Structure, Composition, and Morphology of Aluminum–Nickel Alloys Electrodeposited from Dimethyl Sulfone Baths

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ABSTRACT

It is difficult to perform the electrodeposition of aluminum alloys from aqueous solutions. In this study, aluminum–nickel was electrodeposited from an electrolyte containing dimethyl sulfone, AlCl3, and 0.0 mol%–1.0 mol% NiCl2 at deposition potentials ranging from −1.0 to −5.0 V (Al/Al3+). The surface morphologies of the Al–Ni alloys depended on the NiCl2 concentration and the deposition potential. The crystalline structure of the Al–Ni alloys also depended on the NiCl2-concentration. Furthermore, the content of Ni in the Al–Ni alloys increased with increase in the NiCl2 concentration.

Keywords : Electrodeposition, Al–Ni Alloy, Dimethyl Sulfone

1. Introduction

Aluminum–nickel alloys are expected to be used in high-hardness, high-corrosion-resistant coatings.1 It is difficult to perform the electrodeposition of aluminum and Al alloys from aqueous solutions because the standard electrode potential of Al is less noble than the potential required for hydrogen evolution. Therefore, Al coatings and Al–Ni alloys have been electrodeposited using AlCl3/NaCl molten salts.2 However, electrodeposition using molten salts is performed at high temperatures. In addition, it is mandatory to maintain the system under inert atmosphere. Furthermore, Al–Ni alloy coatings have been formed by electrodeposition from an Al-particle-containing Watts bath.3 Al particles dissolved efficiently in the Watts bath, yielding cracked deposits. Alternatively, Al alloys can be electrodeposited from non-aqueous solutions. Al–Ni alloys have been electrodeposited from non-aqueous solutions4 using ion liquids,5 such as 1-ethyl-3-methylimidazolium chloride,6 1-methyl-3-ethylimidazolium chloride,7 and n-butylpyridinium chloride.8 Al,9 Al–silica,10 Al–Ti,11 Al–Zr,12 and Al–TiO213 have been reported to electrodeposit from dimethyl sulfone (DMSO)-containing baths. DMSO exhibits a relatively high conductivity, good thermal stability, low inflammability, and low toxicity, and it is also a low-cost liquid; these characteristics make it one of the liquid candidates for the electrodeposition of Al alloys.

In this study, Al–Ni alloys were electrodeposited at a relatively low temperature of 150°C from an electrolyte containing DMSO2, AlCl3, and NiCl2 without the Al particles. In addition, the surface morphologies, composition, and crystalline structure of the Al–Ni alloys were investigated.

2. Experimental

Copper sheets with a size of 10 mm × 5 mm were used as cathodes. The Cu cathodes were immersed in dilute nitric acid at 25°C for 1 min, followed by rinsing in water for 1 min using an ultrasonic washer. The electrodeposition bath contained 67.0 mol% of DMSO2 (99.0%, Tokyo Chemical Industry Co., Ltd.), 32.0 mol%–33.0 mol% of AlCl3 (98.0%, Wako Pure Chemical Industries, Ltd.), and 0.0 mol%–1.0 mol% of NiCl2 (95.0%, Wako Pure Chemical Industries, Ltd.). Before electrodeposition, the bath was heated at 150°C for 30 min for dehydration. Al–Ni alloys were electrodeposited by stirring at 1,000 rpm at 150°C under N2. Current and voltage were controlled by a three-terminal method using an electrochemical measurement system equipped with a potentiosat/galvanostat (Hz-7000, Hokuto Denko Corporation). An aluminum sheet with a size of 50 mm × 10 mm and an Al/Al3+ wire with a diameter of 1 mm were used as the anode and reference electrode, respectively. Deposition potentials were adjusted from −1.0 V to −5.0 V.

The surface morphologies of Al–Ni alloys were observed using scanning electron microscopy (SEM, KEYENCE Corporation, VE-8800). Furthermore, the crystalline structure and composition of the Al–Ni alloys were examined using X-ray diffraction (XRD, Rigaku Corporation, RINT2200) and energy-dispersive X-ray spectroscopy (EDS, JEOL Ltd., JSM-6000), respectively. The Ni content was defined as Ni atomic concentration/(Ni atomic concentration + Al atomic concentration).

3. Results and Discussion

Figure 1 shows the SEM images of Al–Ni electrodeposited from 0.0 mol%–1.0 mol% NiCl2-containing baths at deposition potentials ranging from −1.0 to −5.0 V. The surface of Al electrodeposited from the bath without NiCl2 was smooth (Fig. 1(j)). In contrast, with increase in the NiCl2 concentration and deposition potentials, the surface morphologies of the Al–Ni alloys changed from lamellar waves to large nodule structures. With increasing deposition potential, the surface morphologies of the Al–Ni alloys electrodeposited from 0.1 mol% NiCl2-containing baths varied from eddy-like to wave-like lamellar structures (Figs. 1(a), (b), (c)). In contrast, nodules with a size greater than 10 μm and cracks were observed on the surface of Al–Ni electrodeposited from a 0.5 mol% NiCl2-containing bath.
containing bath. With increasing deposition potential, the growth of islands was observed (Fig. 1(d), (e), (f)). Furthermore, nodules with fine particles were observed on the surface of Al–Ni electro-deposited from a 1.0 mol% NiCl₂-containing bath. At noble deposition potential, the islands aggregated, according a size of approximately 30 µm (Fig. 1(g), (h), (i)). These results indicated that with increasing deposition potential, the direction of growth changes from eddy-like to wave-like structures, aggregating islands; with increasing NiCl₂ concentration, the dimension of growth changes from lamellar waves to nodule structures.

Figure 2 shows the XRD patterns of the Al–Ni alloys electro-deposited from 0.0 mol%–1.0 mol% NiCl₂-containing baths at different deposition potentials. Peaks corresponding to Al(111) and Al(200) were observed on Al electrodeposited from the bath without NiCl₂. In contrast, Al(200) peaks were observed, in addition, weak Al(111) peaks were observed on Al–Ni electrodeposited with 0.1 mol% NiCl₂ at higher deposition potential. Although Al(200) peaks were observed, Al(111) peaks were not observed on Al–Ni electrodeposited with 0.5 mol%. Furthermore, noble deposition potential provided lower XRD peaks. Both Al(200) and Al(111) peaks were not observed on Al–Ni electrodeposited with 1.0 mol% NiCl₂. No peaks related to Ni and AlₓNiy were observed on all samples. These results indicate that the introduction of higher concentration–NiCl₂ and the noble deposition potential prevents the growth of Al(111), furthermore the growth of Al(200). The structure of Al–Ni electrodeposited with higher NiCl₂ concentrations of 1.0 mol%, was amorphous.

With the increase in the NiCl₂ concentration in the electrodeposition baths at deposition potentials less noble than −2.0 V, the content of Ni in the Al–Ni alloys increased (Fig. 3). Approximately 8 at% of Ni was included in the Al–Ni alloy electrodeposited from the 1.0 mol% NiCl₂-containing bath at a deposition potential of −3.0 V. The decrease in the Ni content at a deposition potential of −5.0 V corresponded to the preferential deposition of Al. The Al–Ni alloy electrodeposited from the 0.5 mol% NiCl₂-containing bath included 1 at%–4 at% of Ni. The reason of high Ni content of Al–Ni alloy electrodeposited from the 0.5 mol% NiCl₂-containing bath at −1 V was not clear at the present status. Marginal Ni content was observed in the Al–Ni alloy electrodeposited from the 0.1 mol% NiCl₂-containing bath.

The increase of NiCl₂ concentration in the baths increased Ni content in the Al–Ni alloys, however, the increase of NiCl₂ concentration and the noble deposition potential deteriorated the film crystallinity and the surface morphology. The introduction of Ni atoms into the Al lattice led to the breaking of the Al–Al bonds, leading to extinguishing (111)- and (200)-oriented Al and the formation of amorphous Al–Ni alloy electrodeposited from 0.5 and 1.0 mol% NiCl₂-containing baths (Fig. 2). Furthermore, the introduction of Ni atoms aided the three-dimensional growth via the breaking of Al crystals. Consequently, the growth of the deposit changed from lamellar waves to nodule structures (Fig. 1).

4. Conclusions

In this study, Al–Ni alloys were electrodeposited from baths containing DMSO₂, AlCl₃, and 0.0 mol%–1.0 mol% of NiCl₂ at deposition potentials ranging from −1.0 to −5.0 V. The crystalline structure, composition, and surface morphology of the Al–Ni alloys...
depended on the NiCl₂ concentration and deposition potentials. The content of Ni in the Al–Ni alloys increased with increase in the concentration of NiCl₂ in the baths. With increasing NiCl₂ concentrations and noble deposition potentials, the surface morphologies of the Al–Ni alloys changed from lamellar waves to large nodule structures. The precipitation of Al crystals was suppressed by the introduction of NiCl₂. Al–Ni electrodeposited from 0.1 mol% NiCl₂ comprised (111)- and (200)-oriented Al crystals. Nevertheless, Al(111) peaks were not observed for Al–Ni electrodeposited with 0.5 mol% NiCl₂, in addition Al(200) peaks were not observed for Al–Ni electrodeposited with 1.0 mol% NiCl₂.

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