1. Introduction

Electrowinning from aqueous solutions is an important process in nickel smelting. 1–3 Nickel electrowinning is performed from sulfate and chloride solutions. Between these solutions, chloride solutions exhibit higher electrical conductivity and diffusion-limiting current density than sulfate solutions, so that the use of chloride solutions is advantageous for electrolysis at high current densities.

Numerous studies have been performed on nickel electrodeposition from chloride solutions, and many of these have reported the mechanical properties and stress states of the nickel deposits. 4–6 However, very few studies have investigated nickel electrowinning from chloride solutions. The color of the nickel deposits is expected to vary depending on the surface texture, codeposition of impurities, surface oxidation, and the contamination of electrolytes into deposits. A more diffuse appearance in the color of nickel deposits is often associated with deterioration in the quality of the deposits. Therefore, stability in the color of such deposits is a necessary feature. We have previously investigated the effects of these impurities on the color and surface morphology of nickel deposits, but the effects of impurities on the color and surface morphology of deposited nickel are not clear. Therefore, this study selected Mn^{2+}, Cr^{3+}, and SO_4^{2−} ions as impurities, which are present in commercial solutions, and investigated the effect of these impurities on the lightness, morphology, current efficiency, and crystal orientation of deposited nickel.

2. Experimental Procedures

Table 1 shows the solution composition and electrolysis conditions for nickel electrowinning. The electrolytic solution was prepared by dissolving fixed amounts of high-grade NiCl_2·6H_2O (350 g·dm^{-3}, 1.47 mol·dm^{-3}) in distilled deionized water. The pH was adjusted to values of 1, 2, or 3 using hydrochloric acid. A standard pH value of 2 was chosen for

<table>
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<th>Bath composition</th>
<th>Table 1 Electrolysis conditions.</th>
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<tr>
<td>NiCl_2·6H_2O</td>
<td>(mol·dm^{-3})</td>
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<tr>
<td>Mn^{2+}</td>
<td>(g·dm^{-3})</td>
</tr>
<tr>
<td>Cr^{3+}</td>
<td>(g·dm^{-3})</td>
</tr>
<tr>
<td>SO_4^{2−}</td>
<td>(g·dm^{-3})</td>
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<td>pH</td>
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<th>Operating conditions</th>
<th>Current density (A·m^{-2})</th>
<th>Amount of charge (C·m^{-2})</th>
<th>Cathode</th>
<th>Anode</th>
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<td></td>
<td>300</td>
<td>7.2 × 10^6</td>
<td>Ti (4 cm × 5 cm)</td>
<td>DSE, Ni</td>
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solutions containing Mn$^{2+}$ and SO$_4^{2-}$ impurities, and a value of 1 was chosen for solutions containing Cr$^{3+}$ ions. Various amounts of Mn$^{2+}$ (1–10 g·dm$^{-3}$), 0.018–0.18 mol·dm$^{-3}$), Cr$^{3+}$ (0.0001–10 g·dm$^{-3}$, 1.9 × 10$^{-5}$–0.19 mol·dm$^{-3}$), and SO$_4^{2-}$ (10–141.5 g·dm$^{-3}$, 0.104–1.47 mol·dm$^{-3}$) were added to the electrolyte as impurities. Mn$^{2+}$, Cr$^{3+}$, and SO$_4^{2-}$ ions were added in the form of MnCl$_2$·6H$_2$O, CrCl$_3$·6H$_2$O, and NiSO$_4$·6H$_2$O, respectively. For the solution containing NiSO$_4$·6H$_2$O, the concentration of NiCl$_2$·6H$_2$O was adjusted to produce a total Ni$^{2+}$ concentration of 1.47 mol·dm$^{-3}$. The cathode and anode consisted of titanium sheets measuring 4 × 5 cm$^2$ with one side sealed with epoxy resin, and a dimensionally stable electrode mesh, respectively. The anolyte and catholyte were separated with filter cloth to prevent chlorine gas from permeating into the catholyte as a result of anode reaction. Prior to electrodeposition, the cathode was immersed in a 48% sulfuric solution at 363 K for 15 minutes to improve adhesion of the nickel deposits. Nickel electrodeposition was conducted in 1.0 dm$^{-3}$ of unagitated solution at 333 K under galvanostatic conditions (300 A$^{-}$) for a constant charge of 7.2 × 10$^5$ C·m$^{-2}$. Unagitated solutions were used for deposition because the electrolyte only circulated in the electrolysis tank during the actual electrowinning, and as a result, is nearly quiescent at the cathode surface. The deposits were dissolved from the cathode using nitric acid. Nickel was quantitatively analyzed by inductively coupled plasma (ICP) spectroscopy, and the current efficiency for nickel deposition was calculated. The cathode potentials during deposition were measured against a saturated Ag/AgCl reference electrode (0.199 V vs. NHE, 298 K) and the potentials were plotted in reference to the NHE electrode.

The lightness of deposits was measured using a colorimeter (CM-512 m3; Konica Minolta Co.). The surface and cross-sectional morphology of the deposited Ni was observed by SEM and the distribution of elements was examined by EDX. Crystal orientations in the deposited nickel were determined using the method of Wilson and Rogers$^{9,10}$ by comparing the X-ray diffraction intensity at (111) to the (222) reflection. To study the hydrolysis behavior of the solutions, pH titration curves were measured using NaOH. A 5.0 mol·dm$^{-3}$ NaOH solution was added to a 1.47 mol·dm$^{-3}$ solution of NiCl$_2$·6H$_2$O and/or a 0.019 mol·dm$^{-3}$ solution of CrCl$_3$·6H$_2$O using a burette.

3. Results and Discussion

3.1 Effect of Mn$^{2+}$ ions

Figure 1 shows the effect of Mn$^{2+}$ ions on current efficiency for nickel deposition in solutions with various pH. In all solutions, the current efficiency for nickel deposition decreased slightly with the addition of Mn$^{2+}$ ions, regardless of pH. The degree of current efficiency decrease was largest in a solution of pH 3. The effect of pH in a Mn$^{2+}$-free solution was to increase the current efficiency of nickel at higher pH values, while solutions containing Mn$^{2+}$ ions displayed the largest current efficiency in a solution of pH 2, and a slightly lower efficiency in a solution of pH 3. ICP spectroscopy confirmed that manganes was not codeposited with nickel.

Figure 2 shows the effect of Mn$^{2+}$ ions on the surface morphology of nickel deposits. Nickel deposited from a Mn$^{2+}$-free solution was composed of pyramidal crystals of several micron in size, with platelets and granular crystals occurring between the pyramidal crystals. Nickel deposited from a Mn$^{2+}$-bearing solution was also composed of pyramidal crystals of several microns, but these were smaller in size than those from the Mn$^{2+}$-free solution. Fine platelet-shaped crystals were not present in nickel deposited from Mn$^{2+}$-bearing solutions, and the amount of fine granular crystals of approximately 1 μm increased.

Figure 3 shows the effect of Mn$^{2+}$ ions on the cross-sectional morphology of nickel deposited. A fibrous texture was observed in a cross-section from the substrate boundary to the upper area of the deposits, indicating a field-oriented texture$^{11}$ with a preferred orientation of certain planes toward...
the electric field during deposition. The fibrous texture was fine-grained in the vicinity of the substrate and became coarser toward the top of the deposits, reflecting an increase in crystal size with increasing deposit thickness. The width of the fibrous-textured region was smaller in solutions containing Mn\(^{2+}\) than that in a Mn\(^{2+}\)-free solution, indicating that the presence of Mn\(^{2+}\) ions resulted in smaller crystal sizes. In terms of surface morphology, the crystal size of deposits was also smaller in solutions containing Mn\(^{2+}\) ions, following the same trend observed in the cross-sectional morphology.

Figure 4 shows the lightness of nickel deposited from solutions containing various amounts of Mn\(^{2+}\) ions. The lightness of deposited nickel decreased with increasing concentrations of Mn\(^{2+}\) in solution. The nickel lightness appears to depend on surface morphology alone because of the absence of codeposited manganese. As shown in Fig. 2, the addition of Mn\(^{2+}\) ions in solution resulted in the disappearance of fine platelet-shaped crystals and greater amounts of 1-μm-size fine granular crystals. This indicates that an increase in irregular reflection of light due to the addition of Mn\(^{2+}\) ions causes decreased lightness of deposited nickel.

Mn\(^{2+}\) ions in solution are oxidized to MnO\(_2\) on the insoluble dimensionally stable electrode (DES). Many fine black particles assumed to be MnO\(_2\) were observed at the barrier membrane between the anode and cathode. Because this MnO\(_2\) may affect the lightness of the deposited nickel, the nickel deposit lightness was measured following nickel deposition performed on a soluble nickel anode to prevent the formation of MnO\(_2\). The result is shown in Fig. 5. Although the lightness of deposited nickel decreased somewhat in the presence of Mn\(^{2+}\) ions using a soluble nickel anode, the degree of decrease was significantly smaller than that obtained using an insoluble DSE anode. This result suggests that MnO\(_2\) formed on the insoluble DSE anode causes a decrease in lightness of the deposited nickel. The surface morphology images in Fig. 2 show that the nickel crystal size was smaller in solutions containing Mn\(^{2+}\) ions than that in a Mn\(^{2+}\)-free solution. This suggests that the MnO\(_2\) formed on the anode is transferred and adsorbed onto the cathode, resulting in both a higher nucleation rate of nickel deposition and suppressed nickel crystal growth. The details of this process should be further investigated in the future.

### 3.2 Effect of Cr\(^{3+}\) ions

Figure 6 shows the effect of Cr\(^{3+}\) ion concentrations on current efficiency for nickel deposition and the chromium content in the deposits. The current efficiency gradually decreased with increasing Cr\(^{3+}\) concentrations in the low-concentration region, whereas it strongly decreased at Cr\(^{3+}\) concentrations above 0.1 g·dm\(^{-3}\). The chromium content in the deposits was close to zero at concentrations below 0.1 g·dm\(^{-3}\), but it significantly increased at greater concentrations. The large decrease in current efficiency for nickel deposition at Cr\(^{3+}\) concentrations above 0.1 g·dm\(^{-3}\) corresponds to this increase in chromium content in the deposits. However, below 0.1 g·dm\(^{-3}\), the very low chromium content in the deposits did not correlate with the current efficiency for nickel deposition, which decreased slightly in the presence of small amount of Cr\(^{3+}\) ions in solution.

Figure 7 shows the surface morphology and EDX spectra of nickel deposited from a solution containing 0.1 g·dm\(^{-3}\) of Cr\(^{3+}\). The majority type of surface morphology of the deposits consists of pyramidal crystals several microns in size, as shown in (a), and some fine granular crystals were observed between the pyramidal crystals. EDX analysis detected only nickel in these majority areas, as shown in (c), reflecting the deposition of metallic Ni. Conversely, a minor portion of the
surface was covered with a mesh-patterned flat surface and several-micron-scale granular crystals were observed, as shown in (b). EDX analysis detected nickel, oxygen, chromium, and chlorine in these areas, as shown in (d), indicating that the chromium and some of the nickel were deposited in the form of oxides and hydroxides. Inductively coupled plasma spectroscopy determined that the chromium content in the deposits was approximately 0.2 mass%.

Figure 8 shows the lightness of nickel deposited from solutions containing various amounts of Cr\(^{3+}\). The nickel lightness significantly decreased with increasing Cr\(^{3+}\) concentrations above 0.001 g dm\(^{-3}\) in solution. At Cr\(^{3+}\) concentrations above 0.1 g dm\(^{-3}\), the chromium content in the deposits increased strongly (Fig. 6), resulting in decreased lightness of the deposited nickel. However, the lightness of deposited nickel still decreased at a Cr\(^{3+}\) concentration of 0.01 g dm\(^{-3}\), although the chromium content in the deposits was nearly zero.

During deposition from solutions containing Ni\(^{2+}\) and Cr\(^{3+}\) ions, the pH is elevated in the vicinity of cathode due to hydrogen evolution, resulting in the formation of metallic oxides or hydroxides through hydrolysis reactions. The critical pH value for Ni(OH)\(_2\) formation was calculated to be 6.0 on the basis of the potential vs. pH diagram for the Ni–H\(_2\)O system\(^{12}\) in a solution containing 1.47 mol dm\(^{-3}\) of Ni\(^{2+}\). Similarly, the critical pH value for Cr(OH)\(_3\) formation was calculated to be 2.1 on the basis of the potential vs. pH diagram for the Cr–H\(_2\)O system\(^{12}\) in a solution containing 0.019 mol dm\(^{-3}\) of Cr\(^{3+}\). Figure 9 shows pH titration curves measured for a solution containing Ni\(^{2+}\) and Cr\(^{3+}\) ions titrated with 5.0 mol dm\(^{-3}\) NaOH. In the solution containing only Ni\(^{2+}\), the increase in pH begins to plateau at a pH of approximately 5.0 and a suspension begins to form in the solution as a result of precipitation. In the solution containing both Ni\(^{2+}\) and Cr\(^{3+}\) ions, the increase in pH plateaus at pH levels of approximately 2.6 with a subsequently pH increase that stalls at a value around 5.0, similar to the results obtained for the solution containing only Ni\(^{2+}\) ions. The pH values at which precipitation began were somewhat different from the critical pH values for Ni(OH)\(_2\) and Cr(OH)\(_3\) formation calculated from the potential vs. pH diagrams. However, Cr(OH)\(_3\) appears to form preferentially at the cathode layer because the critical pH value for Cr(OH)\(_3\) formation is lower than that for Ni(OH)\(_2\).

During nickel deposition, the pH in the vicinity of cathode becomes raised due to reduction of H\(^+\) ions in a side reaction. Since the critical pH value for Cr(OH)\(_3\) formation is lower than that for Ni(OH)\(_2\), Cr(OH)\(_3\) forms at the cathode layer in solutions containing Cr\(^{3+}\) ions. The deposition of iron-group metals such as nickel proceeds through a multi-step reaction.\(^{13}\) Because reaction limited sites are available on which intermediates can adsorb, the deposition of iron-group metals have a high overpotential. Furthermore, deposition is reported to be suppressed by the formation of foreign substances, such as Zn(OH)\(_2\) species, restrict the adsorption sites for the reaction intermediate on the cathode.\(^{14,15}\) As shown in Fig. 6, the decrease in current efficiency for nickel deposition with increasing Cr\(^{3+}\) concentrations in solution is attributed to suppression of nickel deposition due to Cr(OH)\(_3\) formation at the cathode layer. When nickel deposition is suppressed by Cr(OH)\(_3\) formation, nickel appears to be partially incorporated into deposits in non-reduced forms such as oxides and hydroxides, resulting in decreased lightness of the nickel deposi-

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**Fig. 7** SEM images and EDX spectra of nickel deposited from a solution of pH 1 containing 0.1 g dm\(^{-3}\) of Cr\(^{3+}\). (a) Majority surface type, (b) Minor surface type, (c) EDX spectrum of region in (a), (d) EDX spectrum of region in (b).

**Fig. 8** Effect of Cr\(^{3+}\) ions on the lightness of nickel deposited from solutions of pH 1.

**Fig. 9** pH titration curves for nickel and nickel-chromium solutions. (NiCl\(_2\)-6H\(_2\)O 1.47 mol dm\(^{-3}\), CrCl\(_3\)-6H\(_2\)O 0.019 mol dm\(^{-3}\)).
its. When the concentration of Cr\(^{3+}\) in solution increases further, Cr(OH)\(_3\) formed at the cathode layer becomes partially incorporated into the deposited nickel, which may cause the large decrease in deposited nickel lightness.

### 3.3 Effect of SO\(_4^{2-}\) ions

Figure 10 shows the effect of SO\(_4^{2-}\) concentrations in solution on current efficiency for nickel deposition. The current efficiency was almost constant at SO\(_4^{2-}\) concentrations below 50 g·dm\(^{-3}\), but decreased somewhat above 50 g·dm\(^{-3}\), and decreased significantly above 100 g·dm\(^{-3}\).

Figure 11 shows the surface morphology of nickel deposited from solutions containing various amounts of SO\(_4^{2-}\). Ni deposited from a solution containing 10 g·dm\(^{-3}\) of SO\(_4^{2-}\), as well as that from a SO\(_4^{2-}\)-free solution, are composed of polygonal pyramidal crystals of various sizes. The flat areas alongside the polygonal pyramidal crystals were somewhat larger in nickel deposited from a solution containing 20 g·dm\(^{-3}\) of SO\(_4^{2-}\). With increasing concentrations of SO\(_4^{2-}\) above 50 g·dm\(^{-3}\), the polygonal pyramidal crystals disappeared and the flat area increased.

Figure 12 shows nickel crystal orientations deposited from solutions containing various amounts of SO\(_4^{2-}\). Nickel deposited from an SO\(_4^{2-}\)-free solution was largely unoriented, whereas nickel deposited from solutions containing 10–50 g·dm\(^{-3}\) of SO\(_4^{2-}\) exhibited increased preferred orientation of \{110\} planes with higher SO\(_4^{2-}\) concentrations. However, with increasing SO\(_4^{2-}\) concentrations up to 100 g·dm\(^{-3}\), the deposited nickel became less oriented than that from a SO\(_4^{2-}\)-free solution. With further increases in SO\(_4^{2-}\) concentrations up to 141.5 g·dm\(^{-3}\), the preferred orientation of deposited nickel shifted to \{100\} planes.

Figure 13 shows the lightness of nickel deposited from solutions containing various amounts of SO\(_4^{2-}\) ions. The lightness of nickel deposited from a solution containing 10 g·dm\(^{-3}\) of SO\(_4^{2-}\) was nearly identical to that obtained from a SO\(_4^{2-}\)-free solution, while the lightness increased somewhat at 20 g·dm\(^{-3}\) of SO\(_4^{2-}\) and increased significantly at concentrations above 20 g·dm\(^{-3}\). This relationship between the lightness of nickel and the SO\(_4^{2-}\) concentrations corresponded to the relationship between the nickel surface morphology and SO\(_4^{2-}\) concentrations shown in Fig. 11. That is, with increasing SO\(_4^{2-}\) concentrations in solution, polygonal pyramidal crystals disappeared and the area of flat surface increased (Fig. 11), causing increased lightness of deposited nickel.

Figure 14 shows the time dependence of the cathode potential during nickel deposition at 300 A·m\(^{-2}\) in solutions containing various amounts of SO\(_4^{2-}\) ions. In all solutions containing SO\(_4^{2-}\), the cathode potential slightly shifted toward
Effect of Dissolved Impurities on the Lightness and Surface Morphology of Nickel Deposits from Chloride Electrowinning Solutions

To compare each rate-determining step, it is noted that because the sites on which NiOH$_{ad}$ can adsorb are limited, the overpotential for nickel deposition is larger in a sulfate solution than in a chloride solution. In this study, SO$_4^{2-}$ ions was added in the form of NiSO$_4$·6H$_2$O and the concentration of NiCl$_2$·6H$_2$O was adjusted to maintain a constant total concentration of Ni$_{total}$ ions in solution. Therefore, the concentration of Cl$^-$ ions decreased with increasing SO$_4^{2-}$ concentrations in solution. In solutions containing 141.5 g·dm$^{-3}$ of SO$_4^{2-}$, the concentration of Cl$^-$ was zero. Therefore, in this study, with increasing amounts of SO$_4^{2-}$, nickel deposition appears to simultaneously proceed by the multi-step reaction described by eqs. (4)–(6) in addition to the reactions in eqs. (1)–(3). With greater overpotential for metal deposition, the crystal nucleation rate prevails over the growth rate, which results in smaller crystal sizes. In this study, significant variability in the morphology of deposited nickel depending on SO$_4^{2-}$ concentrations (Fig. 11) appears to be caused by a change in overpotential for deposition. On the other hand, Pangarov calculated the relative work required for two-dimensional nucleation of various crystal planes. Assuming that two-dimensional nuclei generating the smallest nucleation work form at a given crystallization overpotential, he examined the overpotential dependence of the preferred orientation for various metals deposited from aqueous solutions. According to Pangarov, the preferred orientations of face-centered cubic nickel are {111} planes at low overpotential, {100} planes at intermediate overpotential, and {110} planes at high overpotential. That is, the preferred orientation of the deposited Ni changes from {111} to {100} and then to {110} planes with increasing nickel deposition overpotential. In this study, the increase in {110} plane orientation with increasing SO$_4^{2-}$ concentrations in the region of 10–50 g·dm$^{-3}$ of SO$_4^{2-}$ (Fig. 12) is attributed to increases in overpotential that reach the high overpotential region. However, with increases of SO$_4^{2-}$ up to 100 g·dm$^{-3}$, the deposited nickel begins to display less oriented textures, and with further increases in SO$_4^{2-}$ up to 141.5 g·dm$^{-3}$, the preferred orientations of nickel switches to {100} planes, which cannot be explained by the overpotential theory of Pangarov. The texture of the deposited metal is reported to shift from a field-oriented texture type, with a preferred orientation of specific planes, to an unoriented dispersed type with increasing overpotential for deposition. For a solution with 100 g·dm$^{-3}$ of SO$_4^{2-}$ in this study, the texture of deposited nickel seems to shift to the unoriented dispersed type. In the case of 140 g·dm$^{-3}$ of SO$_4^{2-}$, because the concentration of Cl$^-$ ions in solution is zero, the difference in deposition mechanisms between a chloride solution [(1)–(3)] and a sulfate solution [(4)–(6)] possibly affects the crystal orientation of deposited nickel, but the details of this explanation are ambiguous, and further investigation is required.

4. Conclusion

The effect of dissolved impurities on the lightness, surface morphology, and current efficiency of nickel deposited from a chloride electrowinning solution was investigated. In solutions containing 10 g·dm$^{-3}$ of Mn$^{2+}$, the current efficiency for nickel deposition decreased slightly, and the crystal size of the deposited nickel decreased. The lightness of deposited nickel decreased when the concentration of Mn$^{2+}$ ions exceeded 1 g·dm$^{-3}$. When nickel deposition was performed using a soluble nickel anode to prevent formation of MnO$_2$ at the anode, the nickel lightness was higher than that obtained using an insoluble anode, suggesting that MnO$_2$ formation at the insoluble anode caused the decrease in nickel lightness. In solutions containing Cr$^{3+}$ ions, the current efficiency of nickel gradually decreased with increasing concentrations of Cr$^{3+}$, and significantly decreased at Cr$^{3+}$ concentrations above 0.1 g·dm$^{-3}$. The lightness of deposited nickel greatly decreased with increasing Cr$^{3+}$ concentrations above 0.001 g·dm$^{-3}$. In solutions containing Cr$^{3+}$ ions, Cr(OH)$_3$ formation at the cathode layer is presumed to suppress nickel deposition, resulting in some codeposition of NiO and
Ni(OH)$_2$ along with nickel, which causes decreased current efficiency and nickel lightness. However, in solutions containing SO$_4^{2-}$ ions, the current efficiency of nickel decreased slightly at SO$_4^{2-}$ concentrations above 50 g·dm$^{-3}$, and significantly decreased above 100 g·dm$^{-3}$. The lightness of deposited nickel somewhat increased at SO$_4^{2-}$ concentrations of 20 g·dm$^{-3}$, and greatly increased above 20 g·dm$^{-3}$. Since the overpotential for nickel deposition increases with the concentration of SO$_4^{2-}$, the surface of the deposited nickel becomes smooth, resulting in an increase in lightness.

REFERENCES