Development of a Liquid-Phase Ion Gun and Its Application for Sulfidation of Silver Surface

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A system for safe generation of sulfide ions was established by using the microelectrode technique in order to investigate sulfidation of the metal surface of silver. Both silver microelectrode sulfidation and silver sulfide reduction on the microelectrode were reversible in Na₂S solution and corresponded to Ag₂S formation and HS⁻ generation, respectively. Cathodic polarization of Ag₂S, which covered the silver microelectrode, in pH 8.4 boric-borate buffer solution successfully generated HS⁻ above a glass or silver substrate. Concentration of HS⁻ in the vicinity of the substrate was dependent on the distance between the microelectrode and the substrate. The silver substrate was locally sulfidated by HS⁻ generated from the microelectrode. However, at potentials higher than 0.14 VRHE, local sulfidation of the silver substrate was independent of the substrate potential. It is thought that mass transport of HS⁻ is dominant for sulfidation of the silver substrate.

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Manuscript submitted November 17, 2014; revised manuscript received December 17, 2014. Published January 13, 2015.

Metallic materials are widely used in many fields and various environments. However, metals show susceptibility to sulfidation in environments containing sulfide ions and cause various types of sulfide-induced corrosion such as general corrosion, localized corrosion, and stress corrosion cracking. Considerable experience has been acquired concerning corrosion behavior of metals in sulfide-induced corrosion.2–5 Many researchers have attempted to create a sulfide ion-containing environment by flowing H₂S gas6–8 or adding Na₂S9–11 into aqueous solutions in order not to control concentration of sulfide ions but also to investigate sulfidation behavior of metals. However, it was difficult to concentrate with an infinitesimal amount of sulfide ions on a local area. Moreover, sulfide ions can produce H₂S which is an extremely toxic gas and accelerates degradation of the experimental specimens of metallic materials by producing protons and sulfide ions in aqueous solutions. It is vital to establish safe experimental systems for handling the risk factors that should be limited to release of a small amount of sulfide ions.

The microelectrode technique is widely used to elucidate the corrosion of various metal surfaces.12–15 Krawiec et al. investigated the localized corrosion behavior of a magnesium alloy by means of the micro-capillary cell technique.12 Zhang et al. studied local anodic dissolution reaction at the crack tip on a pre-cracked steel specimen using the scanning vibrating electrode technique (SVET) and local electrochemical impedance spectroscopy (LEIS).16 Lister et al. reported imaging of localized S concentrations dissolved from inclusions in stainless steel by using scanning electrochemical microscopy (SECM).17 Vuillemin et al. injected an aggressive ion-containing solution with a micro-capillary on a stainless steel surface for elucidating depassivation of the surface.18 The use of a liquid-phase ion gun (LPIG) is a microelectrode technique, type of SECM, and is effective to control the release of infinitesimal anions from a microelectrode.19–21 Fushimi et al. investigated the local degradation mechanism of a passive film on iron by using a local chloride ion generation system.19 They also reported that depassivation susceptibility of iron was dependent on applied potential and electric field as well as solution pH.18 Falkenberg et al. reported the mechanism of single pit initiation and growth on a copper surface by using the combination of an electrochemical quartz crystal microbalance (EQCM) and LPIG.19 Gabrielli et al. also reported that depassivation susceptibility of iron was dependent on solution pH.20

Despite the fact that an LPIG is suitable for releasing anions above metal surfaces, it has only been used for a system of chloride ion generation. The use of an LPIG can be an alternative application for sulfidation ion generation. In this study, an LPIG was used as a safe system for generation of sulfide ions for the first time. Electrochemistry of an LPIG as a generator of sulfide ions and its application for sulfidation on a silver surface is discussed.

Experimental

A silver wire with a purity of 99.9% and a diameter of 500 μm was embedded in a glass capillary with an outer diameter of 1 mm using an epoxy resin. The cross section of the silver-glass capillary tip was used as a silver microelectrode after mechanical polishing with SiC papers down to 4000 grit and rinsing with distilled water. Figure 1 shows an optical microscopic image of the tip of the fabricated silver microelectrode. A silver plate with a purity of 99.9% and a surface area of 0.8 cm² was prepared as a substrate electrode. The silver substrate was mounted in an epoxy resin mechanically grounded with SiC papers down to 800 grit and then rinsed with distilled water.

Electrochemical experiments of using silver microelectrode and/or the substrate electrode were carried out in a four-electrode electrochemical cell of 100 cm³ in volume with a platinum counter electrode and an Ag/AgCl/sat. KCl reference electrode. However, all the potentials in this study were with respect to the reversible hydrogen electrode (RHE) potential. Cyclic voltammetry (CV) of the silver microelectrode was conducted in a potential range between 0.38 and –0.06 V_RHE in 0.1 mol dm⁻³ Na₂S solution (pH 13.4) at a scan rate of 20 mV s⁻¹. After a steady state had been obtained in CV, the microelectrode was polarized at 0.3 V_RHE in the same solution until the electric charge of 10 mC, Q_charg, was consumed. On the other hand, potentiodynamic polarization of the silver substrate was performed in a potential range from 0.7 to 1.1 V_RHE at a scan rate of 1 mV s⁻¹ in pH 8.4 boric-borate buffer solution.

Figure 2 schematically depicts the experimental setup for liquid-phase ion gun. An optical microscope with a resolution of 5 μm and a stepping motor stage (SGSP20–35, Sigma Koki) with an incremental motion of 0.1 μm were used to control the distance between the microelectrode and substrate of a grass plate or silver electrode. The silver microelectrode was positioned above the substrate with a distance of 125, 250, 500, 750, 1000 or 10000 μm. A bipotentiostat (HAL-1512mM2, Hokuto Denko) independently controlled potentials of the microelectrode and the substrate. The microelectrode potential, Eₑₑ₂, was initially kept at 0.4 V_RHE for 100 s and then changed to 0.0 V_RHE, whereas the silver substrate potential, Eᵦᵦₑₑ, was potentiostatically controlled at 0.04, 0.14, 0.24, 0.34, 0.54, 0.64 or 1.00 V_RHE. The silver substrate was also polarized at the same potential condition.

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without microelectrode polarization as a control experiment. In all electrochemical tests, consistency was confirmed more than 3 times by repetition with different specimens with the same conditions. A scanning electron microscope (SEM; JSM-6510LA, JEOL) was used to observe the morphology of the silver surface. An X-ray diffraction (XRD) meter (RINT 2000 Ultima, Rigaku) with CuKα radiation was used to examine silver surfaces. XRD patterns were identified with JCPDS files (Ag2S: No. 14–0072 and Ag: No. 04–0783).

Results and Discussion

Electrochemical reaction of a silver microelectrode.— Figure 3a shows cyclic voltammograms of a silver microelectrode in deaerated 0.1 mol dm−3 Na2S solution. The CV curve reaches in a steady state within a few cycles. The anodic current at potentials higher than ca. 0.2 VRHE and the cathodic current at potentials lower than ca. 0.2 VRHE seem to bring about sulfidation of silver and reduction of silver sulfide, respectively. The electric charge consumed during CV increases during the anodic current flow, while it decreases to zero during the cathodic current flow (Figure 3b), indicating that anodic and cathodic reactions of silver are reversible during the CV in solution. The XRD pattern of the silver electrode polarized at 0.3 VRHE for 5.1 C cm−2 (Figure 4) suggests the formation of Ag2S. Ag was also detected from the XRD pattern of the silver electrode. Since the solubility of Ag2S is small (Ksp = 7.2 × 10−50),21 little Ag2S was dissolved from the microelectrode.

The results demonstrate that the anodic reaction of silver and the cathodic reaction of silver sulfide correspond to the following backward and forward reactions in an aqueous solution, respectively:

\[
\text{Ag}_2\text{S} + \text{H}_2\text{O} + 2e^- \rightleftharpoons 2\text{Ag} + \text{HS}^- + \text{OH}^- , \quad [1]
\]

where the reduction of Ag2S means generation of HS− into the solution. Standard potential of Eq. 1 is as follows:22

\[
E = -0.274 - 0.0295 \text{pH} - 0.0295 \log[\text{HS}^-]. \quad [2]
\]

From Eq. 2, an HS− concentration [HS−] of 10−2 to 10−3 mol dm−3 can be estimated at E = 0.19 VRHE in pH 13.4. In any case, the silver sulfide surface generates HS− during cathodic polarization. In the following experiments, a silver microelectrode covered with silver sulfide (Ag/Ag2S microelectrode) was used as an LPIG for generating sulfide ions by forming Ag2S on the silver microelectrode with the consumption of electric charge for 10 mC.

HS− generation above a glass substrate.— Figure 5a shows transients of current, Ime, flowing through an Ag/Ag2S microelectrode and electric charge, Qme, consumed on the microelectrode when the microelectrode potential, Eme, was changed from 0.4 to 0.0 VRHE above 0.4 VRHE for 5.1 C cm−2 in 0.1 mol dm−3 Na2S solution. Marks (circle and triangle) were attributed to JCPDS files of Ag2S: No. 14–0072 and Ag: No. 04–0783, respectively.

Figure 1. Optical microscopic top view image of a silver microelectrode tip.

Figure 2. Schematic diagram of the electrochemical set-up used.

Figure 3. (a) Cyclic voltammograms of a silver microelectrode in 0.1 mol dm−3 Na2S solution. The potential scan rate was 20 mV s−1. (b) Transient of electric charge consumed during CV.

Figure 4. XRD pattern of the silver surface polarized at 0.3 VRHE for 5.1 C cm−2 in 0.1 mol dm−3 Na2S solution. Marks (circle and triangle) were attributed to JCPDS files of Ag2S: No. 14–0072 and Ag: No. 04–0783, respectively.

Figure 5. Transient of current, Ime, and transient of electric charge, Qme, of Ag/Ag2S microelectrode as Eme was changed from 0.4 to 0.0 VRHE above 0.4 VRHE for 5.1 C cm−2 in 0.1 mol dm−3 Na2S solution.
a glass substrate in pH 8.4 boric-borate buffer solution. No cathodic current flows through the microelectrode during a polarization at 0.4 V_RHE for 100 s and cathodic current flows when the Ag/Ag_2S microelectrode is polarized at 0.0 V_RHE. A current spike of ca. −4 μA at the beginning is due to charging of double layer capacitance at the Ag/Ag_2S microelectrode surface, while the following cathodic current is due to the generation of HS^−. Cathodic current for HS^− generation gradually increases and shows current peaks at 500–2000 s depending on the distance between the microelectrode and the substrate. Although the same electric charge of −10 mC is consumed regardless of the distance to the substrate, it can be clearly seen in Figure 5b that peak current increases and peak appearance time decreases with increase in the distance. This indicates that generation of HS^− from the microelectrode is strongly dependent on the geometry of the narrow space between the microelectrode and glass substrate. Assuming that HS^− does not diffuse from the narrow space between the microelectrode and substrate with a distance of 125 μm to solution bulk, the amount of HS^− for completion of generation is 5.2 × 10^-8 mol. Since the volume of a cylindrical solution between a microelectrode and a substrate is ca. 9.8 × 10^-4 dm^3, a concentration of HS^− is estimated at 5.3 × 10^-1 mol dm^-3. Although pH can change during a generation of HS^− by Eq. 1, the change of pH by a dissociation of HS^− is negligible during the generation because the acid dissociation constant pK_a of HS^− is 11.96 at 291 K. Therefore, the narrow space is concentrated by HS^− during the generation. Highly concentrated HS^− might clog the space and lead to decrease in further HS^− generation. Generation and concentration of a certain amount of HS^− existing in the narrow space result in extension of HS^− generation period.

HS^− generation above a silver substrate.— Figure 6 shows the dynamic polarization curve of a silver electrode in pH 8.4 boric-borate buffer solution. The corrosion potential is shown in 0.73 V_RHE. This is similar to the standard equilibrium potential of the Ag/Ag^+ system, assuming [Ag^+] = 10^-6 mol dm^-3 in the Ag-H_2O system at 298 K.

$$\text{Ag} = \text{Ag}^+ + e^- \quad [3]$$

$$E = 0.799 + 0.05916 \log[\text{Ag}^+] \quad [4]$$

The anodic current is attributed to general dissolution of Ag at potentials between 0.73 and 1.6 V_RHE. At potentials higher than 1.6 V_RHE, however, oxide of Ag forms as follows:  

$$2\text{Ag}^+ + 3\text{H}_2\text{O} = \text{Ag}_2\text{O}_3 + 6\text{H}^+ + 4e^- \quad [5]$$

$$E = 1.670 - 0.0886p\text{H} - 0.0295 \log[\text{Ag}^+] \quad [6]$$

Figure 7a shows transients of currents I_sub and I_me of the Ag/Ag_2S microelectrode and silver substrate, respectively, in a pH 8.4 boric-borate buffer solution when potential of the microelectrode E_me was changed from 0.4 to 0.0 V_RHE. With potential of the substrate E_sub being kept at 1.00 V_RHE. As discussed above, the generation of HS^− indicates a cathodic current flowing through the microelectrode, although the current spike for charging is observed at the beginning. After 1–2 ks from onset of the HS^− generation, peaks are seen in both I_sub and I_me. The value of I_me is almost constant, while that of I_sub is dependent on the distance between the microelectrode and the substrate. Distance independency of I_sub disagrees with the case on a glass substrate. Thus, the HS^− generation is affected by reaction of HS^− with the substrate as well as diffusion in the narrow space.

Figure 7b shows the electric charge Q_sub consumed at the silver substrate as a function of the electric charge Q_me consumed at the Ag/Ag_2S microelectrode during the generation of HS^−. The value of Q_sub increases linearly with increase in Q_me. The slope of the linear relation between Q_sub and Q_me increases with decrease in the distance between electrodes. The slope at the distance of 125 μm is close to −1, demonstrating that an anodic current equivalent to the cathodic current for HS^− generation flows through the silver substrate. It is thought that the anodic reaction on the substrate is dominantly affected by HS^− generated from the microelectrode. From the larger space between electrodes, a large amount of HS^− can diffuse out to the solution bulk instead of the silver substrate surface. The shortage of HS^− diffusion results in a decrease of the anodic current.

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but also other areas are sulfidized by HS
sulfidation efficiency seems to be constant. It is thought that not only
out to the solution bulk. At distances of more than 500
means loss of substrate sulfidation. This is due to diffusion of HS
substrate is completely sulfidized with all of the HS
is efficiency of the substrate sulfidation. When the ratio is unity, the
attributes 10.5 mC, which is larger than the electric charge
sub and
end includes an additional electric charge
me consumed at the silver substrate and Ag/Ag2S microelectrode, respectively.
me.charge
sub and
me.charge
sub.end compared with
me.charge
sub.end, which is the charge of
sub.end to
me.charge
sub.end against 0
μm, however,
sulfidation efficiency seems to be constant. It is thought that not only
the area of the silver substrate surface adjacent to the microelectrode
but also other areas are sulfidized by HS
diffused to the solution bulk.

On the other hand, a protrusion of silver built up on the microelectrode
surface using the Ag/Ag2S microelectrode in this study. Figures 10a and 10b show transients of currents
sub, the cathodic current for HS
sub, and the anodic current for HS
of
E
was polarized at various values of
sub. Regardless of the values of
sub, the cathodic current for HS
generation shows almost the same behavior, suggesting that HS
generation is not affected by the silver substrate potential. However, the current flowing through the
silver substrate is strongly associated with the applied potential. As seen in Fig. 6, the silver substrate is oxidized and this leads to the
flow of an anodic current at potentials higher than 0.73 V
RHE. While sulfide or water is reduced at lower potentials. Figure 10c shows
the relation between electric charges
sub and
me consumed at the silver substrate and Ag/Ag2S microelectrode, respectively.

Figure 11 shows the electric charge
sub.end consumed at the substrate until completion of HS
sulfidation efficiency of the substrate at potentials higher than 0.64
microelectrode and substrate, respectively. The slope corresponds to
the relation between electric charges
sub and
sub.end, which is the charge of
sub.end when the silver substrate
me.charge
sub.end increases with distance in the
distance. Since an oxidation current of ca. 1.1 \times 10^{-7} A flows during
polarization of the silver substrate at 1.0 V
RHE without the presence of HS
, the value of
sub.end includes an additional electric charge for the oxidation of silver. In order to consider only sulfidation of the
silver substrate, the electric charge
sub.end, which is the charge of
sub.end by the electric charge consumed for the oxidation, is also plotted in Fig. 9. Extrapolation of
sub.end against 0 μm gives 10.5 mC, which is larger than the electric charge
me.charge
for sulfidation of the microelectrode. The ratio of
sub.end to
me.charge
is efficiency of the substrate sulfidation. When the ratio is unity, the
substrate is completely sulfidized with all of the HS
generated from the microelectrode. The sulfidation efficiency is unity at distances less than
30 μm. Conversely, shortage of
sub.end compared with
me.charge
means loss of substrate sulfidation. This is due to diffusion of HS
out to the solution bulk. At distances of more than 500 μm, however,
sulfidation efficiency seems to be constant. It is thought that not only
the area of the silver substrate surface adjacent to the microelectrode
but also other areas are sulfidized by HS
diffused to the solution bulk.

Figure 7. (a) Transients of currents
sub and
me flowing through the Ag/Ag2S microelectrode and silver substrate electrode, respectively, when potential
me of the microelectrode was changed from 0.4 to 0.0 V
RHE while the silver substrate electrode was polarized at
sub = 1.0 V
RHE in pH 8.4 boric-borate buffer solution. The microelectrode, charged Ag2S of 10 mC, was positioned above the substrate with a distance of 125, 250, 500, 750, or 1000 μm. (b) Relation between electric charges
sub and
me consumed at the silver substrate and Ag/Ag2S microelectrode, respectively.

Figure 8. (a) SEM images and (b) XRD pattern of the silver substrate surface after HS
generation at the potential 0.0 V
RHE with a distance of 125 μm.
Figure 9. Electric charge $Q_{\text{sub.end}}$ consumed at the silver substrate until the HS$^-$ generation of 10 mC is completed as a function of the distance $d$. The charge $Q'_{\text{sub.end}}$ was $Q_{\text{sub.end}}$ subtracted by that consumed for substrate oxidation in a separate experiment without the microelectrode.

Figure 10. (a, b) Transients of currents $I_{\text{me}}$ and $I_{\text{sub}}$, and (c) relation between electric charges $Q_{\text{sub}}$ and $Q_{\text{me}}$ when potential $E_{\text{me}}$ was changed from 0.4 to 0.0 V_RHE with the substrate polarized at $E_{\text{sub}} = 0.04, 0.14, 0.24, 0.34, 0.54, 0.64$, or $1.00$ V_RHE. The interelectrode distance was kept at 250 $\mu$m.

Figure 11. Electric charge $Q_{\text{sub.end}}$ consumed at the silver substrate until HS$^-$ generation of 10 mC is completed as a function of the substrate potential $E_{\text{sub}}$. The charge $Q'_{\text{sub.end}}$ was subtracted from $Q_{\text{sub.end}}$ by that of $Q_{\text{sub.control}}$ consumed for oxidation.

Potential of LPIG as a sulfide ion generation apparatus.— In general experiments to investigate a sulfidation of silver, Ag$_2$S layer forms on the silver surface in the presence of sulfide ions-containing media such as H$_2$S, K$_2$S and Na$_2$S. The sulfidized layer in this study by using Ag/Ag$_2$S microelectrode (Fig. 8) is Ag$_2$S. This result is not new findings. However, we have successfully developed a very safe sulfide ion generator with an amount of HS$^-$ of $5.2 \times 10^{-8}$ mol. A generation of HS$^-$ is possible to concentrate with an infinitesimal amount of HS$^-$ on a local area for the first time. Although the local concentration HS$^-$ for sulfidation is estimated as 0.5 mol dm$^{-3}$, the average concentration of HS$^-$ is lower than 0.5 ppm in the electrochemical cell of 100 cm$^3$ in volume until the completion of HS$^-$ generation. This is sufficiently smaller than the ceiling limits of H$_2$S in air,
20 ppm.28 We consider that this experimental system is fairly safe for an HS− generation apparatus.

The relatively large (500 μm in diameter) microelectrode does not show a fine steady state during the HS− generation. Electrochemical reactions on Ag/Ag2S electrode include a generation of HS− and OH− as well as a formation of porous Ag layer. From the interface of Ag/Ag2S, HS− and OH− should diffuse across the Ag layer to solution. We consider that it is difficult to reach a fine steady state in potentiostatic polarization because of the complexity of HS− generation process, even if the ultra microelectrode is used.

Galvanostatic polarization of the Ag/Ag2S microelectrode also enables generation of HS−. Providing a constant rate of HS− generation is beneficial and effective for investigating the charge-transfer controlling process of sulfidation. After the galvanostatic generation, however, hydrogen gas might be generated accompanying a potential shift to a less noble direction and could damage the formed silver sulfide layer. Although it is difficult to generate HS− at a constant rate by potentiostatic polarization of the microelectrode, no hydrogen gas evolves and no products are damaged. The establishment of a safe system for generation of sulfide ions will contribute to precise investigation of the sulfidation in various media not only on a silver surface but also on various metal surfaces.

Conclusions

Development of a system for safe generation of sulfide ions and sulfidation of a silver surface was attempted for the first time using a microelectrode technique. Cyclic voltammetry and XRD revealed that the electrochemical reactions were reversible as anodic Ag2S formation on the Ag microelectrode and cathodic HS− generation of the Ag/Ag2S microelectrode in Na2S solution. The Ag/Ag2S microelectrode successfully generated HS− by cathodic polarization in pH 8.4 boric-borate buffer solution. Generation of HS− ions was strongly dependent on diffusion of HS− ions from the microelectrode to the substrate surface and solution bulk. The substrate potential as well as diffusion of HS− influences sulfidation of the silver substrate. Sulfidation by using the Ag/Ag2S microelectrode is safe and effective to investigate the mechanism and kinetics of sulfidation in various media not only on a silver surface but also on various metal surfaces.

Acknowledgments

This work supported by “Nanotechnology Platform” Program of the MEXT, Japan and by a Grant-in-Aid for Scientific Research (B) 25289235 and Japan Society for Promotion of Science fellowship by a Grant-in-Aid for No. 260061.

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