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研究課題名（和文）Electrodeposition of supersaturated aluminum-based solid solutions for maximizing strength and corrosion resistance

研究課題名（英文）Electrodeposition of supersaturated aluminum-based solid solutions for maximizing strength and corrosion resistance

研究代表者
張　澤磊（ZHANG, Zelei）

京都大学・工学研究科・特定助教

研究者番号：90913400

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研究成果の概要（和文）：アルミニウム（Al）合金の異種微細構造は、α-Al固溶体マトリックスと粗大な金属間化合物から構成され、機械的および防食特性のバランスをとる上で課題を提起しています。過飽和の固溶体は、この課題に対処することが期待されます。本研究では、単一相の過飽和Al(Fe)およびAl(Si)固溶体が電着されました。FeまたはSi還元に関与する活性種は、スペクトル解析とDFT計算により明らかにされました。Al(Fe)は、機械的および防食特性の同時改善を示しましたが、Al(Si)はよりコンパクトでない微細構造を持ち、失敗しました。さらに、Al(Fe)およびAl(Si)の熱分解は、200 °C以上で抑制されました。

研究成果の学術的意義や社会的意義
Al alloys are subject to the conflict between strength and corrosion resistance. This research gives high-strength but also corrosion-resistant Al-Fe alloys, thanks to a homogeneous microstructure.

研究成果の概要（英文）：The heterogeneous microstructure in aluminum (Al) alloys, composed of an α-Al solid solution matrix and coarse intermetallics, presents a challenge in balancing mechanical and anti-corrosion properties. Supersaturated Al-based solid solutions are expected to address this issue. In this study, supersaturated Al(Fe) and Al(Si) solid solutions with a single phase have been electrodeposited in chloroaluminate ionic liquids (ILs). The active species responsible for Fe or Si reduction have been identified through spectral analysis and DFT calculations. Al(Fe) deposits show simultaneous improvements in mechanical and anti-corrosion properties, while Al(Si) exhibits a less compact microstructure, leading to failure. Furthermore, thermal decomposition of Al(Fe) and Al (Si) deposits can be suppressed above 200 °C.

研究分野：材料加工および組織制御関連

キーワード：Electrodeposition　Al alloys　Hardness　Corrosion resistance

１．研究開始当初の背景

Aluminum (Al) is a key material covering various engineering devices. However, the heterogeneous microstructure in aluminum (Al) alloys, consisting of an *a*-Al matrix and intermetallic particles (IMPs), as a consequence of traditional precipitation strengthening, poses a challenge of balancing mechanical and corrosion-resistant properties [1]. The supersaturated Al-based solid solutions with a homogeneous microstructure will inherently resolve the conflict between strength and corrosion resistance, receiving renewed attention [2].

２．研究の目的

The non-equilibrium alloying techniques enable alloying elements (*M*) remaining in Al(*M*) solid solutions below eutectic or peritectic temperatures. Among a series of non-equilibrium alloying techniques, electrodeposition is a more flexible approach to produce Al(*M*) alloys. This research project aims to produce a series of supersaturated Al(*M*) (*M*: Fe and Si) solid solutions through electrodeposition in ionic liquids (ILs), simultaneously maximizing the strength and corrosion resistance of Al.

３．研究の方法

The 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) or trihexyl(tetradecyl)-phosphonium chloride ([$P_{6,6,6,14}$]Cl)−aluminum chloride ($AlCl_3$, molar fraction x = 0.67) IL was prepared in an argon-filled glovebox, where 0.10 mol L^{-1} iron chloride ($FeCl_2$) or 2.5 mol L^{-1} silicon chloride ($SiCl_4$) could dissolve completely to form [EMIm]Cl−$AlCl_3$−$FeCl_2$ and [$P_{6,6,6,14}$]Cl−$AlCl_3$−$SiCl_4$ baths at room temperature. The spectroscopic techniques, including NMR, Raman and UV−Vis, combined with DFT calculations, were employed to elucidate the possible speciation mechanism of $FeCl_2$ and $SiCl_4$ in chloroaluminate ILs. Potentiostatic electrodeposition was conducted in a three-electrode cell at ambient temperature, consisting of a quasi-reference electrode (QRE) Ag wire, a counter electrode (CE) Al sheet, and a working electrode (WE) Cu sheet. In addition, scanning electron microscope (SEM), high-resolution transmission electron microscope (HRTEM), X-ray diffraction (XRD), nanoindentation, and cyclic polarization were performed to characterize the morphology, phase composition, mechanical and corrosion-resistant properties of the deposits.

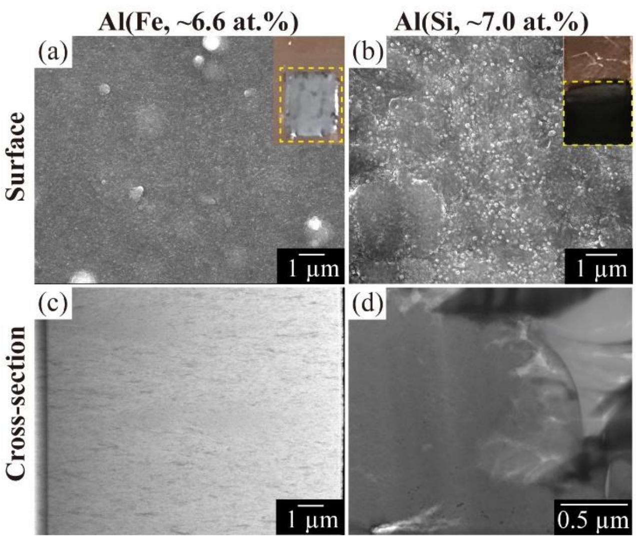

Figure 1 Surface and cross-section morphologies of (a, c) Al(Fe, ~6.6 at.%) and (b, d) Al(Si, ~7.0 at.%) deposits. Insets show the photographs of samples.

４．研究成果

In this study, supersaturated Al(Fe) and

Al(Si) solid solutions with a single phase have been obtained using the [EMIm]Cl−$AlCl_3$−$FeCl_2$ and [$P_{6,6,6,14}$]Cl−$AlCl_3$−$SiCl_4$ baths, respectively. (Fig. 1). The $FeCl_2$ dissolved in Lewis-acidic ILs is assumed to form Cl-bridged $[Fe(AlCl_4)_4]^{2-}$ based on spectral analysis and DFT calculations, while the $SiCl_4$ remains its neutral composition. The $[Fe(AlCl_4)_4]^{2-}$ and $SiCl_4$ together with the $Al_2Cl_7^-$ species supports the reduction and deposition of Al(Fe) and Al(Si) alloys, respectively.

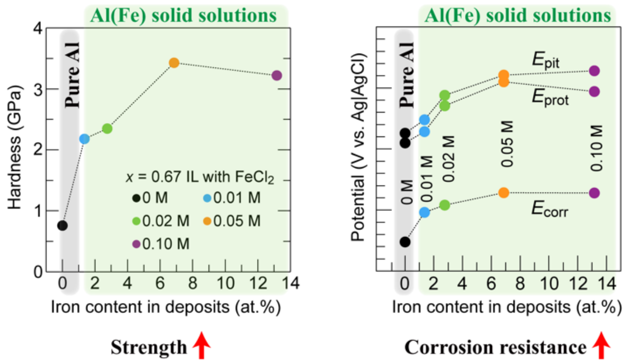

Figure 2 Hardness, corrosion potential (E_{corr}), pitting potential (E_{pit}), and protective potential (E_{prot}) of pure Al, and Al(Fe) deposits. The deposits were obtained potentiostatically at −1.7 V *vs.* Pt QRE from imidazolium chloroaluminate ILs with $FeCl_2$ concentration ranging from 0 to 0.10 mol dm^{-3}.

The supersaturated Fe solutes significantly strengthens the Al matrix, with the hardness of Al(Fe, 6.6 at.%) surpassing that of any commercial Al alloys and other binary Al-based solid solutions (Fig. 2). Moreover, the Al(Fe) deposits demonstrate superior anti-corrosion performance compared to pure Al. The homogeneous microstructure and extended Fe solubility within Al(Fe) solid solutions inherently contributes to a simultaneous improvements in mechanical and anti-corrosion properties.

The Al-Si alloy deposits also exhibit a single phase, with the solid solubility of Si in the Al matrix reaching up to approximately 12 at.%. Despite the fact that Al(Si) deposits exhibit higher hardness than pure Al, their microstructures require further modification to become more compact.

Additionally, the thermal decomposition of supersaturated Al(Fe) and Al(Si) solid solutions could be suppressed over 200 °C, indicating their promising potential for practical applications.

＜引用文献＞

[1] Y. Zhou, X. Jia, J. Li, G. Guan, X. Ma, J. Zhang, Appl. Surf. Sci. 590 (2022) 153108.

[2] J. Chen, J.W. Xiao, C.Y. Hung, W.B. Wang, J. Zhao, F.M. Michel, C. Deng, W.J. Cai, Corros. Sci. 198 (2022) 110137.

５．主な発表論文等

〔雑誌論文〕　計2件（うち査読付論文　2件／うち国際共著　0件／うちオープンアクセス　0件）

１．著者名 Zhang Zelei、Kitada Atsushi、Fukami Kazuhiro、Murase Kuniaki	４．巻 16
２．論文標題 Annealing, solvation, and mirror-plating effects in phosphonium chloroaluminate ionic liquids	５．発行年 2022年
３．雑誌名 Nano Research	６．最初と最後の頁 3348～3357
掲載論文のDOI（デジタルオブジェクト識別子） 10.1007/s12274-022-4999-6	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Zhang Zelei、Kitada Atsushi、Fukami Kazuhiro、Murase Kuniaki	４．巻 35
２．論文標題 Aluminum Electroplating on AZ31 Magnesium Alloy with Acetic Anhydride Pretreatment	５．発行年 2022年
３．雑誌名 Acta Metallurgica Sinica (English Letters)	６．最初と最後の頁 1996～2006
掲載論文のDOI（デジタルオブジェクト識別子） 10.1007/s40195-022-01453-z	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

〔学会発表〕　計3件（うち招待講演　0件／うち国際学会　1件）

１．発表者名 Koki Nishioka, Zelei Zhang, Kazuhiro Fukamia, Kuniaki murase
２．発表標題 Electrodeposition of Al-Si Supersaturated Solid Solution in Phosphonium Ionic Liquids
３．学会等名 International Conference on Surface Engineering (ICSE2023) & Regional INTERFINISH 2023 for 60th Anniversary of Korean Society of Surface Science and Engineering（国際学会）
４．発表年 2023年

１．発表者名 西岡幸城，Zelei Zhang，深見一 弘，邑瀬邦明
２．発表標題 ホスホニウム系イオン液体を用いたAl-Si過飽和固溶体電析
３．学会等名 表面技術協会第148回講演大会
４．発表年 2023年

１．発表者名 ZHANG Zelei
２．発表標題 Electrodeposition of Al(Fe) Supersaturated Solid Solutions from 1-Ethyl-3-methylimidazolium Chloroaluminate Ionic Liquids
３．学会等名 第24回関西表面技術フォーラム
４．発表年 2022年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関