A Liquid-phase Ion Gun Technique for Generating Sulfide Ions on Metal Surfaces

Jun-Seob Lee^{1)*} and Koji Fushimi²⁾

¹⁾ *Department of Metallurgy and Advanced Materials Engineering, Changwon National University*

²⁾ *Faculty of Engineering, Hokkaido University*

* **Corresponding Author** 20 Changwondaehak-ro Uichang-gu Changwon-si, Gyeongsangnam-do 51140, Korea
Email: junseobleee@changwon.ac.kr

A new liquid-phase ion gun (LPIG) technique was developed for safe generation of sulfide ions on metal surfaces in solution, though the LPIG was originally a local chloride ion-generating system used to investigate localized corrosion on metal surfaces as an application of scanning electrochemical microscopy. A silver/silver sulfide microelectrode was used as a liquid-phase sulfide ion gun (LPSIG) instead of a silver/silver chloride microelectrode of an LPIG. Cathodic polarization of the LPSIG microelectrode resulted in the generation of hydrogen sulfide ions in the vicinity of the microelectrode and provided a safe electrochemical environment containing hydrogen sulfide ions. The generation of hydrogen sulfide ions from the LPSIG and the degradation behavior of surfaces of a silver or a type-316L stainless steel are mainly reviewed here. The potential of the LPSIG technique for investigation of hydrogen sulfide-induced corrosion is also discussed.

Key words : Microelectrode, Sulfide ion, Scanning electrochemical microscopy

1. Introduction

In the oil and gas mining industry, metallic materials frequently undergo general corrosion, localized corrosion and stress corrosion cracking induced by aggressive environments containing hydrogen sulfide (H_2S). Studies on corruptions induced by H_2S generally require the use of H_2S gas for dissolving H_2S in a solution with a relatively high concentration^{1)–3)}. For example, H_2S gas was purged using a pressure of 5.0 kPa to 5.0 mM of dissolved H_2S in an acidic solution to characterize corrosion products formed on type-316L stainless steel²⁾. However, H_2S gas is toxic and safety standards for the use of H_2S gas limit the concentration of H_2S gas to be used to, for example, below 20 ppm⁴⁾. Thus, the establishment of a safe experimental condition to use H_2S gas is an extremely important issue for the study of H_2S -induced corrosion. As an alternative method to the utilization of a corrosive environment containing H_2S ^{5)–7)}, the use of sodium sulfide (Na_2S) has been attempted. For example, a sulfur compound was formed on the surface of type-304 stainless steel in a sealed electrochemical cell, in which 15 ppm of H_2S was produced by mixing an Na_2S solution and H_2SO_4 ⁷⁾. Although the use of sulfide ions (S^{2-}) in an aqueous solution might be effective for realizing a safe environment containing H_2S , it was difficult to control its concentration in the sealed cell.

A liquid-phase ion gun (LPIG) technique, in which a silver/silver chloride (Ag/AgCl) microelectrode was cathodically polarized in the vicinity of a metal surface, was useful for generating infinitesimal amount of chloride ions (Cl^-) on a localized area of a metal surface⁸⁾. Control of the first working electrode of the LPIG as a Cl^- generator and operation of the second working electrode

of a metal specimen by a bipotentiostat enabled the measurement of the electrochemical behavior on a localized metal surface in a highly concentrated Cl^- environment. The LPIG was used to investigate degradation behaviors of passive surfaces of iron^{8),9)} and copper¹⁰⁾, and the breakdown mechanism⁸⁾ or anisotropic breakdown⁹⁾ of the passive film formed on an iron surface was reported.

To generate hydrogen sulfide ions (HS^-) instead of Cl^- , a liquid-phase sulfide ion gun (LPSIG) has been developed. A silver/silver sulfide ($\text{Ag}/\text{Ag}_2\text{S}$) microelectrode was cathodically polarized in the vicinity of a metal surface. Since the amount of HS^- generated from the LPSIG microelectrode could be controlled electrochemically as in the case of using an LPIG, the use of an LPSIG would be a potential method for investigation of sulfide-induced corrosion of metals. In this paper, the development of an LPSIG and applications of the LPSIG to local sulfidation of an Ag specimen and to local degradation of a type-316L stainless steel surface are described and the potential of an LPIG and an LPSIG for H_2S -induced corrosion of metals is discussed.

2. Experimental procedures

2.1 Electrodes and specimens

A microelectrode of the LPSIG was fabricated from a silver wire with a diameter of 500 μm by embedding in a 1-mm diameter glass capillary with epoxy resin and polishing the tip of the embedded silver wire with SiC papers down to 4,000 grit. The microelectrode was polarized at -0.70 V versus an Ag/AgCl reference electrode in a saturated KCl solution (SSE) in 0.1 M Na_2S solution (pH 13.4) until the electric charge of 10 mC was consumed to form sulfides on the silver microelectrode.

Plates of silver (AG-403518, Nilaco) with an area of 0.80 cm^2 and type 316L stainless steel (782560, Nilaco) with an area of 0.07 cm^2 were independently used as specimens for LPSIG measurements. Wires of tungsten (W-461167, Nilaco) and silver (AG-401167, Nilaco), both with a diameter of $100 \mu\text{m}$, were also used as sensors of pH and HS^- concentration, respectively. After embedding in epoxy resin and mirror-like polishing, these materials were used as substrate electrodes against an LPSIG microelectrode that was used as a tip electrode in LPSIG-mode scanning electrochemical microscopy (SECM).

2.2 Experimental systems

Fig. 1 shows experimental set-ups for LPSIG and SECM measurements. De-aerated pH 8.4 buffer (aqueous solution of $0.15 \text{ M H}_3\text{BO}_3$ and $0.15 \text{ M NaB}_4\text{O}_7$) was mostly used as the electrolyte solution in an acrylic resin cell of 100 cm^3 in volume with a platinum counter electrode and the SSE reference electrode. To polarize a substrate electrode, a bipotentiostat (HAL-1512 mM2, Hokuto Denko) or a potentiostat (SP-150, Biologic) was used. The bipotentiostat was also used to polarize a microelectrode potentiostatically (Fig. 1a), while the combination of a current source (SS7012, HIOKI) and an electrometer (R8240, Advantest) was used with the potentiostat to polarize the microelectrode galvanostatically (Fig. 1b). The position of the microelectrode relative to the substrate

was controlled by an X-Y-Z stage (SGSP20-35, Sigma Koki). An optical microscope was also used to adjust the inter-electrode distance between the microelectrode and substrate electrode.

2.3 Electrochemical measurements

The substrates used for measurements were a glass plate, a silver plate, a silver microelectrode, a tungsten microelectrode, and a type-316L stainless steel plate. With inter-electrode distances of 125 to $10,000 \mu\text{m}$, potentiostatic or galvanostatic polarization of the LPSIG microelectrode was conducted to generate HS^- above the substrate surface. The LPSIG microelectrode was polarized at $-0.70 \text{ V}_{\text{SSE}}$ in the case of potentiostatic generation, while a cathodic current of $-3.0 \mu\text{A}$ was flowed through the microelectrode for galvanostatic generation. The glass substrate was insulating. The substrate electrodes of the silver plate and stainless steel plate were polarized potentiostatically, while the substrate microelectrodes were in an open circuit condition and their potentials were monitored to sense pH and HS^- concentration $[\text{HS}^-]$ during the LPIG operation. It was found in a separate experiment¹¹⁾ that the potential of the tungsten substrate microelectrode was a function of solution pH as follows:

$$E_{\text{W}}/\text{V}_{\text{SSE}} = 0.0310 - 0.0425 \text{ pH}. \quad (1)$$

HS^- is present with OH^- during the LPIG operation as follows:

Additionally, the solubility product of Ag_2S is very small ($K_{\text{sp}} = 7.2 \times 10^{-50}$ at 298 K) in aqueous solutions¹²⁾. $[\text{HS}^-]$ was calculated from the potential of a silver substrate microelectrode and the solution pH by the standard potential of silver electrode in an HS^- -containing aqueous solution¹³⁾ as follows:

$$E_{\text{Ag}}/\text{V}_{\text{SSE}} = -0.077 - 0.0295 \text{ pH} - 0.0295 \log [\text{HS}^-]. \quad (3)$$

After the LPSIG operation against the substrate electrode of stainless steel, impedance measurement and Mott-Schottky (M-S) analysis were conducted at the same potential as that during the LPSIG superimposed a sinusoidal voltage with an amplitude of $\pm 10 \text{ mV}$ at a frequency of 15 Hz . In the M-S analysis, the potential applied was decreased down to $-0.40 \text{ V}_{\text{SSE}}$ in steps of 20 mV . Furthermore, after the LPSIG operation against the stainless steel substrate polarized at $0.40 \text{ V}_{\text{SSE}}$ for 100 s , the surface was measured by tip generation/substrate collection mode SECM, in which a platinum microelectrode with a diameter of $30 \mu\text{m}$ and the steel were polarized at 0.60 and $-0.20 \text{ V}_{\text{SSE}}$, respectively, in pH 8.4 buffer containing 1.0 mM hydroxymethyl ferrocene (FcMeOH), and the microelectrode was scanned in X and Y directions while keeping an interelectrode distance of $20 \mu\text{m}$.

Fig. 1 Schematic diagrams of LPSIG-mode SECM set-ups for (a) potentiostatic generation and (b) galvanostatic generation.

2.4 Surface analyses

Auger electron spectroscopy (AES) and X-ray

photoelectron spectroscopy (XPS) were conducted for the surface of the type-316L stainless steel substrate polarized without or with the LPSIG operation. In AES with an apparatus (JAMP-9500F JEOL), an electron beam diameter of $30\text{ }\mu\text{m}$ (10 keV, 15 nA) with Ar^+ sputtering at an etching rate of 3.2 nm min^{-1} equivalent to silica was used for obtaining a depth profile of the steel surface. In XPS using an apparatus (JPS-9200 JEOL), a monochromatic Al K α (15 keV, 10 mA) was irradiated to a detection area with a diameter of 1 mm. Photoelectron spectra were deconvoluted using SpecSurf software (JEOL).

3. Results and discussion

3.1 LPSIG operation above a glass surface

Fig. 2a shows transients of a current flowing through an LPSIG microelectrode above a glass plate substrate when the potential was changed from -0.30 to $-0.70\text{ V}_{\text{SSE}}$ in pH 8.4 boric acid-borate buffer solution. Transients of the electric charge Q_{LPSIG} consumed by the LPSIG microelectrode are also shown. These transients are functions of the distance between the microelectrode and the substrate surface. Although no cathodic current flows through the microelectrode during polarization at

Fig. 2 (a) Transients of LPSIG current I_{LPSIG} and electric charge Q_{LPSIG} when the LPSIG microelectrode potential was changed from -0.30 to $-0.70\text{ V}_{\text{SSE}}$ from 0.10 ks in pH 8.4 boric acid-borate buffer solution above a glass plate substrate with distances of 125, 250, 500, 1,000 and 10,000 μm . (b) Peak current I_{peak} of the LPSIG microelectrode as a function of distance d . Reproduced with permission from *J. Electrochem. Soc.*, **162**, C115 (2015) Copyright © 2015, The Electrochemical Society.

$-0.30\text{ V}_{\text{SSE}}$, polarization at $-0.70\text{ V}_{\text{SSE}}$ from 100 s allows the flow of a significant cathodic current associated with the forward reaction of Eq. 2, which is generation of both HS^- and OH^- . This current gradually increases and peaks at 1-3 ks, depending on the distance as shown in Fig. 2b. Highly concentrated HS^- and OH^- generated from the microelectrode could clog the narrow space between the microelectrode and the substrate surface. However, the cathodic current diminishes at 4-6 ks when Q_{LPSIG} reaches -10 mC . This is mainly because of the limitation on the generation of HS^- from the LPSIG microelectrode, corresponding to complete consumption of sulfides charged on the microelectrode surface. After the polarization, the formation of a porous silver product on the microelectrode surface was also observed. This is probably due to the change in ionic conduction at the $\text{Ag}/\text{Ag}_2\text{S}/\text{solution}$ interfaces, that is a silver product. The change in cathodic current transients and the formation of a silver product by potentiostatic polarization make the reduction of silver sulfide complicated.

An alternative method to reduce silver sulfide is galvanostatic polarization. Fig. 3 shows potential transients of the LPSIG microelectrode when the microelectrode was galvanostatically polarized at $-3.0\text{ }\mu\text{A}$ above a tungsten substrate electrode and a silver substrate electrode at an interelectrode distance of $125\text{ }\mu\text{m}$ in pH 8.4 boric acid-borate buffer solution. The potential of the microelectrode shifts from 0.16 to $-0.72\text{ V}_{\text{SSE}}$ and the potentials of the tungsten and silver substrate electrodes also shift from original open circuit potentials to more negative potentials, corresponding to the generation of OH^- and HS^- . The concentrations of OH^- and HS^- calculated by Eqs. 1 and 3

Fig. 3 Changes in potential of the LPSIG microelectrode, tungsten microelectrode substrate, and silver microelectrode substrate during galvanostatic polarization of the LPSIG microelectrode at $-3.0\text{ }\mu\text{A}$ above the microelectrode substrate with an interelectrode distance of $125\text{ }\mu\text{m}$ in pH 8.4 boric acid-borate buffer. The values of pH and $[\text{HS}^-]$ were calculated using Eqs. 1 and 3, respectively. Reproduced with permission from *J. Electrochem. Soc.*, **162**, C685 (2015) Copyright © 2015, The Electrochemical Society.

(Fig. 3) were more stable after the microelectrode polarization than after the potentiostatic polarization. The shift of $[\text{OH}^-]$ is smaller than that of $[\text{HS}^-]$ due to the buffer effect of the solution, while $[\text{HS}^-]$ reaches the order of 10^{-2} M, suggesting that the LPSIG technique is effective for forming a concentrated HS^- environment on the substrate surface

Fig. 4a shows the maximum concentration $[\text{HS}^-]_{\text{max}}$ of HS^- on a substrate surface obtained with a silver substrate microelectrode as a function of the distance between the LPSIG and the substrate during potentiostatic polarization. The value of $[\text{HS}^-]_{\text{max}}$ is almost zero, meaning that HS^- generated from the bulk solution is completely diluted. However, $[\text{HS}^-]$ increases exponentially with a decrease in the distance and $[\text{HS}^-]_{\text{max}}$ reaches 14.5 mM at $125\mu\text{m}$, suggesting that a very small distance between the LPSIG microelectrode and the substrate is effective for concentrating HS^- on the substrate surface. According to Eq. 2, the silver sulfide reduction generating HS^- is also accompanied by the generation of OH^- . However, the maximum concentration $[\text{OH}^-]_{\text{max}}$ of OH^- on a substrate surface is relatively stable as shown in Fig. 4b, whereas $[\text{OH}^-]_{\text{max}}$ was larger during galvanostatic polarization as shown in Fig. 3. The value of $[\text{OH}^-]_{\text{max}}$ is almost constant at $10^{-5.3}$ M regardless of the distance between the LPSIG microelectrode and substrate. This is due to the buffer effect of the solution used ($\text{pH} = 8.4$).

In a stagnant, highly conducting electrolyte solution, the mass transport of dissolving products from the electrode is controlled by the diffusion described as Fick's second law:

$$\frac{\partial c}{\partial t} - D \nabla^2 c = 0, \quad (4)$$

where c and D are the concentration and diffusion coefficient of diffusing species, respectively, and t is time. The concentration profiles of species generated from an LPSIG microelectrode in solution can be estimated from Eq. 4. In the boundary condition, concentration gradients at insulating surfaces and bulk solution are defined as follows:

$$\nabla c = 0. \quad (5)$$

At the interface between the LPSIG microelectrode and solution, concentration gradients of HS^- and OH^- in the normal direction were determined from an LPSIG current measured. In an initial condition, $[\text{HS}^-] = 0$ M and $[\text{OH}^-] = 10^{-5.6}$ M. Diffusion coefficients¹⁴⁾ $D(\text{HS}^-) = 1.73 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D(\text{OH}^-) = 5.27 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ were also used. The values of $[\text{HS}^-]_{\text{max}}$ and $[\text{OH}^-]_{\text{max}}$ that were numerically calculated using a finite element method solver of COMSOL Multiphysics™ 5.0 are also plotted in Figs. 4a and 4b, respectively. The calculated value of $[\text{HS}^-]_{\text{max}}$ is in relatively good agreement with the measured value, though the calculation does not consider a chemical balance of OH^- or H^+ that is strongly related to water ionic products in the presence of boric acid-borate buffer. Conversely, the diffusion of HS^- might be enhanced by the buffering effect because the consumption of OH^- accelerates the forward reaction of Eq. 2. Since the forward reaction of Eq. 2 at the LPSIG surface is limited because an electric charge of 10 mC was consumed for the formation of Ag_2S , the diffusion reduces the value of $[\text{HS}^-]$ on the substrate surface in competition with the generation of HS^- . The geometry of the space between the LPSIG and the substrate strongly determines the diffusion and concentration of HS^- .

3.2 Local sulfidation of a silver surface

Fig. 5a shows transients of the current flowing through the LPSIG microelectrode and silver substrate electrode in pH 8.4 buffer when the potential of the microelectrode was changed from -0.20 to $-0.70 \text{ V}_{\text{SSE}}$ and the potential of the substrate electrode was kept at $0.30 \text{ V}_{\text{SSE}}$. The cathodic current flowing through the LPSIG micro electrode, indicating the generation of HS^- as shown in Fig. 2a, increases and decreases, showing a peak within 1.5 ks regardless of the interelectrode distance. Almost corresponding to the microelectrode current, anodic current flows through the silver substrate electrode and shows a peak. In Fig. 5b, the electric charge $Q_{\text{Ag sub}}$ consumed on the silver substrate electrode increases linearly with the electric charge Q_{LPSIG} consumed on the LPSIG microelectrode during HS^- generation. The slope of the relationship becomes steeper as the distance decreases and becomes almost -1.0 as shown in Fig. 5c.

Fig. 6a shows an SEM image of the silver substrate electrode surface after the LPSIG operation at a distance of $125\mu\text{m}$. On the local surface facing the LPSIG

Fig. 4 Measured and calculated maximum concentrations of (a) HS^- and (b) OH^- at the peak current of LPSIG microelectrode during potentiostatic polarization of the LPSIG microelectrode as a function of interelectrode distance.

Fig. 5 (a) Transients of currents flowing through the LPSIG microelectrode and silver substrate electrode polarized at $0.10 V_{SSE}$ when the LPSIG microelectrode potential was changed from -0.20 to $-0.70 V_{SSE}$ in pH 8.4 boric acid-borate buffer with an interelectrode distance of 125, 250, 500 or $1,000 \mu m$. (b) Relation between electric charges consumed by the LPSIG microelectrode Q_{LPSIG} and the silver substrate electrode $Q_{Ag sub}$. (c) Slope $dQ_{Ag sub}/dQ_{LPSIG}$ of (b) as a function of d . Reproduced with permission from *J. Electrochem. Soc.*, **162**, C115 (2015) Copyright © 2015, The Electrochemical Society.

Fig. 6 (a) SEM image and (b) XRD pattern of the silver substrate surface after the LPSIG potentiostatic operation with $d = 125 \mu m$. Reproduced with permission from *J. Electrochem. Soc.*, **162**, C115 (2015) Copyright © 2015, The Electrochemical Society.

microelectrode, formation of a circle-like product can be seen. The diameter of the product is about $1,000 \mu m$, which coincides with the diameter of the glass sheath of the LPSIG. The product was identified as Ag_2S by using XRD patterning as shown in Fig. 6b. It is suggested that the silver substrate surface is sulfidized by HS^- generated from the LPSIG microelectrode with the backward reaction of Eq. 2. From this point, the slope in Fig. 5c corresponds to the efficiency for sulfidation. It would become unity as the distance decreases to a value as small as the diameter of the LPSIG microelectrode. In this condition (at $0.30 V_{SSE}$), conversely, sulfidation of silver occurs electrochemically. When the silver substrate was polarized at potentials lower than $-0.16 V_{SSE}$, on the other hand, the electrochemical sulfidation was suppressed and the sulfidation efficiency became a value smaller than zero.

3.3 Application to local sulfidation of type-316L stainless steel surface

Local generation of HS^- by the LPSIG operation was effective for investigating sulfidation of the silver substrate electrode surface. Local HS^- generation should also be effective for sulfidating other material surfaces. It was therefore applied to type-316L stainless steel and used to

investigate its local sulfidation. In this case, galvanostatic polarization was used for the generation of HS^- instead of potentiostatic polarization because of the ease of controlling the concentration. Fig. 7a shows double logarithmic plots of the substrate current density and time during potentiostatic polarization of a type-316L stainless steel substrate electrode at $0.40 \text{ V}_{\text{SSE}}$ in pH 8.4 boric acid-borate buffer, while the LPSIG microelectrode was galvanically polarized at $-3.0 \mu\text{A}$ for 100, 150, or 600 s, corresponding to concentrations of HS^- of 1.5, 2.2, or $2.8 \times 10^{-3} \text{ M}$, respectively, at an interelectrode distance of $125 \mu\text{m}$. The substrate current decreases with time, indicating the formation of an insulating film such as oxide film. However, the current density after polarization for 100 s increases and the slope of the plot decreases with increase in $[\text{HS}^-]$ supplied from the LPSIG operation, indicating that the resistivity of the insulating film becomes small in the presence of HS^- . This was also confirmed from impedance measurement at 15 Hz, at which the capacitive property of the steel surface is dominant, after the LPSIG operation (Fig. 7b). The value of Z increases with time, suggesting that the donor density of the film decreases due to aging. The Z at the same time

after the operation depends on $[\text{HS}^-]$ and becomes smaller with an increase in $[\text{HS}^-]$. This means that the donor density in the oxide film is strongly related to HS^- in the solution at the initial stage of passivation. Fig. 7c shows an M-S plot of the substrate electrode after film formation at $0.40 \text{ V}_{\text{SSE}}$ with the LPSIG operation. The positive slope indicates that the film has an n-type semiconductive property. Since the slope is inversely proportional to donor density of the film, it is clear that the donor density increases with an increase in $[\text{HS}^-]$. A more defective film therefore forms in a solution containing a larger concentration of HS^- .

Fig. 8 shows a tip generation/substrate collection mode SECM image of a steel surface after the LPSIG operation when the substrate was polarized at $0.40 \text{ V}_{\text{SSE}}$. During the SECM measurement, the platinum tip microelectrode was polarized at $0.60 \text{ V}_{\text{SSE}}$ to oxidize FcMeOH and to generate FcMeOH^+ , while the substrate electrode was polarized at $-0.20 \text{ V}_{\text{SSE}}$ to reduce and collect FcMeOH^+ . The reactivity of reduction on the substrate is affected by the electron transfer reaction through the oxide film on the substrate electrode^{15)–17)}. It is apparent that a circle-shaped local surface of stainless steel with a diameter of approximately

Fig. 7 (a) Double logarithmic plot of current density and time during potentiostatic polarization of the type-316L stainless steel substrate electrode at $0.40 \text{ V}_{\text{SSE}}$ after the LPSIG operation at $-3.0 \mu\text{A}$ for 0, 0.1, 0.15, and 0.6 ks, corresponding to local concentrations of HS^- of 0.0, 1.5, 2.2 and 2.8 mM, respectively. (b) Transients of impedance $|Z|$ measured at a frequency of 15 Hz after the LPSIG operation and (c) Mott-Schottky plots of the steel after polarization at $0.40 \text{ V}_{\text{SSE}}$ with the LPSIG operation. Reproduced with permission from *J. Electrochem. Soc.*, 162, C685 (2015) Copyright © 2015, The Electrochemical Society.

Fig. 8 Tip current image of tip generation/substrate collection mode SECM of the type-316L stainless steel surface after potentiostatic polarization at $0.40 V_{SSE}$ with the LPSIG operation for local concentration of HS^- of 2.8 mM. Reproduced with permission from *J. Electrochem. Soc.*, **162**, C685 (2015) Copyright © 2015, The Electrochemical Society.

$500 \mu m$, which is similar to the diameter of the LPSIG microelectrode, has relatively high reactivity for reduction of $FcMeOH^+$. The local surface of stainless steel in the vicinity of the LPSIG microelectrode becomes defective due to a high concentration of HS^- and allows electron transfer reaction more frequently than other surface.

The local substrate surface after the LPSIG operation was also analyzed by AES and XPS. Fig. 9 shows depth profiles of concentration ratios obtained by AES with Ar^+ sputtering. The surface is primarily covered with oxides of iron and chromium with a thickness of approximately 3 nm regardless of the LPSIG operation. In the LPSIG operation, however, S is incorporated at the outermost surface of the oxide and approximately 10% of the iron is enriched in the outer oxide film. Fig. 10 shows XPS $S 2p_{3/2}$ spectra for the substrate surface in a solution with and without the LPSIG operation. Peaks for S species identified as sulfate, sulfite, and sulfide were observed in/on the oxide surface when the LPSIG operation was conducted, while no peak for S species was observed without the LPSIG operation. It is thought that HS^- generated from the LPSIG operation is adsorbed on the substrate, incorporated into the oxide film, and oxidized to tetra- or hexa-valent species.

A passive film formed on a stainless steel surface in an alkaline aqueous solution mainly consists of oxide and/or hydroxide^{18)–21)}. In a solution containing HS^- , the formation of sulfate and/or sulfite can compete with the formation of oxide and/or hydroxide, though $[HS^-]$ at the local surface is 10^5 -times smaller than $[OH^-]$. It is assumed that HS^- in the solution adsorbs and forms sulfide on the surface and the adsorbed divalent S is oxidized, resulting in the introduction of donor levels such as metal cations and/or oxygen vacancies in the oxide film as well as surface states on the film. The formation of donor and surface states would also be related to the applied potential of the substrate electrode as well as the HS^- concentration on the surface. If the solution is enriched with H^+ and/or H_2S , an oxide film is a major

Fig. 9 Atomic ratios of (a) O or S and (b) Fe, Cr and Ni to major elements Fe, Cr, Ni, Mo, O, and S calculated from AES depth profiles of the type-316L stainless steel surface with or without the LPSIG operation at a potential of $0.40 V_{SSE}$. The depth profiled with Ar^+ sputtering is equivalent to 0.06 nm s^{-1} for SiO_2 . Reproduced with permission from *J. Electrochem. Soc.*, **162**, C685 (2015) Copyright © 2015, The Electrochemical Society.

Fig. 10 Photoelectron spectra of $S 2p_{3/2}$ of the type 316L stainless steel surface with or without the LPSIG operation at potential of $0.40 V_{SSE}$. Reproduced with permission from *Electrochim. Acta*, **220**, 304 (2016) Copyright © 2016, Elsevier.

product and the surface is no longer passive state. Sulfate, sulfite and/or sulfide, depending on the potential, would be formed on the surface.

3.4 H_2S generation by local acidification

The value of $[HS^-]_{max}$ on a substrate surface with an interelectrode distance of $125 \mu m$ described above was 52 nM. It is too small to show a severe environment such

as a condition containing H_2S , because the amount of generated HS^- is determined by the electric charge to form Ag_2S on the Ag microelectrode. In order to overcome this drawback of the LPSIG, the polarization of a Pt microelectrode in Na_2S aqueous solution has been used for local sulfidation of the Fe-Cr alloy surface²²⁾. During anodic polarization of the Pt microelectrode in a narrow space between the microelectrode and the alloy surface, H_2S was concentrated to a concentration as high as the Na_2S concentration of the solution used and induced local sulfidation of the alloy surface. The sulfidation behaviors were dependent on the microelectrode current, interelectrode distance, substrate electrode potential, and Cr concentration in the alloy.

4. Conclusions

Operation of an LPSIG technique, which is cathodic polarization of silver/silver sulfide microelectrode, enables the generation and concentration of HS^- locally in the vicinity of the microelectrode on the substrate surface. The generation of HS^- was fully controlled by electrochemical reaction and following mass-transport, and a maximum concentration of 10 mM and average concentration of $0.5\ \mu\text{M}$ were achieved on the substrate surface and in the whole solution, respectively. The distribution of HS^- and OH^- from the LPSIG to the substrate surface was also related to the buffering effect of the solution.

Electrochemical measurements and surface analyses revealed that the LPSIG operation was effective for investigating the effects of HS^- on substrate surfaces of silver and type-stainless steel stainless steel. The silver surface with an interelectrode distance of less than $125\ \mu\text{m}$ could be sulfided with a current efficiency of 100%, while type-316L stainless steel at potentials higher than $0.40\ \text{V}_{\text{SSE}}$ was passivated but allowed the formation of a defective oxide film. It was clear that the sulfidation was dependent on the electrode potential as well as HS^- concentration.

In order to achieve a higher concentration of HS^- and a more acidic local environment, a new type of LPSIG has been developed. The LPSIG technique is useful for investigation of the degradation behavior of metallic

material surfaces by sulfide ions and for evaluation of their degradation resistances with a small electrochemical cell in a laboratory room. The LPIG technique is also expected to be applied in corrosion science and engineering fields to provide other aggressive anions such as thiosulfate, sulfate and sulfite bromide, iodide, and fluoride.

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要 旨

溶液中の金属表面に硫化物イオンを安全に発生させるための新しい液中イオン銃技術を開発した。これまでの液中イオン銃 (LPIG) は局所的な塩化物イオン発生システムであり、走査型電気化学顕微鏡法の応用技術として金属表面の局部腐食挙動を調べるために使われてきた。LPIG の銀/塩化銀微小電極の代わりに、銀/硫化銀微小電極を液中硫化物イオン銃 (LPSIG) として用いた。LPSIG 微小電極のカソード分極により、微小電極近傍において硫化水素イオンが発生し、硫化水素イオンを含む安全な環境を供給することができた。ここでは主に、LPSIG からの硫化水素イオンの発生に加え、これを適用した銀表面や 316L ステンレス鋼表面の変質挙動について解説する。硫化水素イオンによる腐食の調査手段としての LPSIG 技術の潜在能力についても議論する。

キーワード 微小電極, 硫化物イオン, 走査型電気化学顕微鏡法