A Scanning Laser-Enhanced Electrochemical Microscope for Hydrogen detection (H-SLEEM) has been developed in order to in-situ visualize the distribution of hydrogen localized on a steel surface. Introduction and detection of hydrogen for the steel sheet was conducted by hydrogen permeation technique with a pair of electrochemical cells. When the hydrogen detection side under hydrogen permeation is irradiated with focused Ar laser, anodic current relating to hydrogen oxidation reaction is thermally enhanced at the irradiation spot and then anodic current increment corresponding to the hydrogen permeation rate at the spot is expected to be determined. In the case that whole the hydrogen detection side was irradiated with diffused laser, the anodic current increased and the current increment increased with an increase in the hydrogen permeation current. The use of focused laser also permitted the measurement of the anodic current increment depending on the hydrogen permeation current. The modulated laser provided more stable and reproducible current increment. When the specimen whose hydrogen entry side was masked except for a small exposed area in center was employed and the modulated laser was raster-scanned under hydrogen permeation, a very clear image of the two-dimensional distribution in the current increment corresponding to local hydrogen permeation rate on the detection side was obtained. It is concluded that the H-SLEEM can successfully visualize the localized hydrogen distribution on the steel surface.

KEY WORDS: scanning laser-enhanced electrochemical microscope; hydrogen embrittlement; carbon steel; hydrogen permeation; visualization.
tained. Raster-scanned laser irradiation, therefore, can produce two-dimensional distribution of the current increment corresponding to distribution of electrochemical reaction rate on the polarized surface (cf., Sec. 2 in detail). We had successfully applied the technique to visualizing the localized corrosion of stainless steels in solutions. As mentioned, the technique can in-situ visualize the distribution of electrochemical reaction rate of the surface of a specimen polarized in a solution, so that it is also expected to obtain in-situ and quantitative distribution of localized hydrogen on specimen during hydrogen permeation technique. In this study, we have tried to develop a new SLEEM for hydrogen detection (H-SLEEM) in order to in-situ visualize two-dimensional distribution of permeating hydrogen localized on steel surface in an aqueous solution under hydrogen permeation.

2. Principle

Figure 1 shows an illustration of principle for the H-SLEEM. Hydrogen permeation through a metallic sheet is conducted by using the conventional hydrogen permeation technique with a modified Devanathan-Stachurski cell. A hydrogen entry and a detection sides of the metallic specimen contact with an electrolyte and an alkali solution, respectively. Hydrogen enters from a hydrogen entry side naturally in acid solution or electrochemically in solutions. The hydrogen detection side is kept at a passivation potential, and the hydrogen reaching the detection side is simultaneously oxidized to proton electrochemically. Accordingly, hydrogen permeation rate can be estimated by the increment of anodic current, which denotes hydrogen permeation current. In order to improve the sensitivity of the measurement of the hydrogen permeation current, the hydrogen detection side is covered with thin Ni plating. In this study, the hydrogen detection side is irradiated with a focused laser beam through the alkali solution. The irradiated site is then heated up locally and the electrochemical reactions at that site is thermally activated, so that the anodic current should increase. If the increment of anodic current by the laser irradiation depends on the hydrogen permeation current without laser irradiation, the laser irradiation technique is able to determine the hydrogen permeation rate at the small irradiation site in-situ in the solution.

Furthermore, the two-dimensional distribution of hydrogen permeation rate is expected to be obtained by using the raster-scanned laser beam technique. Passive film of Ni possesses n-type semiconductor property whose bandgap is 3.45±0.1 eV \(^{23}\) so that some photocurrent is induced by irradiating the light with a wavelength less than 360 nm. The light source employed in this study is Ar laser, whose wave length and photoenergy are only 514.5 nm and 2.41 eV, respectively. Therefore, the Ar laser is expected not to produce the photocurrent, but to induce only the thermally-enhanced current. Razzini et al. have already developed a similar laser technique, but the technique is based on the detection of photocurrent by using the laser with higher photoenergy or the metallic materials whose passive film has a bandgap lower than the photoenergy of the irradiation light. \(^{22,23}\)

3. Experimental

A block diagram of the H-SLEEM is illustrated in Fig. 2. A light source is an Ar laser (NEC Co. Ltd., GLG3280) which has a single wave length and a maximum power of 514.5 nm and 800 mW, respectively. The laser beam, which can be mechanically modulated by a mechanical chopper (NF Circuit Block Co. Ltd., 5584A), is introduced into an optical microscope (Lasertec Co. Ltd., 1LM15) by using a single-phase optical fiber. An intensity of Ar laser emitted at a terminal of the optical fiber is measured by a laser power meter (Neo Ark Co. Ltd., PM250). The laser beam is focused by an objective lens with long working distance, and emitted on a specimen surface through a test solution.

Schematic of a pair of electrochemical cells of modified Devanathan–Stachurski type is shown in Fig. 3. The cells are separated by a metal sheet which acts as bi-electrode and is electrochemically controlled by a bi-potentiostat (Toho Giken Co. Ltd., PS12): One side (hydrogen entry side, lower) in contact with an electrolyte is galvanostatically polarized. The opposite side (hydrogen detection side, upper) in contact with 1 M NaOH solution is potentiostatically polarized at 0 V against an Ag/AgCl (3.3 M KCl, room temperature) reference electrode. These solutions are fully deaerated by nitrogen gas, and circulated between the cell and a vessel at 2.0 ml min \(^{-1}\) by a roller pump (Furue Science Co. Ltd., VT1). The cell for hydrogen detection has
4. Results and Discussion

4.1. Continuous Irradiation of Diffused Laser

First of all, a terminal of the optical fiber was directly faced to the window of the cell in a distance of about 50 mm, and the whole surface of the detection side (10 mm in diameter) was irradiated with diffused laser as-emitted from a quartz window through which the electrode surface is irradiated with the laser, and thickness of the electrolyte layer is reduced to be 1.5 mm to avoid attenuating the laser intensity. The cell is mounted on an X-Y stage (Sigma Koki Co. Ltd., MIN160XY) to move the irradiation spot on the specimen surface two-dimensionally.

An increment of the anodic current induced by the irradiation of the modulated laser beam is measured by a lock-in amplifier (NF Circuit Block Co. Ltd., L15640) connected to the bi-potentiostat through a filter (NF Circuit Block Co. Ltd., 3611) and a differential amplifier (NF Circuit Block, 5307). The X-Y stage controller and the lock-in amplifier are connected to a personal computer (Compac Co Ltd., Deskpro) through GPIB interface to automatically control the irradiation spot and to collect the output voltages of the lock-in amplifier at the irradiation location. Optical images are also obtained in-situ by using a charge coupled device camera system equipped with the optical microscope to confirm the irradiation site.

Material used was SM400B carbon steel (C: 0.13, Si: 0.19, Mn: 0.69, P: 0.011, S: 0.007 in mass%, and Fe: bal.) sheet, whose thickness was about 1 mm. The steel sheet was cut and mechanically polished to #1500 followed by chemical polishing in the solution consisting of HF (6 m\(^{-3}\)) and H\(_2\)O\(_2\) (94 m\(^{-3}\)). A hydrogen detection side of the specimen was Ni-plated in a Watt bath (NiSO\(_4\)·6H\(_2\)O: 250 kg m\(^{-3}\), NiCl\(_2\): 45 kg m\(^{-3}\), H\(_3\)BO\(_3\): 40 kg m\(^{-3}\)) at 10 A m\(^{-2}\) for 7 min. The thickness of Ni plate was about 100 nm. Test solution of the hydrogen entry and the detection sides were 0.1 M Na\(_2\)SO\(_4\) and 1.0 M NaOH, respectively. The temperature of the solution was kept at 24°C.

Steady state anodic current at the hydrogen detection side was about 8 nA (104 \(\mu A\) m\(^{-2}\)). Under the steady state anodic current, the solution was poured and contacted to the hydrogen entry side without galvanostatic operation, and then the anodic current was the same, did not increase at all for 24 hr. This fact means that amount of permeating hydrogen is too small to be detected or no hydrogen permeates in this condition. The laser irradiation under this condition increased the anodic current, as shown in Fig. 4(a). The laser-induced current increment was almost the same as that before the solution was poured into the hydrogen entry cell. The increase in the current is, therefore, due to thermal activation of passivation reaction of Ni. In the case that a cathodic current density of 17.2 A m\(^{-2}\) was galvanostatically applied to the hydrogen entry side after the anodic current on the opposite side became steady stage, the total anodic current before laser irradiation increased because of addition of the hydrogen permeation current, and the steady state current was about 170 nA (2200 \(\mu A\) m\(^{-2}\)). Furthermore, it was obvious that the laser irradiation under the steady-state current condition produced a larger current increment in comparison to that without hydrogen permeation, as shown in Fig. 4(b). The difference value between the increments of anodic current under the conditions with and without hydrogen permeation corresponds to the increment of thermally-activated reaction of the hydrogen oxidation.

The current increments in 20 s after the irradiation to the specimen with and without hydrogen permeation (\(\Delta I(D)\)) were obtained from the transition curves of the anodic current as shown in Figs. 4(a) and 4(b), respectively, and the difference between the current increments (\(\Delta I(D) = \Delta I(D) - \Delta I(NH)\)) was plotted against steady state anodic current density without the laser irradiation (\(i_{DS}\)) in Fig. 5. It is clearly seen that \(\Delta I(D)\) starts to increase from \(i_{DS}\) of 200 \(\mu A\) m\(^{-2}\) and increases almost linearly with an increase in \(i_{DS}\) in the log–log scale. The fact clearly demonstrates that this laser technique has a potential to estimate hydrogen permeation rate at the laser irradiation site.
4.2. Continuous Irradiation of Focused Laser

The hydrogen detection side which was anodically polarized was irradiated with the laser beam finely focused by the optical microscope. A laser intensity and a magnification of an object lens were 30 mW and $10^{10}/H_{1100}$, respectively.

In order to confirm the effective diameter of the laser spot, the laser was scanned one-dimensionally on the hydrogen detection side with a small shielding material of PTFE sheet. Figure 6 shows the anodic current ($I_D$) profile along the laser scanning line from the shielding material to the specimen surface under hydrogen permeation (steady state anodic current: 216 nA). A step distance, a total scan distance, and a laser irradiation time at a given position were 10 μm, 400 μm, and 0.5 s, respectively. Forward-and-backward scans were conducted twice. As can be seen, $I_D$ drastically changed at the specimen/the shielding material interface, and difference of $I_D$ at the interface was about 0.2 nA. The diameter of the laser spot estimated from the distance of the slope region was about 60 μm in this case.

The profile was less reproducible because $I_D$ without irradiation was frequently drifted in sub nA scale although quite stable in hundred nA scale.

The technique was applied to the specimen of which a half of the hydrogen entry side was masked with epoxy resin to avoid entry of hydrogen from the area. The two areas whose opposites were unmasked and masked were irradiated with the focused laser. This condition expects that the each irradiation area has a different hydrogen permeation rate. Figure 7(a) shows the relationship between $\Delta I_L$ and $I_{DS}$, where $\Delta I_L$ are obtained from the anodic current increment in 10 and 20 s after the irradiation and $I_{DS}$ is total anodic current under steady state before laser irradiation, which is almost the same as hydrogen permeation current. The figure demonstrates that $\Delta I_L$ can be obtained from $I_{DS}$ of 50 nA, and has a positive correlation with $I_{DS}$ even by using the focused laser. Moreover $\Delta I_L$ at the area whose opposite was not masked was larger than that at the area whose opposite was masked. Therefore, the facts strongly indicate that the fine laser beam can detect the distribution of permeating hydrogen rate quantitatively. It was also seen that $\Delta I_L$ from the site whose opposite site was covered with epoxy resin increased with an increase in $I_{DS}$, and the reason will be described later.

Figure 7(b) shows the relationship between $\Delta I_L$ and the laser intensity. In this case, $I_{DS}$ was 410 nA. It was found in this figure that $\Delta I_L$ at the area whose opposite was not masked was larger than that at the area whose opposite was masked at the laser intensity of more than 30 mW. This means that the laser intensity of more than 30 mW is necessary to detect the difference in $\Delta I_L$ relating to the hydrogen permeation rate.

By the line scan of the fine laser, detection of the one-dimensional distribution of permeating hydrogen on the hydrogen detection side was tried. In this study, the specimen whose hydrogen entry side was masked in half as men-
tioned before was employed. A laser intensity and a laser irradiation time at a given position were 30 mW and 20 s, respectively. $I_{DS}$ was 550 nA. The result is shown in Fig. 8. A plateau region in $\Delta I_L$ was found in the area of which opposite side was not masked to permit hydrogen entry. While, $\Delta I_L$ gradually decreased as the laser moved to the site whose opposite side was masked to prevent hydrogen entry. The same trend was also observed in the reverse scan. Hydrogen entering from the unmasked hydrogen entry side diffuses to the whole hydrogen detection side. Hydrogen permeation rate is dependent on the diffusion distance by Fick’s law about diffusion, so that the hydrogen permeation rate is the highest and homogeneous in the center area of the hydrogen detection side whose opposite side is unmasked, and decreases as the position on the hydrogen detection side becomes far from the center area. Since $\Delta I_L$ correlates with hydrogen permeation rate, the observed distribution in $\Delta I_L$ is considered to agree with that in the hydrogen permeation rate. Therefore, it is concluded that the laser technique can visualize the line profile of distributed hydrogen permeation rate.

4.3. Irradiation of Modulated and Focused Laser

In order to achieve more clear visualization of the distribution of permeating hydrogen, the above technique requires more stable and precise measurement of the irradiation-induced current increment. However, the total anodic current always drifted in nA scale which was the same order as that of the irradiation-induced current increment, so that $\Delta I_L$ was often hard to be measured reproducibly. Accordingly, modulated laser irradiation technique was tried to be applied hereafter.

The laser beam was modulated by the mechanical chopper which was located in front of the laser source. An amplitude of the anodic current oscillation synchronized with the laser modulation was detected with the lock-in amplifier connected with the bi-potentiostat. A modulation frequency of 5.1 Hz was adopted. The following was confirmed in advance: When the hydrogen detection side polarized anodically was not irradiated with the modulated laser, none of output of the lock-in amplifier was indicated. Some value of the output was obtained under irradiation of the modulated laser to this surface without hydrogen permeation. In addition of the hydrogen permeation operation to this specimen condition, the output was enlarged much more. The behavior will be described later. In the case that the modulation frequency was varied from 1 to 25 Hz, the output was maximum at a modulation frequency around 5 Hz and almost none at the frequency of more than 20 Hz.

An effective diameter of the laser spot in this system was estimated by using the method mentioned before. An intensity of the laser was 40 mW. The effective diameter as a function of the object lens was summarized in Table 1. It was found that an increase in the magnification of the object lens led to a decrease in the diameter of the laser spot. However, the diameter was not accurately reduced corresponding to the magnification of the lens. The higher magnification lens must produce the finer spot of the laser, and a high energy density is then supplied to the spot. The spot is then heated up much more than that by using a low magnification lens, and the effective area of thermally-activated reaction on the surface becomes larger than the spot size of the laser estimated by its magnification. This may be the reason why the effective laser spot is not so sufficiently reduced by the high magnification lens.

Dependence of the increment of anodic current converted from the output of the lock-in amplifier ($\Delta I_L$) on the total anodic current including hydrogen permeation current under steady state ($I_{DS}$) was investigated. An increase in $I_{DS}$ is due to an increase in hydrogen permeation rate. $I_{DS}$ before hydrogen permeation was about 20 nA. In this study, the half-masked specimen as mentioned before was used. The result is shown in Fig. 9. It was found that $\Delta I_L$ started to increase at an $I_{DS}$ of 300 nA, which indicates that the sensitivity of detection of permeating hydrogen is lower than...
that in the use of the non-modulated fine laser as shown in Fig. 7(a). In the measurement, the laser modulation frequency was about 5 Hz, which means that the laser irradiation time per one cycle is about 0.1 s (non-irradiation time was also about 0.1 s per cycle). The short irradiation time is considered to result in the low sensitivity of detection of permeating hydrogen. The figure also demonstrates that logarithm of \( D_I \) increases linearly with an increase in logarithm of \( I_{DS} \) in the hydrogen permeation area. There is a breakpoint at an \( I_{DS} \) of about 900 nA, but the reason is not clear right now.

\( D_I \) in the area whose opposite side was masked was three or four times smaller than that in the area whose opposite side was not masked. In addition, the value of \( D_I \) in the area whose opposite was masked increased with an increase in \( I_{DS} \), because some amount of laterally diffusing hydrogen may reach the laser spot site in the area as mentioned before.

Laser scanning test was conducted by using the specimen of which the hydrogen entry side was masked with PTFE tape except for a small oval area in center. The schematic view of the specimen arrangement is shown in Fig. 10. An intensity of the modulated laser, a modulation frequency, and a total anodic current were 82 mW, 5.1 Hz, and 1 000 nA, respectively. In addition, a step distance and a laser irradiation time at a given position were 300 \( \mu \)m and 0.5 s, respectively. A line profile of \( D_I \) measured along the arrow line was shown in Fig. 11. The characteristics of the location is added to the bottom of the figure (cf., Fig. 10). The following features can be seen clearly: Almost none of \( \Delta I_{H} \) was obtained in the O-ring region, which resulted from that the laser did not reach the specimen surface. When the laser spot reached the surface from the O-ring region, \( \Delta I_{H} \) was increased steeply. The value was the same as that before hydrogen permeation. As the laser spot approached to the center, \( \Delta I_{H} \) became plateau or gradually increased. When the laser spot moved into the center region where the hydrogen directly permeated, \( \Delta I_{H} \) remarkably increased.

Next, the laser spot was raster-scanned in the region of 9 mm×9 mm (rectangle mark, E, in Fig. 10) under the same conditions as above. The two-dimensional distribution in \( \Delta I_{H} \) was obtained as shown in Fig. 12 in contour style. It was found that the hydrogen detection area within the O-ring was identical to the area of \( \Delta I_{H} \) value of more than 3.0 nA. Furthermore, \( \Delta I_{H} \) was the highest in the center area where hydrogen directly permeated to the hydrogen detection side. The area of an \( \Delta I_{H} \) value of 6.0 nA, which is about a half bandwidth of the peak indicated in Fig. 11, is quite the same shape as the center area in Fig. 10. The image consisted of the output data of 961 points (31 spots×31 spots) and was obtained in 480 s, but there was only negligible drift in the imaging time, compared with the profile in Fig. 4. It indicates that this modulated laser technique can produce the more reproducible image. Since \( \Delta I_{H} \) corresponds to the hydrogen permeation rate at a laser spot, the distribution image of \( \Delta I_{H} \) is considered to coincide with that of permeating hydrogen. Therefore, it is concluded that the H-SLEEM can successfully visualize the hydrogen dis-
tribution on the hydrogen detection side in-situ.

5. Conclusions

In order to visualize hydrogen distribution on the metal surface in the aqueous solution in-situ, the H-SLEEM was successfully developed. The modulated laser technique provided the reproducible images of the distribution of permeating hydrogen on the hydrogen detection side of the steel under hydrogen permeation.

The followings will be future works for this study: Optimum conditions (laser spot diameter, laser intensity, anodic current density, holding time of laser spot, and so on) will be determined for obtaining more detailed distribution image. In addition, the technique will be applied to reveal hydrogen distribution of the materials which actually suffered hydrogen embrittlement.

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REFERENCES