Slippery liquid-infused porous surfaces on aluminum for corrosion protection with improved self-healing ability

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KEYWORDS: Slippery liquid-infused porous surface, aluminum, corrosion, self-healing, lubricant additive

ABSTRACT

Slippery liquid-infused porous surfaces (SLIPSs) can be formed by impregnating lubricants in porous surfaces with low surface energy. In this study, SLIPSs have been obtained on practically important aluminum with a porous anodic alumina layer by impregnating lubricants containing

organic additives. The additive-containing lubricants change the surface slippery even without the prior organic coating of the porous alumina surface. The additive-containing SLIPSs reveal low water sliding angle of <5º and markedly improved corrosion resistance in an acetic acid solution containing chloride. The SLIPSs are formed by the in situ adsorption of the organic additives on the porous alumina surface. The scratched defects induce corrosion of the organic coating-type SLIPSs, whereas the additive-containing SLIPSs sustain the high corrosion resistance even after introducing scratch defects. The adsorption of the organic additive in lubricants and refilling of the lubricant are responsible for the self-healing of the corrosion resistance. Thus, the additive-containing SLIPSs are promising self-healing corrosion-resistant surfaces.

1. INTRODUCTION

Advanced surface technology for metallic materials is of scientific interest and practical importance to prevent corrosion in aggressive service environments. The formation of passive films on metals and alloys can effectively suppress corrosion because of blocking the direct interaction of the metal substrate with the corrosive media.[1] However, stable passive films do not always develop on metallic materials in a range of corrosive service environments. Thus, novel coating and surface modification technologies are necessary to avoid the environmental degradation of metallic materials.

The development of liquid-repellent surfaces is a promising approach to avoid the corrosion of metals and alloys.[2-3] Superhydrophobic surfaces, which reveal water contact angles of >150º and low sliding angles of usually <5º, can repel aqueous solutions readily and rapidly. The

superhydrophobic surfaces are obtained by surface roughening and the reduction of surface energy, for instance, by an organic coating of metallic materials.[4-6] Under the superhydrophobic condition, the air is trapped between the rough surface and liquid, reducing the contact area of liquid to the solid surface (Cassie-Baxter state).[7] Consequently, liquid droplets are readily rolling off from the slightly tilted superhydrophobic surfaces. Because of the presence of the organic coating and trapped air, the superhydrophobic surfaces on metals and alloys reveal the high corrosion resistance due to the ready removal of corrosive liquid. However, the corrosion resistance of the superhydrophobic surfaces is not generally durable because of mechanical damage of the micro-/nano-rough surfaces and the chemical degradation of organic coatings. The transition from the Cassie-Baxter state, in which air pockets are present in the rough surface, to the thoroughly wetted Wenzel state under pressure impingement is another degradation mode of superhydrophobicity. These degradations induce corrosion of metallic materials. The superhydrophobic coatings made of carbon fibers, which were grown on a zinc substrate, initially exhibited good corrosion resistance; however, the coatings were unstable over long-term immersion in a 3.5% saline solution and induced corrosion.[8]

Wong et al. reported slippery liquid-infused porous surfaces (SLIPSs) in 2011 as a novel liquid-repellent biomimetic surface.[9] The SLIPSs, which can be fabricated by impregnating lubricant oil into the porous solid surface with low surface energy, possess excellent repellency of a wide range of liquids, including low surface tension oils, expanding their applications to anti-fouling, anti-biofouling, self-cleaning, anti-icing, droplet manipulation, and corrosion protection. The self-healing properties of SLIPS due to the mobility of lubricant trapped inside the pores are significant characteristics for practical applications, particularly for corrosion protection.

The corrosion-resistant SLIPSs were first reported by Qiu et al. in 2014.[10] They fabricated the SLIPSs on Cu, Cu alloy, Al-Mg alloy, and low alloy steel by infiltrating perfluorinated lubricant into a 3D sponge-like carbon fiber matrix, which was prepared onto the metal substrates. Thus-prepared SLIPSs performed exceptionally high corrosion resistance in NaCl solution. It was also reported that SLIPSs on aluminum had great potential for inhibiting microbially influenced corrosion in a marine environment.[11] The crucial role of SLIPSs in impeding corrosion was the suppression of the settlement of sulfate-induced bacteria, regardless of the type of lubricant. Lee et al. demonstrated that a solvent exchange method effectively filled the porous anodic alumina nanochannels with lubricant.[12] The SLIPS thus formed on aluminum exhibited markedly improved corrosion resistance even in aggressive HCl solution. The high self-healing ability of SLIPSs for corrosion protection has been confirmed in several reports.[12-17] The defect sites, such as cracks, were refilled with lubricant, contributing to the long-term corrosion protection.

However, the SLIPSs need a hydrophobic solid surface, and thin organic coatings, including a self-assembled monolayer, must be developed on metals to make the surface hydrophobic. If the hydrophobic surface is damaged mechanically, the hydrophilic metallic surface is exposed. Such regions risk corrosion even if the lubricant is refilled because SLIPS are not stable on the hydrophilic surface. Herein we investigated the formation of SLIPSs on an aluminum substrate without an organic coating and their corrosion protection behavior. Organic additives, which possess adsorption ability on the alumina surface, were introduced into the lubricants. The porous substrate used in this study was the anodized aluminum, which possessed a porous alumina layer with many cylindrical pore channels. The present study demonstrated the highly improved self-healing corrosion resistance by utilizing the additive-containing SLIPSs.

2. EXPERIMENTAL SECTION

The substrate used in this study was a 99.5 mass% aluminum sheet of 0.3 mm thickness. After ultrasonic cleaning in acetone for 10 min, the aluminum substrate was anodized to form a nanoporous anodic alumina layer at 40 V in stirred 0.3 mol dm^{-3} oxalic acid aqueous electrolyte at 303 K for 30 min with a Pt counter electrode. The anodized aluminum was then immersed in 5 wt% phosphoric acid solution at 303 K for 15 min for pore widening to ~50 nm. The thickness of the porous alumina layer was ~8 μm, as shown in **Figure S1**. Some of the anodized substrates were coated with tetradecylphosphonic acid (TDP: Sigma-Aldrich) by immersing the substrate into 1.0 mmol dm^{-3} TDP-ethanol solution for two days for reducing the surface energy.

Three types of lubricants were used in this study; polydimethylsiloxane (PDMS: Shinetsu silicone, KF-96), polymethylhydrosiloxane (PMHS: Shinetsu silicone, KF-99), and perfluopropolyether (PFPE: Dupont, Krytox GPL100). **Table 1** summarizes the physical properties of these lubricants. The organic additives used in this study were trimethoxyoctylsilane (TMS: Sigma-Aldrich), 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FAS: Sigma-Aldrich), 1-decanethiol (DCT: Tokyo Chemical Industry), 1H,1H,2H,2H-perfluorodecanethiol (FDT: Sigma-Aldrich), and 8-quinolinol (QNL: Fujifilm Wako Chemical). It is known that alkylphosphonic acids are strongly adsorbed on the aluminum surface,[18-20] promising as organic additives. However, they were not soluble in the lubricants used in this study. The concentration of the additives in lubricant was generally 2.0 mass%, but only 0.1 mass% was added for FAS and QNL because of limited solubility. The anodized aluminum substrate was immersed ultrasonically in the additive-free and additive-containing lubricants for 10 min to impregnate the lubricants into nanopore channels. The extra lubricant on the surface was removed by tilting the specimen at 45º in the air. Hereafter, the coating-type SLIPS is

expressed as, for instance, PMHS@TDP, whereas the additive-type SLIPS is, for instance, TMS/PMHS.

Table 1. Physical properties of lubricant oils used in this study.

Lubricant	Kinematic viscosity at 25ºC ($mm^2\ s^{-1}$)	Surface tension at 25ºC ($mN\ m^{-1}$)	Pour point (ºC)
PDMS	100	20.9	-50
PMHS	20	20.8	-73
PFPE	12.4	15.5	-70

The surfaces and fracture cross-sections of the specimens were observed by a field-emission scanning electron microscope (ZEISS, Sigma-500), operated at 1.5 kV. The elemental depth profiles of the specimens were obtained using a glow discharge optical emission spectroscope (GDOES: Jobin Yvon, 5000RF) of 13.56 MHZ and power of 35 W under a pulse mode of a duty cycle of 0.25 and a frequency of 200 Hz in Ar atmosphere (1.0 kPa). The light emission from each element was monitored with a sampling interval of 0.01 s.

The static water contact angle was measured by a contact angle meter (Kyowa Interface Science, DM-DE1) using a water droplet (4 μL) and analyzed by FAMAS software. The water sliding angle on the specimen was also measured by tilting the specimen stage using a water droplet (10 μL).

The corrosion behavior was examined by potentiodynamic polarization measurements (Ivium, ConpactStat) at a potential sweep rate of 1.0 mV s^{-1}. The electrolyte used in this study was an acidic solution containing 2 g dm^{-3} acetic acid and 10 g dm^{-3} NaCl (pH 3) at 298 K. A three-electrode electrochemical cell with a Pt counter electrode and an Ag/AgCl reference electrode was used. The self-healing behavior was examined by introducing the cross-cut scratch defects

into the lubricant-infiltrated specimens, with the scratch penetrating through the porous alumina film to the aluminum substrate.

3. RESULTS AND DISCUSSION

Figure 1 shows static water contact angles of the anodized Al substrates with and without TDP coating and lubricants. The anodized Al substrate, before the coating or lubrication, is hydrophilic with a water contact angle of 42.9 ± 0.8º (**Figure 1a**). The TDP coating changes the surface to hydrophobic, and its water contact angle increases to 117.3 ± 2.1º (**Figure 1b**). Similarly, the lubricant-containing surfaces (**Figure 1c-1g**) reveal hydrophobicity with water contact angles between 97 – 118º. The presence of additives in lubricant slightly influences the static water contact angle.

The water droplet on the anodized Al substrate was highly adherent on the surface, even after the TDP coating; the water droplet was not rolling off even after tilting perpendicularly on the substrate with and without the TDP coating. The impregnation of lubricants changed the surface slippery. **Table S1** summarizes the sliding angles of a water droplet on various specimens. The TDP-coated Al substrate with PDMS lubricant becomes SLIPS, with the water sliding angle as low as 2.0º. When the PDMS lubricant was impregnated into the coating-free porous alumina layer, the water droplet was stuck on the surface, confirming the necessity of reducing solid surface energy.[9] However, when PDMS lubricant contains alkylsilane (TMS and FAS) additives, the lubricated surface becomes slippery even without the TDP coating with a sliding angle less than 5º, as shown in **Table S1**. The formation of SLIPSs without the TDP coating is dependent on the type of organic additives. Aklylthiols and quinolinol additives were not suitable in forming the coating-free SLIPSs for PDMS lubricant, probably because of weak adsorption of

these additives on the alumina surface. Findings suggest that the adsorption of the additives occurs on the porous alumina surface, reducing the surface energy and generating a slippery surface.

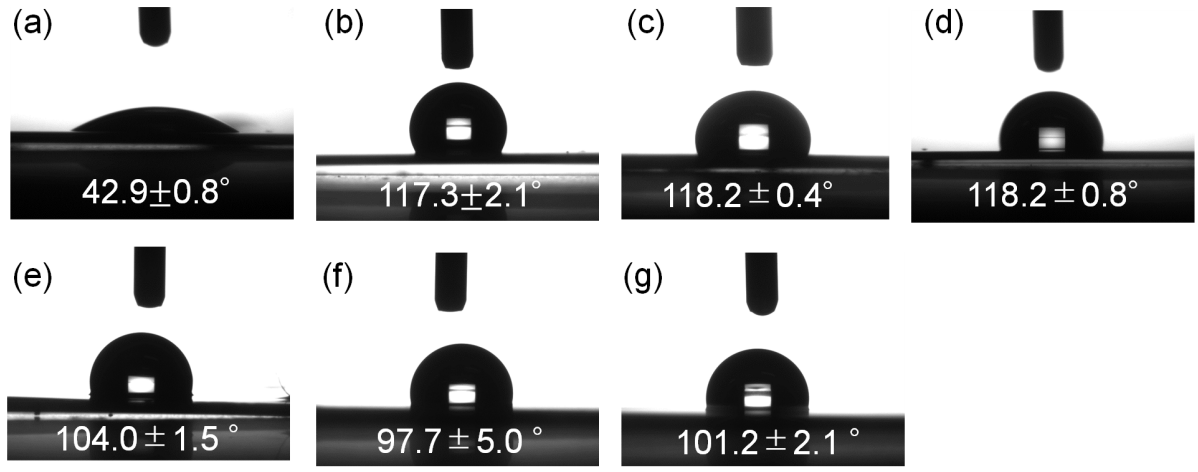

Figure 1. Static water contact angles on (a) the anodized aluminum substrate without coating and lubricant and with (b) TDP coating, and (c) PMHS@TDP, (d) TMS/PMHS, (e) PDMS@TDP, (f) TMS/PDMS, (g) FAS/PDMS SLIPSs.

The influence of the type of additives for PMHS lubricant is different from that for PDMS to form SLIPSs. The alkylthiol and quinolinol additives, in addition to the alkylsilane additives, in PMHS change the surface to SLIPSs. Such difference should come from the fact that the PMHS-lubricated surface is slippery without the TDP coating and additives; the water sliding angle is as low as 3.3º, as shown in **Table S1**. The PMHS lubricant contains a Si-H bond, which is reactive to the substrate surface (**Scheme S1**). It was reported that a thin PMHS layer, 2-10 nm thick, was adherently formed on a range of substrates, including Al substrate, showing small sliding angles of <8º for liquid droplets with surface tensions ranging from 20.5 to 72.8 mN m^{-1}.[21] The

adsorption of PMHS reduces the surface energy of the porous alumina layer, producing SLIPSs without prior organic coating. Because of such reactivity of PMHS, a wide range of additives are effective in developing SLIPSs without the TDP coating. The FAS-containing PFPE also forms a slippery surface without the TDP coating.

Although the additive-containing lubricants developed SLIPSs without an organic coating, the slippery surface was not obtained immediately after impregnating the lubricants. **Figure 2** shows the change in the water sliding angle with the lubricant impregnation time. When PDMS lubricant was used (**Figure 2a**), the water sliding angle was >20º; however, the water sliding angles on the FAS/PDMS and TMS/PDMS reduced gradually to less than 5º with the impregnation time. The DCT/PDMS and FDT/PDMS did not show sliding of water even after impregnation for 7 d. Thus, the type of additives, probably their adsorption ability, is crucial for forming SLIPSs without organic coating. It was reported that the alkyl silanes could form self-assembled monolayers on an aluminum surface through a condensation reaction between Si-OR and surface Al-OH group.[22-23] Thus, the FAS and TMS can be chemisorbed on the alumina surface formed by anodizing the aluminum substrate, reducing the surface energy. In contrast, alkyl thiols are not suitable molecules for forming self-assembled monolayers on oxides, although it is well known that they are best on noble metals, such as gold and copper.[22] Thus, the addition of thiols, DCT and FDT, in PDMS did not well chemisorb on the alumina surface, not making the surface SLIPS; only alkyl and fluoroalkyl silanes, TMS and FAS, which chemisorb on the alumina surface, are effective additives to PDMS in making SLIPS without the prior organic coating.

Different behavior was found when PMHS, forming SLIPSs without additives and coatings, was used as a lubricant. The TMS/PMHS and FAS/PMHS showed low sliding angles of <5º

regardless of the impregnation time (**Figure 2b**). However, the addition of DCT, FDT, and QNL in PMHS changed to the non-sliding surface at a short impregnation time. The additives may impede the reaction of PMHS with the alumina surface for chemical adsorption, although the long impregnation time changed these surfaces to SLIPS; the sliding angle of the FDT/PMHS reduced to <5º after the impregnation for 7 d. Movie S1 to S3 shows the sliding of a water droplet on the as-anodized Al substrate, TDM@PMHS, and TMS/PMHS specimens, which were tilted to 10º. The water droplet stuck on the as-anodized Al surface (Movie S1), while both the TDM@PMHS (Movie S2) and TMS/PMHS (Movie S3) surfaces were essentially slippery. Interestingly, the water sliding on the additive-type TMS/PMHS surface is faster than that on the coating-type PMHS@TDP, although the same lubricant was used. The enhanced sliding rate on the TMS-added lubricant may be associated with the change in the lubricant viscosity.

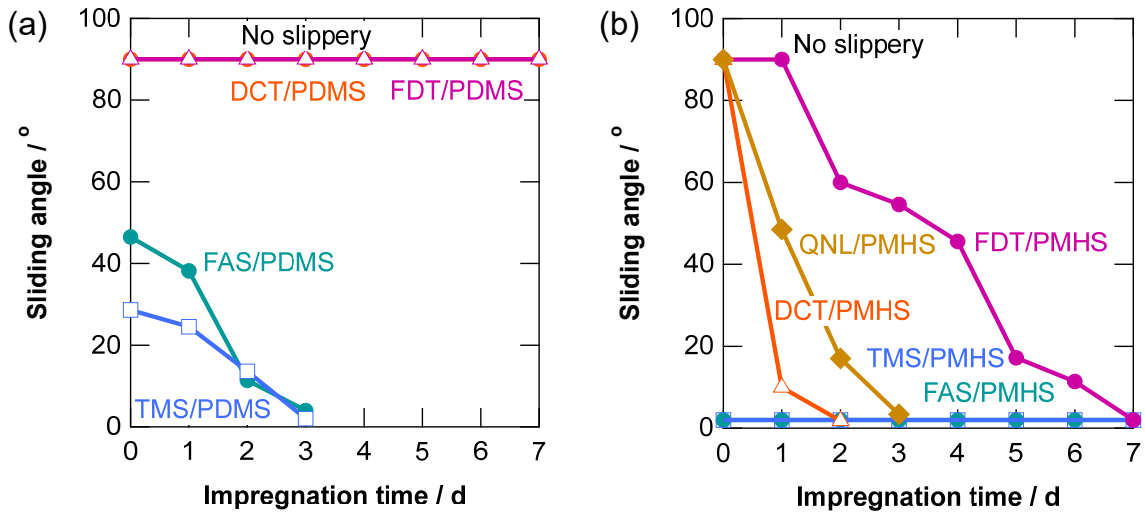

Figure 2. Change in the water sliding angle with the impregnation time of (a) PDMS and (b) PMHS lubricants containing additives.

As described above, the formation of SLIPSs without a low-surface-energy coating on anodized Al should be associated with the in-situ adsorption of the additives. In order to confirm the additive-adsorption, GDOES elemental depth profile analysis was conducted after removing the lubricant layer by washing. **Figure 3** shows the depth profile of the anodized aluminum substrate with PDMS, TMS/PDMS, and FAS/PDMS lubricants. The intensity of aluminum is relatively constant during sputtering of the porous anodic alumina layer, followed by a steep increase in the intensity at the metal/film interface. The silicon is present in the porous anodic alumina layer for all three specimens, but the specimens with TMS and FAS additives reveal the enhanced intensity of silicon. The increased intensity reflects the adsorption of the TMS and FAS molecules on the surface of pores, and the adsorption reduces the surface energy, contributing to the formation of SLIPSs.

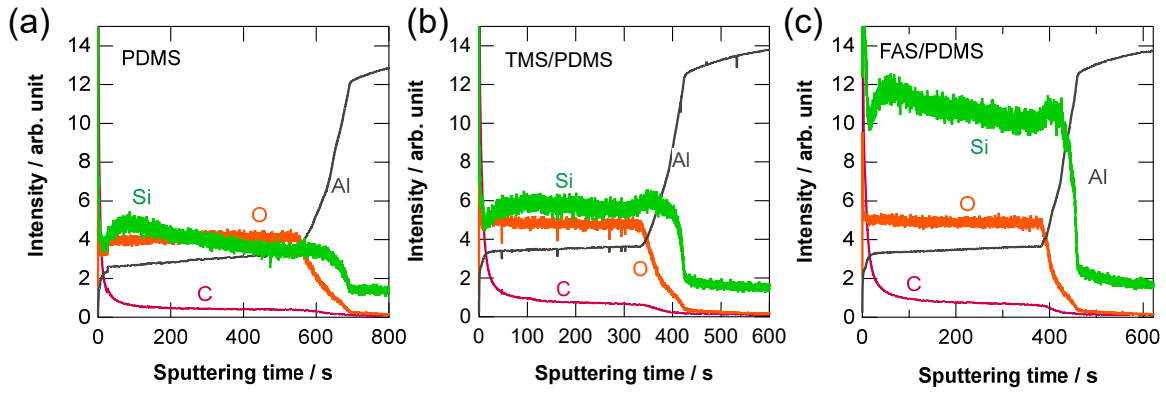

Figure 3. GDOES elemental depth profiles of the anodized aluminum specimens with (a) PDMS, (b) TMS/PDMS, and (c) FAS/PDMS lubricants. The lubricant was removed by washing in toluene before the analysis.

The corrosion behavior of the SLIPSs specimens was examined by potentiodynamic polarization in acetic acid containing chloride. **Figure 4a** shows the potentiodynamic polarization curves of TMS/PDMS, FAS/PDMS, PDMS@TDP SLIPS specimens, as well as the anodized aluminum substrate without coating and lubricant. Compared with the as-anodized Al substrate, the anodic current density decreases markedly for the SLIPS specimens. The corrosion current density of the as-anodized specimen is ~10^{-6} A cm^{-2}, whereas the SLIPS specimens show the corrosion current in the order of 10^{-10} A cm^{-2} or less. Thus, the additive-type SLIPSs exhibit high corrosion resistance, similar to the coating-type SLIPS.

As described above, the PMHS lubricant forms SLIPS without additive and coating. However, the corrosion resistance of the PMHS SLIPS is not improved; the corrosion current density of the PMHS SLIPS is even slightly higher than that of the as-anodized Al (**Figure 4b**). The corrosion current density of the PMHS SLIPS decreases only under the presence of the TDP coating or TMS and FAS additives. Thus, the formation of SLIPS itself is not a prerequisite in improving the corrosion resistance. The PMHS@TDP SLIPS shows a steep anodic current rise at -0.50 V vs Ag/AgCl, associated with pitting corrosion. Such current rise is absent up to -0.1 V vs Ag/AgCl for the TMS/PMHS and 0.3 V vs Ag/AgCl for the FAS/PMHS, indicating that these additives appear to be also effective in suppressing the localized corrosion. The low current density of the TMS/PMHS maintains even after immersion in the corrosive solution for one week, revealing the durability of the corrosion resistance (**Figure 4c**). The SLIPSs formed by adding thiol molecules (DCT or FDT) or QNL in PMHS improve corrosion resistance, although DCT is slightly less effective in reducing the corrosion current (**Figure 4d**).

When PFPE fluorine-based lubricant is used (**Figure 4e**), the corrosion resistance depends on the type of additives and coating. Combining the fluoroalkylsilane additive and fluorine-based

lubricant shows the lowest corrosion current density; the alkyl coating and alkylsilane additive are less effective in improving the corrosion resistance. This trend suggests that matching the surface energy of solid and lubricant is an important factor in reducing the corrosion current. It should be worth mentioning that the importance of matching the surface energy of the underlying substrate and lubricant on the stability of the lubricant layer on the porous substrate was reported previously. [9]

The water sliding angle reduces gradually to <5º with the lubricant impregnation time when the DCT/PMHS and FDT/PMHS are used (**Figure 2b**). The corrosion current density also changes with the impregnation time (**Figure 4f**). The DCT/PMHS at a short impregnation time of ~10 min (DCT/PMHS-F) shows a comparable corrosion current density with the as-anodized Al. However, the corrosion current density is reduced approximately three orders magnitude after impregnation for 3 d, at which the surface changes to SLIPS. Similarly, the FDT/PMHS exhibits highly improved corrosion resistance after changing to SLIPS by impregnating for 7 d. Thus, the formation of SLIPS by adsorbing the additives on the alumina surface is of importance in improving the corrosion resistance of Al.

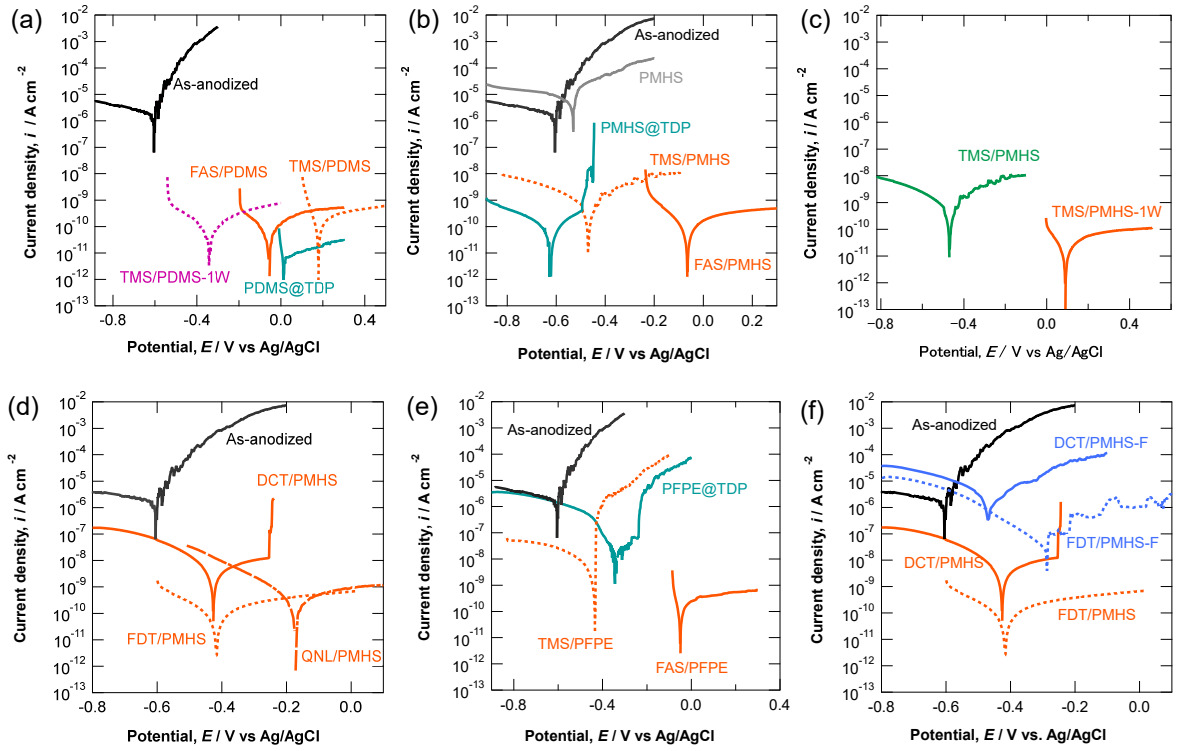

Figure 4. Potentiodynamic polarization curves in 2 g dm^{-3} acetic acid containing 10 g dm^{-3} NaCl (pH 3) of (a) as-anodized aluminum and additive-containing PDMS and PDMS@TDP SLIPSs, (b) as-anodized, additive-free and additive-containing PMHS and PMHS@TDP SLIPSs, (c) TMS/PMHS SLIPS, (d) as-anodized aluminum and DCT, FDT and QNL-containing PMHS SLIPSs, (e) as-anodized and additive-containing PFPE and PFPE@TDP SLIPSs and (f) as-anodized aluminum and the DCT- and FDT-containing PMHS before and after changing to SLIPSs. The specimens depicted as "-1W" were polarized after immersing in the corrosive solution for one week.

The corrosion-resistant SLIPSs have been reported in the past decade.[12, 15-17, 24-28] These SLIPSs used an organic coating before impregnating lubricants. It is likely that the mechanical damage of the coated solid surface reduces the stability of SLIPSs and causes degradation of corrosion resistance. The additive-type SLIPSs may have an advantage for self-healing. Even if

the surface is mechanically damaged, the additive molecules can be adsorbed again on the damaged surface, reducing the surface energy. Thus, the recovering of the corrosion resistance is highly expected.

In order to examine the self-healing behavior of the additive-containing SLIPSs, we introduced a cross-scratch on the SLIPSs (**Figure 5a**). Then, the corrosion behavior was evaluated through potentiodynamic polarization. The scratch penetrated through the porous alumina layer into the metal substrate, and the Al metal substrate was exposed directly to the lubricant. **Figure 5b** discloses the high corrosion resistance of the organic coating-type PMHS@TDP degraded considerably after introducing the scratch (PMHS@TDP-SC); both cathodic and anodic current densities increased more than three orders magnitude. In particular, a steep increase of anodic current occurs from the corrosion potential, suggesting the pitting corrosion at the scratched area.

In contrast, the additive-type TMS/PMHS SLIPS maintains the low corrosion current density even after introducing scratch defects (TMS/PMHS-SC). In the additive-type SLIPSs, the scratch defects are effectively healed by the adsorption of the TMS additive, recovering the stability of SLIPS. **Figure 5c** also demonstrates the similar low corrosion current density of TMS/PDMS-SC. Thus, the additive-type SLIPS exhibits highly improved self-healing properties in terms of corrosion protection.

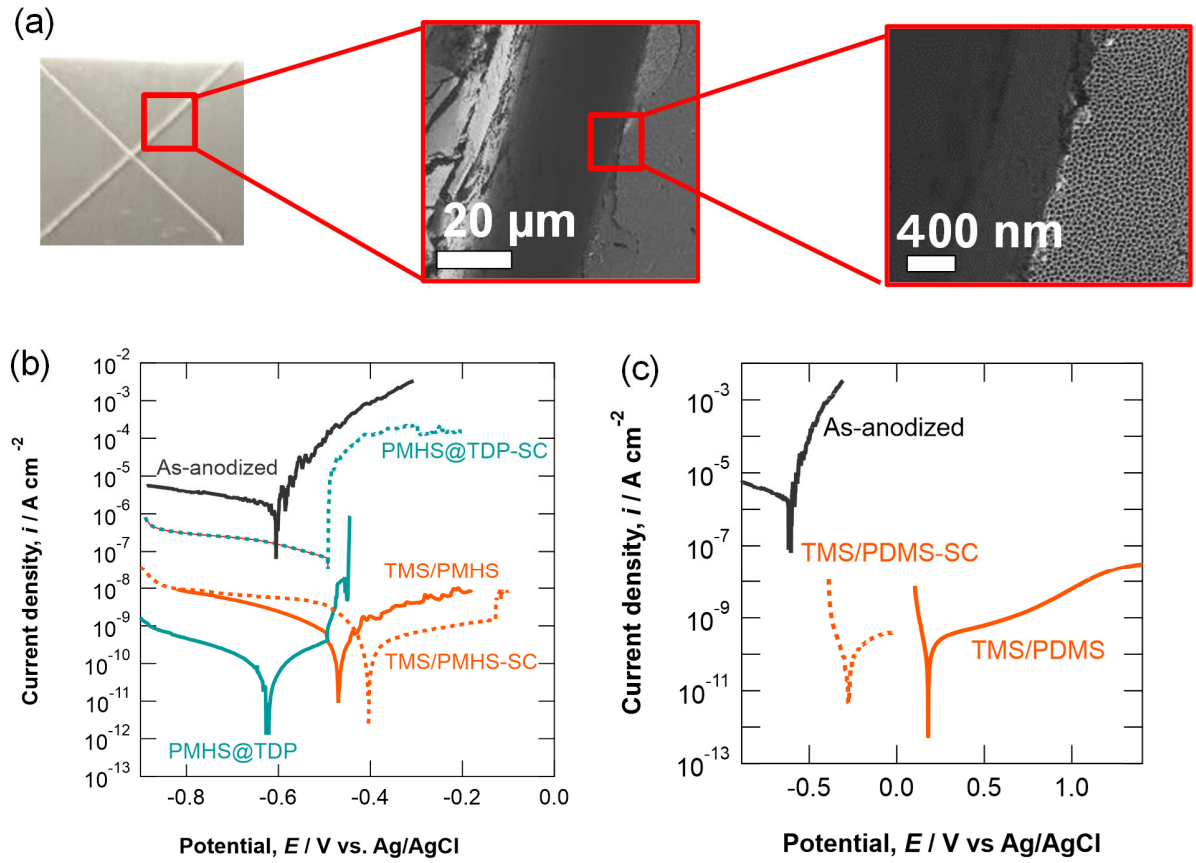

Figure 5. (a) Optical and scanning electron micrographs of the anodized aluminum with cross-scratch defects and potentiodynamic polarization curves in 2 g dm^{-3} acetic acid containing 10 g dm^{-3} NaCl (pH 3) of (b) the PMHS@TDP and TMS/PMHS SLIPSs and (c) the TMS/PDMS SLIPSs with and without the scratch defects.

As shown in **Figure 2**, thiol-type additives need a long impregnation time of ≥2 d to get a slippery surface with a sliding angle <5º. Such SLIPSs do not show immediate self-healing for corrosion protection (**Figure 6**). The FDT/PMHS SLIPS, which shows the low corrosion current density, reveals highly increased cathodic and anodic current density after introducing the scratch defects (FDT/PMHS-SC). The DCT/PMHS SLIPS, which is less corrosion resistant than

the FDT/PMHS, shows an increase in the corrosion current density of nearly one order of magnitude after the scratch (**Figure 6a**). The TMS/PDMS needs 3-d-impregnation for making SLIPS with a water sliding angle of <5º (**Figure 2a**). However, the introduction of scratch defects does not increase the corrosion current density (**Figure 6b**). The TMS/PDMS is slippery even at a short impregnation time, although the water sliding angle is ~30º. Even if the sliding angle is high, the slippery surface is sufficient to maintain the high corrosion resistance of the additive-containing SLIPSs.

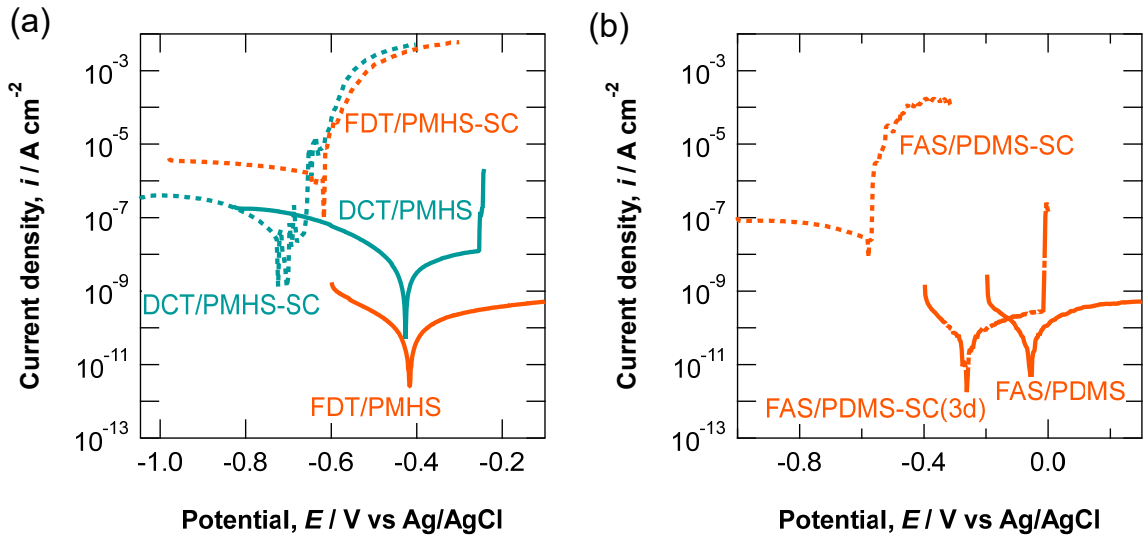

Figure 6. Potentiodynamic polarization curves in 2 g dm^{-3} acetic acid containing 10 g dm^{-3} NaCl (pH 3) of (a) the DCT/PMHS and FDT/PMHS and (b) FAS/PDMS SLIPSs with and without the scratch defects.

The long-term self-healing ability was also examined by introducing the scratch defects after immersion of the SLIPS specimens in the chloride-containing acetic acid for one week. Both TMS-containing PDMS and PMHS SLIPSs were scratched after immersion in the corrosive

solution for one week (**Figure 7a**). The type of lubricants influences self-healing durability. The TMS/PMHS does not possess durability; the corrosion current density increases after introducing the scratch defects. In contrast, the low current density of the TMS/PDMS remains almost unchanged even after scratch. Findings indicate that only the PDMS lubricant containing TMS exhibits the long-term ability of self-healing.

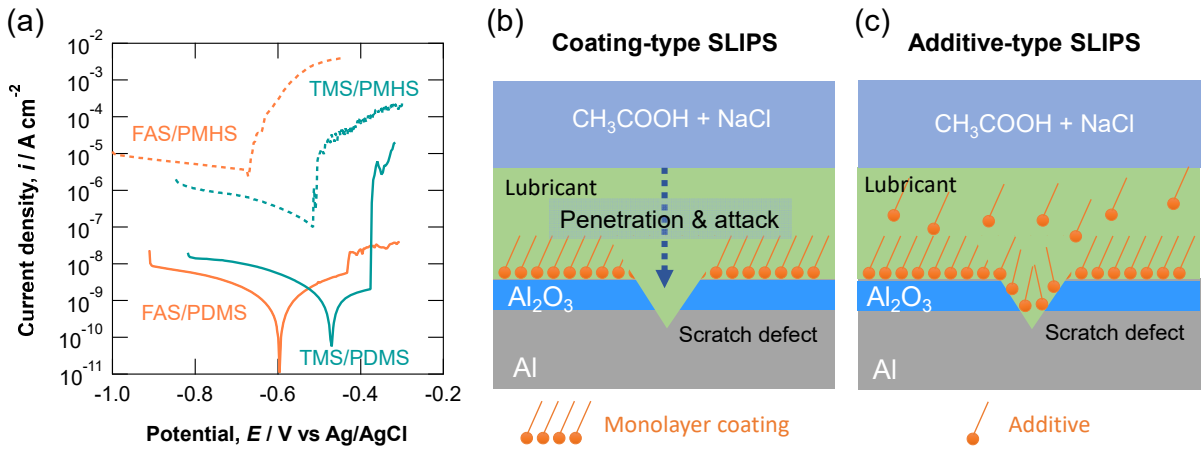

Figure 7. (a) Potentiodynamic polarization curves of the additive-type SLIPSs measured after immersion in 2 g dm^{-3} acetic acid containing 10 g dm^{-3} NaCl (pH 3) for one week and subsequent introduction of the scratch defects, and schematic illustrations of (b) coating-type and (c) additive-type SLIPSs with a scratch defect.

The adsorption capability of TMS on alumina in the lubricants should be lost after the hydrolysis and subsequent polymerized condensation (Equation 1).

$$\mathrm{RSi(OEt)_3} + 3\mathrm{H_2O} \xrightarrow{\text{hydrolysis}} \mathrm{RSi(OH)_3} + 3\mathrm{EtOH} \xrightarrow{\text{condensation}} \mathrm{RSiO_{1/2}} + \frac{1}{2}\mathrm{H_2O} \qquad (1)$$

The reaction rate of the first hydrolysis can be expressed by equation 2, and the rate constant is dependent upon the concentration of acid or base catalysts:[29]

$$rate = k_{obs}[\mathrm{RSi(OEt)_3}]^m[\mathrm{H_2O}]^n \quad (2)$$

It is known that the PDMS are immissible with water and acetic acid. In contrast, acetic acid is partly missible with the PMHS, promoting the hydrolysis and condensation rate in PMHS. Consequently, the degradation of the self-healing ability of the TMS/PMHS is faster than that of the TMS/PDMS.

Figure 7b and 7c shows schematic illustrations of the coating-type and additive-type SLIPSs with a scratch defect. When a scratch defect is introduced into the coating-type SLIPS, hydrophilic alumina substrate is exposed to lubricant. It was reported that water droplets were not slippery and penetrated through a lubricant layer that was impregnated into the hydrophilic porous substrate.[9] Thus, the exposure of hydrophilic surface by introducing a scratch defect induces the penetration of the corrosive aqueous solution into the substrate, causing the degradation of corrosion protection. In contrast, re-adsorption of additive organic molecules can occur when the scratch defect was introduced to the additive-type SLIPS (Figure 7c), maintaining the high corrosion protection. The self-healing ability may depend on the adsorption rate of the additives, suggesting that alkylsilane additives are better than alkylthiol and quinolinol additives. The stability of the additives is also an important factor in the durability of self-healing.

4. CONCLUSIONS

The corrosion-resistant SLIPSs with high self-healing ability are developed on Al substrate. A lubricant containing an organic additive, which can adsorb on a porous surface, is impregnated into the porous alumina layer formed by anodizing of Al substrate. An organic coating, reducing the surface energy, is usually necessary to form SLIPSs. However, the impregnation of the additive-containing lubricant directly into the hydrophilic anodized Al substrate can make a slippery surface because of the in situ adsorption of the organic additive on the alumina surface. The anodized Al substrate suffers from corrosion in chloride-containing acetic acid aqueous solution. Both coating-type and additive-type SLIPSs improve remarkably the corrosion resistance in this corrosive solution. In addition, the additive-type SLIPSs exhibit better self-healing ability compared with the coating-type SLIPSs; the former SLIPSs maintain high corrosion resistance even after introducing a scratch defect, while the scratch defect induces the corrosion for the coating-type SLIPSs. Thus, the additive-type SLIPSs, developed for the first time in this study, are novel self-healing surfaces with high corrosion resistance.

Supporting Information

The supporting information is available free of charge at https//pubs.acs.org/doi/….

Scanning electron micrographs of surface and cross-section of anodized Al (Figure S1); sliding angles of a water droplet on anodized Al substrate with and without lubricants and TDP coating (Table S1) (PDF).

Water sticking anodized Al surface (MP4)

Water sliding coating-type SLIPS surface (MP4)

Water sliding addtive-type SLIPS surface (MP4)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This paper was supported in part by the Light Metal Educational Foundation, Inc.

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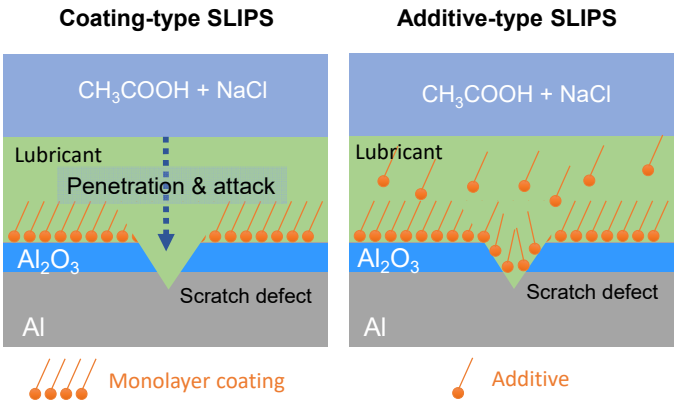
TOC graphic


Coating-type SLIPS
Additive-type SLIPS
CH3COOH + NaCl
Lubricant
Penetration & attack
Al2O3
Scratch defect
Al
CH3COOH + NaCl
Lubricant
Al2O3
Scratch defect
Al
Monolayer coating
Additive