Fundamental Research on Biomedical Application of Al-Mo-Ti Alloy Electrodeposited from AlCl₃–1-Ethyl-3-methylimidazolium Chloride Melt

Tetsuya Tsuda¹,², Satoshi Arimoto², and Susumu Kuwabata²
¹Frontier Research Base for Global Young Researchers
²Department of Applied Chemistry
Graduate School of Engineering, Osaka University
2-1 Yamada-oka, Suita, Osaka 565-0871, Japan
Fax: 81-6-6879-7374, e-mail: ttsuda@ap.chem.eng.osaka-u.ac.jp

The electrodeposition of ternary Al-Mo-Ti alloy was examined in the Lewis acidic 66.7-33.3 percent mole fraction aluminum chloride–1-ethyl-3-methylimidazolium chloride (AlCl₃–EtMeImCl) room-temperature ionic liquid containing both (Mo₆Cl₈)Cl₄ and TiCl₂. All of the electrodeposited Al-Mo-Ti alloys were dense and compact, and they adhered well to the copper substrate. In simulated body fluid, e.g., Ringer’s solution, the Al-Mo-Ti alloy showed better corrosion resistance than pure nickel although it was somewhat inferior to 316 L stainless steel that is one of typical metallic biomaterials. Open circuit experiments in Ringer’s solution suggested that amorphous Al-Mo alloy is superior to Al-Ti and Al-Mo-Ti alloys as a metallic biomaterial because of the formation of more stable passivation layer.

Key words: ionic liquid, molten salt, electrodeposition, aluminum alloy, biomaterial

INTRODUCTION
Supersaturated, single-phase binary aluminum-transition metal alloys show increased resistance to chloride-induced pitting corrosion compared to pure Al. Some examples of these "stainless" aluminum alloys that have been prepared to date include Al-V, Al-Nb, Al-Ti, Al-Cr, Al-Mo, and Al-W [1, 2]. Because the solute metal must be present in the Al at concentrations greatly exceeding their usual equilibrium solubilities (< 1 atomic percent (a/o)) so as to enhance the corrosion resistance, non-equilibrium alloying methods such as melt spinning, ion implantation, and sputter deposition are required to prepare these materials. Isothermal electrodeposition from chloroaluminate ionic liquids, particularly those that are liquid at room-temperature, e.g., AlCl₃–EtMeImCl, offers a low-temperature route to thin films of these interesting and potentially useful materials. All of the alloys cited above have been prepared by electrodeposition from this or related chloroaluminate ionic liquids [3, 4]. Of the electrodeposited alloys in this list, amorphous Al-Mo alloys show the best resistance to chloride-induced pitting corrosion (ca. +0.8 V vs. pure Al) [5]. However, we found that the addition of a relatively small amount of a second transition element, notably Mn, significantly improves the corrosion resistance of the Al-Mo alloy system [6].

In this article, we introduce our recent experiments involving the galvanostatic electrodeposition of ternary Al-Mo-Ti alloy in the Lewis acidic 66.7-33.3 percent mole fraction (m/o) AlCl₃–EtMeImCl room-temperature ionic liquid (described hereafter as 66.7 m/o RTIL) containing both (Mo₆Cl₈)Cl₄ and TiCl₂. The purpose of this investigation is to obtain fundamental data when the Al-Mo-Ti alloy prepared from the 66.7 m/o RTIL is applied to metallic biomedical materials.

EXPERIMENT
Preparation of plating bath
The procedures used for the synthesis and purification of EtMeImCl, the sublimation of AlCl₃, and the preparation of a Lewis acidic 66.7 m/o AlCl₃–EtMeImCl RTIL were identical to those described in previous articles [7-9]. Solutions of Mo(II) and Ti(II) in the 66.7 m/o RTIL were prepared by the addition of anhydrous molybdenum(II) chloride, (Mo₆Cl₈)Cl₄ (Cerac, 99.5 %), and anhydrous titanium(II) chloride (Aldrich, 99.98 %), respectively. After preparing the stock solutions of Mo(II) and Ti(II), the composition of each plating bath was adjusted by combining these stock solutions as needed. All experiments were conducted in an argon gas-filled glove box (Vacuum Atmospheres Company, NEXUS system) with an O₂ and a H₂O content < 1 ppm.

Electroplating
Electroplating experiments were conducted with an EG&G Princeton Applied Research Model 263A potentiostat/galvanostat controlled with EG&G PARC Model 270 software. A coil of 1.0 mm diameter Al wire (Alfa Aesar, 99.999 %) was used as the counter electrode; this electrode was immersed directly in the plating bath and encircled the working electrode. The reference electrode (Al(III)/Al) was constructed by placing a 1.0 mm diameter Al wire (Alfa Aesar, 99.999 %) into a 12 mm diameter Pyrex tube terminated with a porosity E glass frit (Ace Glass) and filling this tube with neat 66.7 m/o RTIL. The Al electrodes were cleaned with a mixture of concentrated H₂SO₄, HNO₃ and H₃PO₄, rinsed with distilled water, and dried under vacuum before use. Copper wire (1.25 mm diameter)
served as the substrates during alloy electroplating experiments. These substrates were electropolished at an anodic current density of 100 mA cm\(^{-2}\) in aqueous 0.236 M CuSO\(_4\) for 1 minute. The Cu wire substrates were held in a fixture that could be rotated with a Pine Instruments AFMSRX electrode rotator. Alloy samples of 5 μm thickness were deposited from ionic liquid solutions of mixtures of both Mo(II) and Ti(II) onto the Cu wire electrodes. The Al alloy-coated substrates were removed from the glove box and cleaned with distilled water. All electroplating experiments were carried out at 523 K.

Characterization of the electrodeposits

The surface morphology of the electrodeposited alloy samples was observed with a Keyence VE-9800 scanning electron microscope (SEM). Alloy composition was measured with an EDAX Genesis-XM2 energy dispersive X-ray spectrometer (EDS) attached to SEM. The composition values reported in this article represent a mean for at least eight measurements that were carried out at different positions. The crystal structure of the electrodeposits was examined by employing a RIGAKU X18 SAXS-IP X-ray diffractometer (XRD) with Cu Kα radiation.

Potentiodynamic pitting corrosion measurements were conducted at 298 K on the resulting Al-Mo-Ti alloys by linear sweep staircase voltammetry at room temperature (298 ± 2 K) in a 0.1 M NaCl aqueous solution. Some samples were examined in physiological saline solution consisting of 137 mmol L\(^{-1}\) NaCl + 2.7 mmol L\(^{-1}\) KCl + 10 mmol L\(^{-1}\) phosphate buffer at pH = 7.4 (298 K) and in Ringer’s solution, which is composed of 38.5 mmol L\(^{-1}\) NaCl + 1.41 mmol L\(^{-1}\) KCl + 1.09 mmol L\(^{-1}\) CaCl\(_2\)·2H\(_2\)O at pH = 6.9 (298 K). Prior to these measurements, the solutions were thoroughly deaerated with nitrogen. A large surface area Pt foil and a Ag/AgCl electrode immersed in a KCl-saturated solution served as the counter and reference electrodes, respectively. The potential values are reported with respect to a NaCl-saturated calomel electrode (SSCE).

RESULTS AND DISCUSSION

Electrodeposition of Al-Mo-Ti alloys

We have already reported cyclic staircase voltammograms recorded at a Pt rotating disk electrode (Pt-RDE) in 66.7 m/o RTIL before and after the addition of (Mg,Cl)\(_2\) or TiCl\(_2\) [10]. As discussed in the article, in the pure melt, a stripping wave for electrodeposited Al initiates at around 0 V, but this wave is replaced by waves corresponding to the stripping of the electrodeposited Al-Mo or Al-Ti alloys in those solutions containing Mo(II) or Ti(II), respectively [5, 11]. Cyclic staircase voltammograms recorded in the 66.7 m/o RTIL containing both Mo(II) and Ti(II), regardless of the Mo(II)/Ti(II) concentration ratio, C\(_{\text{Mo(II)}/\text{Ti(II)}}\), are more or less similar in appearance to that recorded in the Mo(II) solution. This implies that the alloy formation of Al-Mo dominates the ternary Al-Mo-Ti alloy deposition process. In fact, as described later, the Ti content of all the Al-Mo-Ti alloys produced during this investigation was less than 1 atomic percent (a/o).

Figure 1 shows the variation in the Al, Mo, and Ti content of the resulting Al-Mo, Al-Ti, and Al-Mo-Ti electrodeposits as a function of the applied current density. The alloy samples were deposited on copper rotating wire electrode substrates under constant current conditions at a rotation rate of 2000 rpm. The Al content in all of the samples increases with \(j\) because the concentration of precursor ions, Mo(II) and Ti(II), is much smaller than that of Al\(_{2}\)Cl\(_4\) [12]. In the case of the binary Al-Mo and Al-Ti alloys, the Mo and Ti content in these alloys decrease with an increase in \(j\), like previous articles [5, 11], but the Mo content of the Al-Mo alloys is always significantly greater than the Ti content of the corresponding Al-Ti alloys even if the two binary alloys were prepared under identical conditions. This same result carries over to the ternary Al-Mo-Ti alloys. The result could be reconciled in part by considering the diffusion coefficients of Mo(II) and Ti(II), \(D_{\text{Mo(II)}}\) and \(D_{\text{Ti(II)}}\), respectively, in the RTIL [10].

Fig. 1. The relationship between the plating current density and the percent atomic fraction of Al, Mo, and Ti in the deposits. The solution compositions were: (○) 30 mmol L\(^{-1}\) Mo(II); (□) 30 mmol L\(^{-1}\) Ti(II); (▲) 30 mmol L\(^{-1}\) Mo(II) + 15 mmol L\(^{-1}\) Ti(II); (◆) 30 mmol L\(^{-1}\) Mo(II) + 30 mmol L\(^{-1}\) Ti(II); (▼) 15 mmol L\(^{-1}\) Mo(II) + 30 mmol L\(^{-1}\) Ti(II). The temperature was 323 K, and the substrates were rotated at 2000 rpm during electrodeposition.

Figure 2 depicts the surface morphology of Al-Mo-Ti alloys prepared at different current densities under the condition that is \(C_{\text{Mo(II)}}/C_{\text{Ti(II)}} = 2\) with \(C_{\text{Ti(II)}} = 15\) mmol L\(^{-1}\). The alloy produced at ~5 mA cm\(^{-2}\) (Al\(_{93.3}\)Mo\(_{6.0}\)Ti\(_{0.7}\)) is shown in Fig. 2a. The surface of this deposit is covered with elongated carrot-shaped, dendritic nodules that are ~2 to 5 μm in diameter. However, the deposit prepared at ~20 mA cm\(^{-2}\) (Al\(_{93.3}\)Mo\(_{5.0}\)Ti\(_{0.7}\)) consists of asymmetric, fused nodules without crystallographic faces (Fig. 2b). The morphology is similar to the Al-Ti alloy (Fig. 2c) [11] rather than the amorphous Al-Mo alloy [5] and Al-Mo-Mn alloy [6], which are composed of spherical nodules. Before examining these deposits with XRD techniques, we expected that this alloy system would form amorphous metallic glasses similar to those found for Al-Mo [5] and Al-Mo-Mn [6] when the Mo content of these alloys exceeds ~6.5 a/o. The formation of...
These amorphous deposits is usually signaled by the disappearance of the fcc Al reflections and the development of a broad reflection centered at about $2\theta = 41^\circ$. However, even when the total Mo content of the deposit approached 10 a/o, there was no obvious evidence of a metallic glass phase in the Al-Mo-Ti alloy (Fig. 3). Given that no amorphous Al-Ti alloy has been reported to date [11-13], probably Ti atoms in the Al-Mo-Ti alloys act as a barrier to metallic glass formation.

Fig. 2. SEM images of (a, b) Al-Mo-Ti and (c) Al-Ti alloy samples electrodeposited in 66.7-33.3 m/o AlCl$_3$-EtMeImCl. The alloy compositions, current densities, and solution compositions were: (a) Al$_{0.95}$Mo$_{0.05}$Ti$_{0.05}$, -5 mA cm$^{-2}$, 323 K, 30 mmol L$^{-1}$ Mo(II) + 15 mmol L$^{-1}$ Ti(II); (b) Al$_{0.80}$Mo$_{0.20}$Ti$_{0.05}$, -20 mA cm$^{-2}$, 323 K, 30 mmol L$^{-1}$ Mo(II) + 15 mmol L$^{-1}$ Ti(II); (c) Al$_{0.95}$Ti$_{0.05}$, -20 mA cm$^{-2}$, 323 K, 353 L$^{-1}$ Mo(II) + 333 mmol L$^{-1}$ Ti(II). The substrates were rotated at 2000 rpm during electrodeposition.

Corrosion resistance experiments in simulated body fluids

As stated in the Introduction, it is well known that non-equilibrium Al-transition metal alloys are more resistant to chloride-induced pitting corrosion than pure Al [1, 2]. Furthermore, previous researches have shown that such alloys prepared by isothermal electrodeposition in chloroauminate RTILs have almost the same pitting potentials as similar alloys prepared by other non-equilibrium alloying methods such as rapid solidification, ion implantation, and sputter deposition [3]. We attempted to reveal corrosion resistance of the Al-Mo-Ti alloy in simulated body fluids, saline solution and Ringer’s solution, because Al-Ti based alloy is used as one of biomedical and dental implant materials [14], but the pitting potentials were almost the same as those obtained in the NaCl aqueous solution. The Al-Mo-Ti alloys showed better corrosion resistance in Ringer’s solution than pure nickel (ca. +0.00 V vs. SSCE) and were slightly inferior to one of the typical metallic biomaterials, 316 L stainless steel (ca. +0.35 V) [15]. For example, the value for Al$_{0.80}$Mo$_{0.20}$Ti$_{0.05}$ alloy prepared in this study was +0.07 V. Figure 4 shows variations in open circuit potentials of Al-Mo, Al-Ti, and Al-Mo-Ti alloys in Ringer’s solution. All of the alloys reach stable potentials after 5 ~ 15 days due to the formation of passivation layer. The open circuit potential tends to shift positively as the Mo content in the alloys increases. In this investigation, the Al$_{0.95}$Mo$_{0.05}$ alloy with amorphous glass phase indicated the highest open circuit potential, suggesting that Al-Mo alloy system is better biomedical and dental materials than Al-Mo-Ti and Al-Ti alloys if no undesirable biological reaction occurs in the human body.

Figure 5 depicts SEM images of Al-Mo-Ti alloys before and after the pitting potential experiments in saline solution and Ringer’s solution. The surface morphology and the alloy composition appreciably altered after the corrosion resistance tests because Al
preferentially dissolved out from the alloy deposits during the tests.

Fig. 4. Variations in open circuit potentials of Al-Mo, Al-Ti, and Al-Mo-Ti alloys in Ringer’s solution. (●) Al$_{92.0}$Mo$_{8.0}$, (□) Al$_{92.5}$Mo$_{6.7}$Ti$_{0.8}$, (▲) Al$_{96.5}$Mo$_{2.9}$Ti$_{0.6}$, and (◇) Al$_{97.8}$Ti$_{2.2}$.

Fig. 5. SEM images of Al-Mo-Ti alloy (a, c) before and (b, d) after the pitting potential measurements in simulated body fluids: (b) saline solution; (d) Ringer’s solution. The original alloy compositions were (a) Al$_{93.6}$Mo$_{5.7}$Ti$_{0.7}$ and (c) Al$_{94.0}$Mo$_{5.3}$Ti$_{0.7}$.

CONCLUSIONS
The electrodeposition of ternary Al-Mo-Ti alloy was examined in the Lewis acidic 66.7-33.3 mol % AlCl$_3$–EtMeImCl room-temperature ionic liquid containing both (Mo$_6$Cl$_8$)Cl$_4$ and TiCl$_2$. All of the electrodeposited Al-Mo-Ti alloys were dense, compact, and no chloride contamination. In simulated body fluid, the Al-Mo-Ti alloys showed better corrosion resistance than pure nickel and were slightly inferior to 316 L stainless steel. Open circuit experiments for the Al-Mo, Al-Ti, and Al-Mo-Ti alloys produced during this investigation in Ringer’s solution revealed that amorphous Al-Mo alloy system may be superior to Al-Ti and Al-Mo-Ti alloys as a metallic biomaterial.

ACKNOWLEDGMENTS
This research has been carried out at the Frontier Research Base for Global Young Researchers, Osaka University on the Program of Promotion of Environmental Improvement to Enhance Young Researchers’ Independence, the Special Coordination Funds for Promoting Science and Technology, Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) and was supported by Grant-in-Aid for Scientific Research on Priority Area, Area No. 452, “Science of Ionic Liquids” and Grant-in-Aid for Scientific Research, Grant No. 18201022, from MEXT. This research was supported by Core Research for Evolution Science and Technology (CREST) from Japan Science and Technology Agency (JST).

REFERENCES

(Received May 19, 2009; Accepted November 17, 2009)