Structure of Deposits Obtained from Urea-Based Melt Bath Containing Co and La

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Electrodeposition was performed in an unagitated solution from a urea-based melt bath containing Co and La under galvanostatic (10–40 mA·cm⁻²) and couloustatic (10 C·cm⁻²) conditions at 403 K, and the structure of the deposits was investigated. Co deposited in a metallic state at 10 mA·cm⁻², whereas it was incorporated into deposits mainly as an oxide at high current densities of 30 and 40 mA·cm⁻². La codeposited with Co as an oxide irrespective of current density. The content of La₂O₃ increased with current density. The deposits showed a granular crystal structure and became nonuniform crystals comprising large localized granules at high current densities. [doi:10.2320/matertrans.M2011379]

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1. Introduction

A few metals can electrodeposit from an aqueous solution because of competition with hydrogen evolution by electrolysis in an H₂O solvent. Because standard single electrode potentials of Al, Mg, and rare-earth metals, which are expected constituent elements of functional coatings, are significantly less noble than that of hydrogen evolution, they cannot deposit from an aqueous solution. Therefore, many studies have focused on electrodeposition from molten salts, which are stable solvents and have a wider potential window than aqueous solutions.¹⁻⁵ Urea-based melts have recently attracted attention as solvents because their physicochemical properties are similar to those of room-temperature molten salts. The merits of urea-based melts as solvents are that they are inexpensive to synthesize and the solubility of metal salts and metallic oxides is high. Although the deposition of pure Ag, Cu, and some alloys from urea-based melts has been reported,⁶⁻⁸ the structure of the deposits is ambiguous. In this study, Co with a standard single electrode potential E⁰ of −0.277 V and La, which cannot deposit from an aqueous solution because of a significantly less noble potential E⁰ of −2.52 V, are deposited from a urea-based melt and the structure of the deposits is investigated.

2. Experimental

The electrolytic solution was prepared by dissolving reagent grade CoSO₄ (6.0 mmol·L⁻¹), LaCl₃ (0.012 mol·L⁻¹), and NaBr (0.29 mol·L⁻¹). Urea (CH₄N₂O) was dried in advance at 393 K for 7 h in vacuum. Prior to preparing the electrolytic bath, CoSO₄ and LaCl₃ were dehydrated at 427 K for 21 h in vacuum. Electrodeposition was performed in an unagitated solution under galvanostatic (10–40 mA·cm⁻²) and couloustatic (10 C·cm⁻²) conditions at 403 K. Iron sheets measuring 1 × 2 cm² and carbon sheets measuring 5.5 × 5.5 cm² were used as a cathode and an anode, respectively. Polarization curves were measured by the potential sweep method, in which the electrode was polarized from −0.7 V (vs. Pt, Urea + NaBr) to −1.2 V at 1.0 mV·s⁻¹. Cathode potentials were measured using a platinum wire reference electrode. Cathode deposits were dissolved using nitric acid. Co and La contents in the deposits were quantitatively analyzed by inductively coupled plasma spectroscopy, enabling the La content to be calculated. The morphology of the deposits was observed by scanning electron microscopy (SEM). Chemical states of Co and La in the deposits were investigated by X-ray photoelectron spectroscopy (XPS) after sputtering for 4 min with Ar ions.

3. Results and Discussion

Figure 1 shows the relationship between the composition of the deposits and current density. The La content was calculated from the moles of La and Co in the deposits using the following equation.

La content = [mole La/total mole (La + Co)] × 100

The La content was small at low current densities of 10 and 20 mA·cm⁻², whereas it increased at high current densities of 30 and 40 mA·cm⁻².

Figure 2 shows the total polarization curves for deposition from the urea-based melt bath. In the urea-based melt containing only La (③), the current density increased at potentials less noble than −0.9 V (vs. Pt, Urea + NaBr).

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Because no inductively coupled plasma spectroscopy showed deposit on the cathode, it appears that the urea medium and mixed trace water decomposed. Urea medium is reported to be decomposed at $-1.0$ V vs. Pt, Urea$^+\text{NaBr}$. In the urea-based melt containing only Co (2), the current density increased gradually while the cathode potential shifted to a less noble direction than approximately $-0.7$ V. The current density became almost constant at $-0.82$ to $-0.93$ V because of the diffusion limit of Co ions. At potentials less noble than $-0.95$ V, the current density increased as the cathode potential shifted to a less noble direction, similar to the urea-based melt containing only La. In contrast, in the urea-based melt containing both La and Co (1), the current density gradually increased as the cathode potential shifted to less noble than approximately $-0.95$ V and became almost constant at $-0.85$ to $-0.9$ V because of the diffusion limit of Co ions. At potentials less noble than $-0.9$ V, the current density increased abruptly, indicating the decomposition of the urea medium and mixed trace water, similar to that observed in urea-based melts containing only La and only Co. When the cathode is polarized at potentials less noble than $-1.2$ V, the current density seems to increase linearly with polarizing the cathode.

Figure 3 shows the SEM images of the deposits obtained from the urea-based melt bath containing Co and La. The deposits obtained at 10 and 20 mA·cm$^{-2}$ showed an unsmooth granular surface. At 30 mA·cm$^{-2}$, block-like deposits were observed with cracks, whereas at 40 mA·cm$^{-2}$, the deposits showed nonuniform granular crystals composed of large localized granules.

Figure 4 shows the XPS spectra of deposits obtained at various current densities from the urea-based melt bath containing Co and La. The peak of the Co spectrum for the deposit obtained at 10 mA·cm$^{-2}$ was consistent with that of metallic Co, revealing that metallic Co deposited at 10 mA·cm$^{-2}$. However, the peak of the Co spectrum for the deposit obtained at 30 and 40 mA·cm$^{-2}$ was consistent with CoO, indicating that Co was incorporated mainly as an oxide. In contrast, the peaks of the La spectrum were located at the same binding energy irrespective of current density and showed main peaks at 835 and 852 eV and satellite peaks at 840 and 857 eV. The main peaks did not correspond to metallic La but were consistent with those of La oxide. Satellite peaks are known to exist because of electron transfer.
between La and Co. The satellite peaks were consistent with those of La$_2$O$_3$, demonstrating that La was incorporated into the deposit as an oxide. At high current densities of 30 and 40 mA·cm$^{-2}$, both Co and La codeposited mainly as oxides. The reason why Co and La codeposited mainly as oxides seems to be due to the decomposition of mixed trace water. Since the decomposition of water increases with polarizing the cathode potential or increasing the current density, Co codeposited mainly as oxides at high current densities. Urea medium is reported to be decomposed at $\sim$1.0 V vs. Pt, as the result, the cathode potential possibly doesn’t polarize to the equilibrium potential for La deposition.

4. Conclusion

Electrodeposition was performed from a urea-based melt bath containing Co and La, and the structure of deposits was investigated. Co deposited in a metallic state at 10 mA·cm$^{-2}$, whereas it was incorporated into the deposit mainly as an oxide at high current densities of 30 and 40 mA·cm$^{-2}$. In contrast, La codeposited with Co as an oxide irrespective of current density. La$_2$O$_3$ content increased as the current density increased. The deposits showed characteristic granular crystals and became nonuniform crystals composed of large localized granules at high current densities. Co–La alloy was not obtained from a urea-based melt bath in this study because of the decomposition of mixed trace water and urea medium.

REFERENCES