is no conflict of interest.

Acknowledgments

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