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Journal of The Electrochemical Society

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J. Electrochem. Soc. 2012, Volume 159, Issue 4, Pages D225-D229.
doi: 10.1149/2.079204jes

Journal of The Electrochemical Society, **159** (4) D225-D229 (2012)
0013-4651/2012/159(4)/D225/5/$28.00 © The Electrochemical Society

Electrodeposition of Bright Al-Zr Alloy Coatings from Dimethylsulfone-Based Baths

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Electrodeposition of Al coatings from dimethylsulfone ($DMSO_2$)-$AlCl_3$ baths with the addition of $ZrCl_4$ was studied. Although pure Al coatings electrodeposited from the bath without $ZrCl_4$ are lusterless, bright and smooth coatings were obtained when the $ZrCl_4$ content in the baths was 0.005–0.015 mol per 10 mol $DMSO_2$. The Zr content in the coatings varied up to 3.5 at% in proportion to the $ZrCl_4$ content in the baths. The bright Al-Zr alloy coating showed high reflectance of 50–80% in the wavelength range of 450–1000 nm, whereas that of the matte pure Al coating was 10–20%. Morphological observations confirmed a reduction in the grain size of Al and surface leveling caused by the addition of $ZrCl_4$ to the baths. Moreover, a strong ⟨100⟩ preferential orientation of Al crystals was observed for the bright coatings. The bright coating containing ∼3.5 at% Zr had a higher corrosion potential by 0.1 V than the pure Al coating.

[DOI: 10.1149/2.079204jes]

Manuscript submitted October 7, 2011; revised manuscript received December 15, 2011. Published February 1, 2012.

Aluminum offers good corrosion resistance owing to the natural oxide layer formed on its surface and thus can be used as a corrosion-resistant coating for metallic materials. In general, electrodeposition is the preferred method for the fabrication of such coatings because it is simple and cost-effective compared to other common processes such as hot dipping,[1] thermal spraying[2] and chemical vapor deposition.[3] Moreover, electrodeposition has merits that complex-shaped components can be coated and the thickness of the coatings can be easily controlled.

However, it is well known that metallic Al cannot be electrodeposited from commonly-used aqueous solutions, and hence a number of non-aqueous media including aromatic hydrocarbons,[4] etheric solvents[4] and inorganic molten salts[5] have been studied to date. However, they have some drawbacks such as combustibility, high vapor pressure and dendritic growth of deposit. In recent years, ionic liquids, also known as room temperature molten salts, have been extensively explored for the electrodeposition of pure Al as well as Al alloys.[6–12] The ionic liquids are attractive media since they have low vapor pressure, high electrical conductivity and a wide electrochemical window.[6] Dimethylsulfone ($DMSO_2$)-$AlCl_3$ electrolyte is also an attractive medium for the electrodeposition of Al because it is more stable and therefore easier to handle than the conventional media. In this electrolyte, $AlCl_3$ undegoes a solvolysis reaction and forms two soluble species, $AlCl_4^-$ and $Al(DMSO_2)_3^{3+}$ and electrodeposition of Al occurs from the $Al(DMSO_2)_3^{3+}$complex.[17] Smooth, dense Al coatings are reportedly obtained from $DMSO_2$-$AlCl_3$ baths.[13–16,18–20]

Although electrodeposition of Al-Ti,[9,10] Al-Mo,[11] Al-Zr[12] alloys has been studied in ionic liquid systems, electrodeposition of Al alloys from the $DMSO_2$ system has not been studied extensively. To the best of our knowledge, the attempted electrodeposition of Al-Ti alloy by Legrand and co-workers is the only report on electrodeposition of Al alloys from $DMSO_2$ based baths available in the literature.[21,22] Thus, little is known about the effects of secondary metal-elements on the electrodeposition of Al from the $DMSO_2$-$AlCl_3$ electrolytes.

In this paper, we focus on Zr, which is one of the elements known to improve the corrosion resistance of Al.[23,24] Our preliminary experiments confirmed that Zr can be co-deposited with Al from a $DMSO_2$ based bath containing $ZrCl_4$. Furthermore, we found that the brightness of the electrodeposited coatings was drastically enhanced by the addition of $ZrCl_4$. The electrodeposition of bright Al coatings from the $DMSO_2$ system has not been reported so far, although it has been studied in ionic liquid systems.[25] In the present study, the effect of $ZrCl_4$ addition to $DMSO_2$ baths on the brightness, surface morphologies and corrosion resistance of electrodeposited coatings was examined in detail.

Experimental

Electrodeposition.— Copper plates (1.5 cm × 3.0 cm) were used as substrates for the electrodeposition of Al and Al-Zr alloys. Prior to the electrodeposition, the substrates were polished with a SiC paper, and then cleaned by sonication in ethanol. After the cleaning, a part of each substrate was covered with PTFE tape so that a square area (1 cm × 1 cm) would be exposed. The anode was an aluminum plate (2.5 cm × 3 cm), which was polished and rinsed in water and ethanol before the electrodeposition. The Al plate works as a sacrificial anode to maintain the concentration of Al species in the bath.[13]

The plating bath was prepared by mixing $DMSO_2$ (Tokyo Chemical Industry, >99.0%) and $AlCl_3$ (Fluka, anhydrous $\geq$99.0%) at a mol ratio of 10 : 2, and then $ZrCl_4$ (Wako Pure Chemical) was added to the bath. The $ZrCl_4$ content in the bath was varied from 0 mol to 0.015 mol per 10 mol $DMSO_2$ (All the values of $ZrCl_4$ content in this paper describe the amount of $ZrCl_4$ per 10 mol $DMSO_2$). Prior to use, $DMSO_2$ had been dried in a vacuum at 60°C for more than one day. No further purification was conducted. $AlCl_3$ and $ZrCl_4$ were stored in an Ar-filled glove box with a circulation system and used as received. After mixing, they were melted at 110°C.

A conventional two-electrode cell was employed for the electrodeposition. Al-Zr alloys were electrodeposited at constant current density of 60 mA cm^{-2} for 10 min using an electrochemical analyzer (ALS, model 660C). Assuming 100% current efficiency, an Al layer with a thickness of about 12 μm was obtained under the deposition conditions. During the electrodeposition, the bath was stirred at 400 rpm and the temperature of the bath was kept at 110°C with a thermostat. The preparation of the baths and the electrodeposition were carried out in the Ar-filled glove box.

Characterization.— Normal-incidence specular reflectance spectra for the electrodeposited coatings were measured using a multichannel photodetector (Otsuka electronics, MCPD-7700) coupled with an optical microscope (Nikon, Eclipse LV100). Spectra were taken from a 20 μm diameter spot using a 10x objective lens with a numerical aperture of 0.3 with reference to an Al mirror with a 50 nm MgF_2 coating (Sigma Koki Co., Ltd., TFA-25C05-20). The measured data were converted to absolute reflectance with the use of the simulated reflectance spectrum for the mirror. The composition of the coatings was detemined by EDX coupled with an SEM (Hitachi S-3500). XRD patterns were taken by employing a diffractometer (Panalytical, X'Pert PRO-MPD) with Cu-Kα radiation. An FE-SEM (Hitachi, SU6600) was used to observe the surface morphology of the coatings. The roughness was measured by a surface texture measuring instrument (Surfcom 1400D, Tokyo Seimitsu). The parameters for the measurement were cutoff length of 0.8 mm, and cutoff ratio of 300. The scanned length was 3.0 mm and the scan rate was 0.15 mm s^{-1}.

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The roughness was calculated based on ISO '97. The corrosion resistance of the coatings was evaluated by recording potentiodynamic anodic polarization curves in deaerated 0.1 M NaCl solution at ambient temperature, using a potentiostat (Hokuto Denko, HZ-5000) at a scan rate of 0.5 mV s^{-1}. The conventional three-electrode cell was employed for the measurement. The measurement was performed for a circular area with a diameter of 5.8 mm on the surface of the coatings. A Pt coil was used as the counter electrode and an Ag/AgCl electrode (SSE) in a KCl saturated aqueous solution was used as the reference electrode.

Results and Discussion

The electrodeposition of Al from the $DMSO_2$-$AlCl_3$ bath without any additives produces dense, uniform pure Al coatings, but the coatings are lusterless. In contrast, a bright coating was electrodeposited when 0.01 mol $ZrCl_4$ was added to the plating bath. Figure 1 presents photographs comparing the appearance of the coatings electrodeposited from baths without and with 0.01 mol $ZrCl_4$. Whereas the coating obtained in the absence of $ZrCl_4$ is dull-white, that from the $ZrCl_4$-containing bath has a silvery, mirror-like appearance. Normal-incidence reflectance spectra for these coatings show more quantitatively that the coating obtained with incorporation of $ZrCl_4$ has a bright, reflective surface (Figure 2). The reflectance of the matte Al coating without $ZrCl_4$ is as small as 10-20% over the visible and near-infrared region (450–1000 nm). As for the bright coating, even the minimum reflectance is as high as 50% at 450 nm. The reflectance increases at longer wavelengths and approaches 80% in the near-infrared region (800–1000 nm), showing that the bright coating from the $ZrCl_4$-containing bath has over 4-times higher reflectance than the pure Al coating.

In order to examine the effect of $ZrCl_4$ in more detail, electrodeposition was conducted from $DMSO_2$-$AlCl_3$ baths containing various amounts of $ZrCl_4$ at a constant current density of 60 mA cm^{-2}. When the $ZrCl_4$ content was less than 0.005 mol, the electrodeposited coatings were matte. Bright coatings were obtained from the baths with $ZrCl_4$ contents from 0.005 to 0.015 mol. When the $ZrCl_4$ content was higher than 0.015 mol, the color of the coatings turned to dark, and adhesion of the coatings degraded. Such coatings are not suitable for corrosion protection and thus we did not carry out further characterization for the dark coatings.

The relationship between the $ZrCl_4$ content in the plating baths and Zr content in the coatings is shown in Figure 3. The amount of Zr in the coatings varied from 0 at% to 3.5 at% in proportion to the $ZrCl_4$ content in the plating bath, suggesting that the deposition of Zr is diffusion-controlled. The bright coatings contained 1.2–3.5 at% Zr. The EDX analysis also revealed that the coatings contained 0.2 ~ 1.4 at% of Cl and S as impurities.

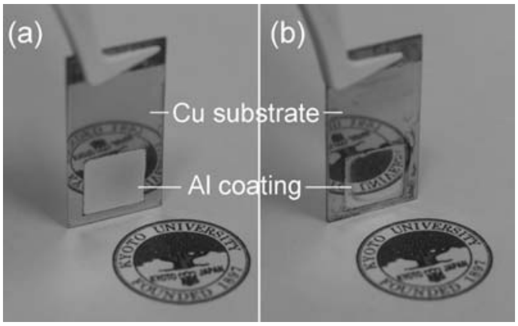

Figure 1. Photographs of (a) matte Al coating and (b) bright Al-Zr coating electrodeposited on Cu substrates from $DMSO_2$-$AlCl_3$ bath containing no and 0.01 mol $ZrCl_4$, respectively.

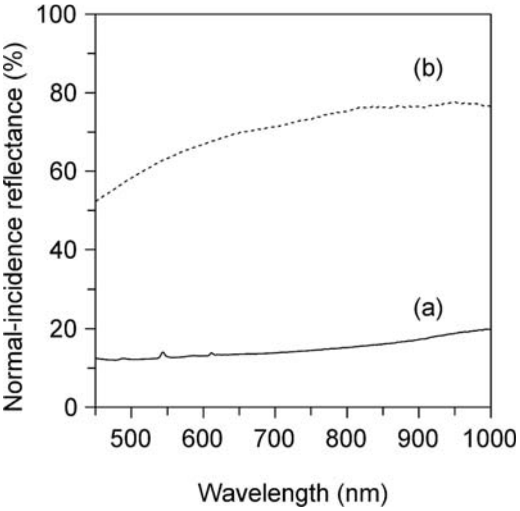

Figure 2. Normal-incidence reflectance spectra of (a) matte Al coating and (b) bright Al-Zr coating electrodeposited on Cu substrates from $DMSO_2$-$AlCl_3$ bath containing no and 0.01 mol $ZrCl_4$, respectively.

The coatings were also examined by XRD (Figure 4). Diffraction peaks corresponding to Al and Cu substrates were confirmed for all the samples. Although the Zr content of the Al-Zr alloy coatings (0.5–3.5 at% Zr) exceeded the maximum solubility of Zr in Al phase (<0.1 at%), no evidence for the formation of Al-Zr intermetallics or metallic Zr was found in the XRD patterns. If Zr is dissolved in the Al phase to form an oversaturated solid-solution, corresponding peak shift should be observed in the XRD pattern of the Al phase. However, no peak shift was observed. This is possibly because most of the Zr deposited is present separately from the Al phase. Secondary phase cannot be detected by XRD because the Zr amounts in the coatings are too small. The diffraction patterns of the pure Al (Figure 4a) and the Al-Zr alloy electrodeposited with the addition of 0.0025 mol $ZrCl_4$ (Figure 4b), which exhibit a matte appearance, are similar to that of an Al powder, indicating that the coatings are composed of randomly orientated Al crystal grains. The diffraction pattern significantly changes when the $ZrCl_4$ content in the bath is raised to 0.005 mol; the intensity of Al 200 diffraction becomes about 40 times greater than that for the pure Al coating (Figure 4c), while the intensity of Al 111 diffraction remains as low as that for the pure Al coating. The strong Al 200 diffraction clearly shows that the Al-Zr alloy coating obtained with 0.005 mol $ZrCl_4$ has a preferrential orientation where (100) planes are parallel to the substrate. Similar XRD patterns are

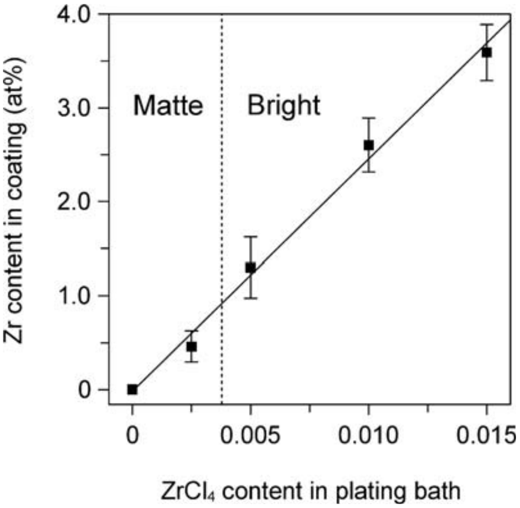

Figure 3. Relationship between $ZrCl_4$ content in the plating bath and Zr content in electrodeposited coating.

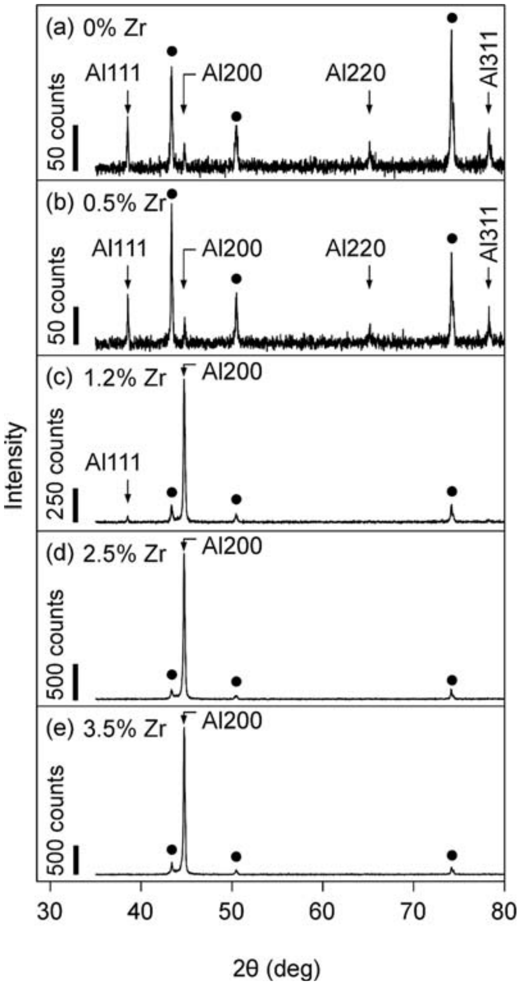

Figure 4. XRD patterns of pure Al and Al-Zr alloy coatings electrodeposited from $DMSO_2$ based baths containing various amounts of $ZrCl_4$: (a) 0 mol (pure aluminum), (b) 0.0025 mol, (c) 0.005 mol, (d) 0.010 mol, and (d) 0.015 mol. Diffraction peaks of Cu substrate are denoted by •.

observed for the coatings obtained from the baths containing 0.01 and 0.015 mol $ZrCl_4$ (Figures 4d and 4e) except that the Al 111 diffraction completely disappears and the Al 200 diffraction becomes more intense. This set of XRD patterns indicates that the Al crystals in the bright coatings have a strong ⟨100⟩ preferrential orientation, while those in the matte coatings have no preferred orientation.

Figure 5 presents SEM images showing typical surface morphologies of the coatings. Randomly-scattered angular grains of Al approximately 5 μm in size can be seen on the surface of the pure Al coating (Figure 5a). A similar morphology, except with the grain size decreased to around 1 μm, can be found on the sample obtained from the bath containing 0.0025 mol $ZrCl_4$ (Figure 5b). In contrast, the grain size of the bright coatings obtained by the addition of of 0.005-0.015 mol $ZrCl_4$ diminished to approximately 20 nm (Figures 5c–5e). As a result, the surfaces of these coatings became smoother than that of the matte pure Al coating. Although the SEM images of the surface of the bright coatings indicated the drastic decrease in the grain size, the XRD peak of the bright coatings was not broadened. This suggests that the bright coatings consist of thin columnar grains grown perpendicularly to the substrate.

The smooth surface of the coatings was also evidenced by roughness measurement (Figure 6). The mean roughness (R_a) of the matte pure Al coating was approximately 0.1μm. The roughness of the coating did not change when 0.0025 mol $ZrCl_4$ was added to the plating bath, whereas the R_a dramatically decreased to 0.01 μm when

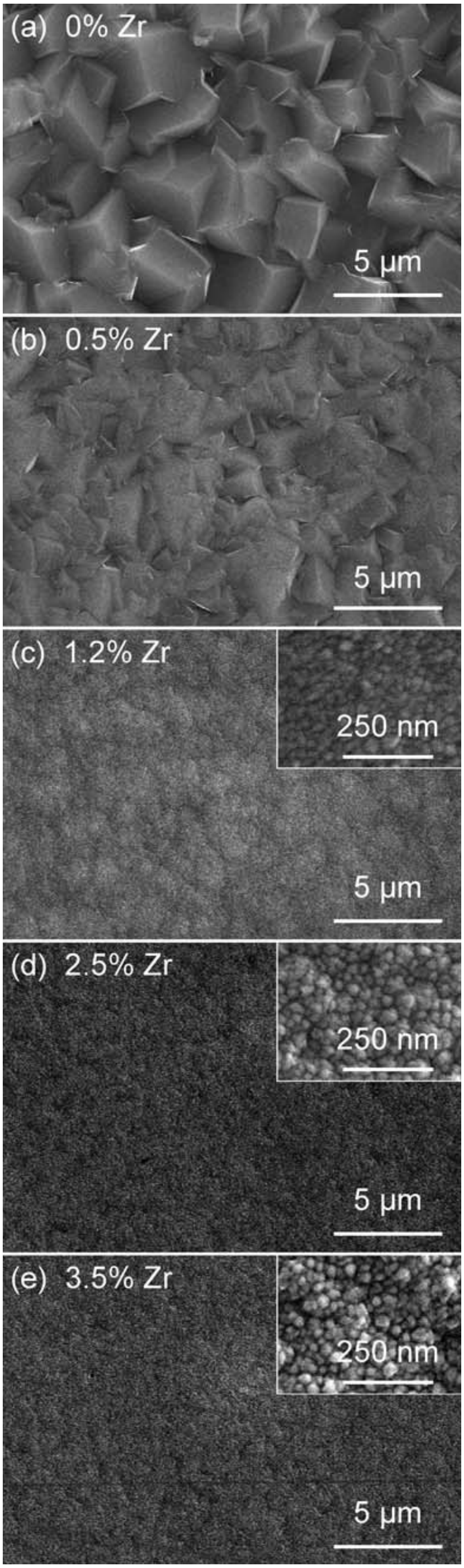

Figure 5. SEM images of the surfaces of pure Al and Al-Zr alloy coatings electrodeposited from $DMSO_2$ based baths containing various amounts of $ZrCl_4$: (a) 0 mol (pure aluminum), (b) 0.0025 mol, (c) 0.005 mol, (d) 0.010 mol, and (d) 0.015 mol.

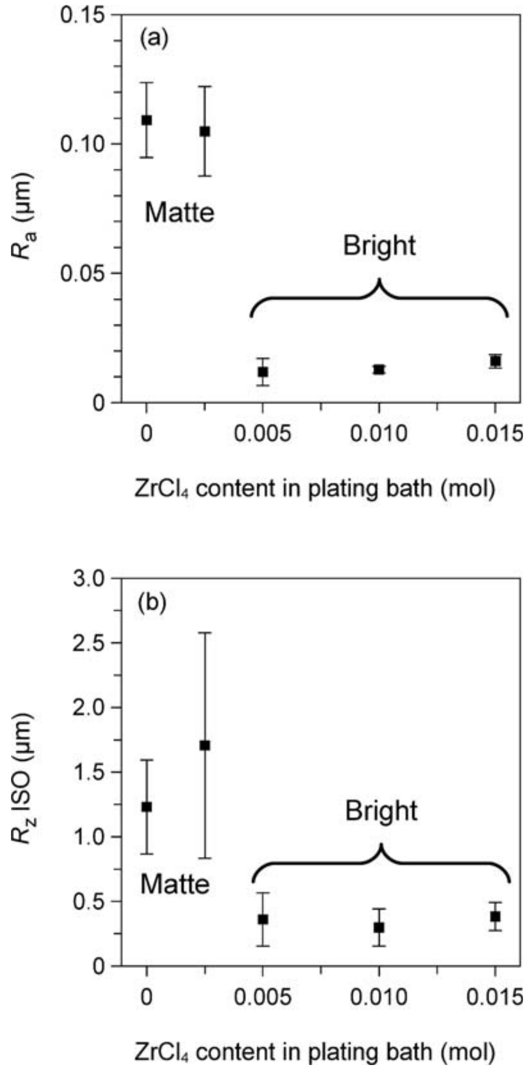

Figure 6. Surface roughness of coatings electrodeposited from $DMSO_2$-$AlCl_3$ baths as a function of $ZrCl_4$ content in the bath: (a) arithmetical mean roughness (b) maximum roughness height (ISO '97).

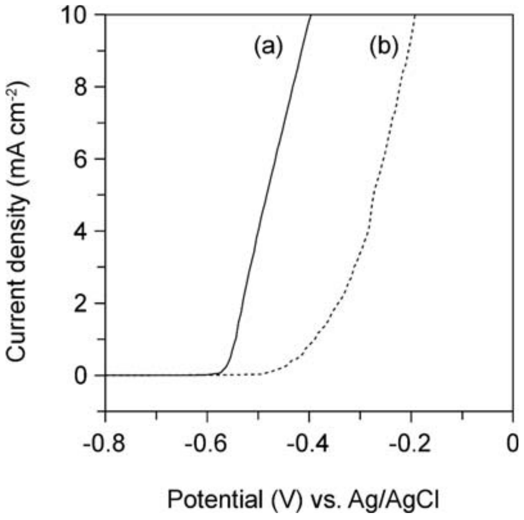

Figure 7. Anodic polarization curves recorded in 0.1 M NaCl aqueous solution for (a) pure aluminum coating and (b) Al-3.5% Zr alloy coating. The Al-3.5% Zr alloy coating was obtained from a bath containing 0.015 mol $ZrCl_4$.

0.005 mol or more $ZrCl_4$ was added to the bath. The maximum height (R_z) varied similarly to R_a and was 1.2-1.7 μm and 0.3 μm for the matte coatings and bright coatings, respectively (Figure 6b). The variations in the surface roughness are in agreement with the surface morphologies of the coatings revealed by the SEM images (Figure 5). The R_a and R_z for the bright coatings obtained in this study are much smaller than the reported values for the bright Al coatings electrodeposited from an ionic liquid bath containing 1,10-phenanthroline as a brightener ($R_a = 0.12$ μm, $R_z = 1.0$ μm),[25] thus showing the better brightening ability of $ZrCl_4$ in the $DMSO_2$ based bath.

The SEM images (Figure 5) and the XRD patterns (Figure 4) show that the grain size and the crystal orientation simultaneously undergo significant changes when 0.005 mol or more $ZrCl_4$ is added to the bath. The grain refinement and preferential crystal orientation are typical phenomena in bright coatings electrodeposited with the aid of brighteners.[26] Additionaly, we carried out cyclic voltammetry in the $DMSO_2$-$AlCl_3$ electrolyte with and without $ZrCl_4$ and confirmed that the reduction current is suppressed when $ZrCl_4$ is present in the electrolyte. For these reasons, we presume that $ZrCl_4$ produces bright coatings by a similar mechanism to the commonly-used brighteners. The proposed mechanism is as follows: Zr(IV) species in a plating bath are preferentially adsorbed onto peaks of Al deposit and particular crystal planes. The adsorbed species suppress the crystal growth of Al in particular crystal directions at the peaks of deposit, leading to the production of preferentially oriented fine crystal grains and a leveled surface with small irregularities. The resulting surface with smaller irregularities than the wavelength of the visible light looks bright and lustrous, because light incident to the surface is reflected without being diffused.

Al-Zr alloys prepared by the electrodeposition from $AlCl_3$-1-ethyl-3-methylimidazolium chloride ionic liquid are reported to have superior corrosion resistance to that of pure Al.[12] In order to examine whether the corrosion resistance of the Al-Zr alloy coatings obtained from the $DMSO_2$ bath is also improved, the corrosion resistance of the pure Al and the Al-3.5% Zr alloy coatings electrodeposited from a $DMSO_2$ bath containing 0.015 mol $ZrCl_4$ was compared by potentiodynamic anodic polarization in a NaCl aqueous solution (Figure 7). The passive region of the pure Al coating lies below −0.6 V vs. SSE followed by a sudden rise in anodic current. The rise in the anodic current is explained by pitting corrosion of Al induced by chloride ions.[23,24] The curve for the Al-Zr alloy displays a wider passive region up to −0.5 V vs. SSE, indicating that the addition of Zr to Al by the electrodeposition from the $DMSO_2$ bath is effective for the enhancement of the corrosion resistance of Al.The shift in the corrosion potential of 0.1 V is comparable to those for the Al-Zr alloys electrodeposited from the ionic liquid bath.[12]

Conclusions

In this paper, we presented the electrodeposition of Al-Zr alloy coatings from $DMSO_2$-based baths. Al-Zr alloy coatings containing up to 3.5 at% Zr were obtained in the presence of $ZrCl_4$ in the baths. The addition of $ZrCl_4$ had the effects of grain refining and surface leveling, resulting in the formation of bright coatings with a silvery, mirror like appearance. The bright Al-Zr alloy coating showed high reflectance of 50–80% in the visible and near-infrared region. Moreover, the addition of Zr to the coating from the $DMSO_2$ bath was confirmed to be effective for the enhancement of corrosion resistance. These results expand the potential applications of electrodeposited Al-Zr coatings to decorative coatings and coatings for optical devices as well as corrosion resistant coatings.

Acknowledgments

The authors thank Kenji Kazumi and Teruyoshi Unesaki for their assistance in SEM observation.

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