Visualize Water in Corroded Region of Painted Steels at a Compact Neutron Source

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Water under a film of paint in corroded steels was visualized using thermal neutrons at the RIKEN-accelerator-based compact neutron source. Two painted plate samples made of normal steel and corrosion-resistant alloy steel were prepared. Both were scratched on the painted surface and then subjected to a cyclic corrosion test to generate blisters caused by under-film corrosion. They were soaked in water for 2 h and then removed from the water. Time dependences of the water distribution in the under-film corrosion were observed using the neutron transmission imaging method for the first time. The alloy sample contained less water than the sample made of normal steel and the water in the alloy escaped from the sample more rapidly than that in the normal steel. We also evaluate the corrosion resistance performance of the painted steel sample.

KEY WORDS: compact neutron source; neutron imaging; water distribution; painted steels; under-film corrosion; corrosion-resistant alloy; normal steel.

1. Introduction

Modern civil structures such as bridges are required to have a low life-cycle cost and a long life. Since the corrosion damage of steel cannot be avoided in practical environments,1) effective countermeasures against corrosion are strongly required. Paint coatings are the most widely used method for preventing the corrosion of general structures.2) On the other hand, it is a challenging task to reduce the life-cycle costs of structures including the initial cost and the maintenance cost for repainting and there are continuous needs of constructions. However there are always budgetary constraints.

In the case of painted steel, water may penetrate under the coating film over time. When defects are formed in the film, the water can penetrate, induce under-film corrosion, and eventually cause blisters on the coating film. Painted steel structures must therefore be repainted periodically, which increases their maintenance cost. Attempts are being made to prolong the life of paint coatings which include the development of heavy-duty coatings and/or alloy steels.3) Until now, these have been three major approaches to research and development to improve the corrosion resistance of paint coatings: (1) Adding suitable alloying elements to the steel can increase the density of the corrosion products, rust layer. This prevents the incursion of water, which directly causes corrosion, and oxygen and chlorine, which are promotors corrosion. As a result, corrosion is inhibited. (2) The combined use of zinc-rich paint and a thick paint improve the durability of the film. (3) A combination of (1) and (2) is applied together.

Thus far, macroscopic observation using optical microscope4) and transmission electron microscope,5) microscopic texture observation by X-ray diffraction6) and Fourier transform infrared spectroscopy,7) X-ray absorption spectroscopy,8) and element analysis by electron probe micro analyzer,9) have been carried out as destructive inspections, to determine the corrosion mechanism of painted steels and evaluate the improvement in the corrosion resistance when employing various countermeasures. Visual observation has been frequently performed, as a means of non-destructive inspection. In addition, corrosion has been evaluated using electrochemical methods.10) However, it is difficult to obtain information on the water content and movement, which cause the corrosions directly, because these probes are not sensitive to water.

The corrosion of steel is generated with existing of water and oxygen in natural environment. The existence of the water is most important factor. Duration of contact among water and bare steel, that means water detention period in the under-film corrosion of steel, may be considered to have
strong correlation with the corrosion. However, studies to prove it are not found. Thus, it is needed to measure the water detention period in the corrosion for the discussion on the corrosion mechanism. The corrosion of painted objects in outdoor environments is promoted by rain and condensation water, which penetrate under the film of the painted steel.

Neutrons are a good probe for investigating the water movement in corroded iron with a radiography technique. We have already observed the distribution of water and the corrosion in steel samples exhibiting under-film corrosion under dry and fully wet conditions.\(^8\)

In this study, the water distributions in samples exhibiting under-film corrosion during a drying process were measured continuously by in situ observation using RIKEN-accelerator-based compact neutron source (RANS). Time dependences of the water distribution were evaluated in terms of the blister shape. Then the observation result that indicates the water, most important factor for the corrosion, dominates the generation of corrosion, are obtained. It will contribute to understand the corrosion mechanism.

2. Experiment

2.1. Neutron Imaging Method

A neutron image is taken by transmitting a neutron beam through a sample onto an imaging detector. Neutrons are a unique probe for water imaging since low-energy neutrons in particular with energy around 25 meV, have a large elastic cross section for hydrogen.\(^9\) Thus, neutrons partially transmitting through water in a sample give contrast in the neutron image.\(^10\) This feature have been used for non-destructive inspection in a variety of cases, for example, water flow in a metal pipe,\(^11\) corrosion inspection of metals,\(^12\) water in concrete,\(^13\) and water in living plants.\(^14\)

We conducted an experiment focusing on this point. The transmission ratio of dry samples in this study was estimated to be 0.56, whereas wet samples were expected to have a transmission ratio of 0.51. The difference in the transmission ratio between the dry and wet samples is considered to be due to the contribution of the water. Thus it is expected that the water distribution in under-film corroded steel can be observed. The details of the procedure for obtaining the water distribution from neutron images will be explained in section 3.1.

2.2. Neutron Source

Figure 1 shows an overview of the RANS. It is composed of four major parts, which are a proton linear accelerator, a target station, neutron guides, and a camera box. Total length is 15 m and the accelerator part is 8 m. The width of the RANS area is 8 m. Protons are accelerated up to an energy of 7 MeV with a maximum average current of 100 \(\mu\)A by a Model PL-7 linear accelerator by AccSys Technology Inc. Figure 2 shows a sketch of the setup from the target station to the camera box. The protons bombard a beryllium target\(^15\) at the center of the target station and then neutrons with an energy of MeV order are generated via the Be(p,n) reaction. The neutrons are slowed by hydrogens in a moderator, downstream, of the beryllium target, which is made of 40 mm-thick polyethylene. Finally, the neutrons from the moderator surface propagate to the downstream camera box through the neutron guides. An opening section of a target station is 15 cm \(\times\) 15 cm. The camera box and the neutron guides are shielded by borated polyethylene. Figure 3 shows the neutron energy spectrum at the sample position, which is 5 m from the moderator. There are a large number of thermal neutrons with energy around 25 meV and fast neutrons with energy around a few MeV.\(^16,17\) The angular divergence of the thermal neutron beam at the sample...
position is 0.03 rad, which is estimated from the geometric configuration of the sample and the neutron source shown in Fig. 2. In this study, thermal neutrons were used to take neutron images.

2.3. Detector System for Imaging

The imaging detector was set downstream of the sample in the camera box. The thermal neutrons transmitted through the sample impact on the LiF/ZnS scintillator (equivalent to BC-704, Saint Gobain) and generate alpha and tritium particles. Then they generate scintillation photons in the scintillator. The photons propagate to a cooled CCD sensor (BITRAN BU-53LN) through a mirror and a focusing lens. The number of photons reaching the CCD sensor is proportional to the neutron intensity at the scintillator. The image sensor is mainly sensitive to thermal neutrons, because fast neutrons make a much smaller contribution to the generation of scintillation photons. The size of the pixels on the image sensor is 80 $\times$ 80 $\mu$m$^2$ at the image on the scintillator. The size of the sensitive area is 146 mm width $\times$ 106 mm height.

2.4. Samples

Two steel plates, a normal steel (SM400) and a corrosion-resistant alloy steel (0.8Cu-0.4Ni-0.05Ti), were prepared. Both were machined to plates of 6 mm thickness, 70 mm width, and 140 mm height. They were coated with epoxy-modified paint with 240 $\mu$m thickness and low corrosion resistance and scratched by a sharp knife to fix the site of the corrosion and simulate a film defect. This scratch is considered to produce region much rougher than that in practical environments. The plates were then subjected to a cyclic corrosion test (CCT), the procedure of which is shown in Fig. 4, to create blisters of under-film corrosion during which the samples were placed horizontally. The salt water spray condition were 1.5 $\pm$ 0.5 ml/h per sample area of 80 cm$^2$ with 5 wt% concentration. These steel plates were prepared as samples for water-imaging experiments. Optical images of the samples are shown in Fig. 5.

2.5. Measurement

Each sample was soaked in water for 2 hours. The saturation of the amount of water contained in the sample was confirmed by the weight change. After the sample was removed from the water, the water on the surface was removed by wiping, then the sample was mounted on a precision balance scale located in front of the image sensor, and was dried in the air. Then neutron images were continuously taken by the image sensor. Neutron exposure started 5 min after the removable of the sample from the water. The average proton current on the Be target was about 15 $\mu$A. The exposure times for each image were 5 min at the beginning of the measurements and 10 min at the end. Total duration of the measurement was 150 min for each sample. The amount of water in the sample was contentiously monitored via the weight variation.

The distances between the samples and the scintillator of the image sensor were 44 mm and 55 mm for the alloy sample and the normal sample, respectively. Thus, a blur of the image due to the angular divergence of the neutron beam was expected to be about 1 mm. The pixel size of the image sensor is enough small. Figure 6 shows neutron images of the normal sample in after the removable of the sample from the water. The average proton current on the Be target was about 15 $\mu$A. The exposure times for each image were 5 min at the beginning of the measurements and 10 min at the end. Total duration of the measurement was 150 min for each sample. The amount of water in the sample was contentiously monitored via the weight variation.

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![Fig. 5. Optical images of samples.](image)

![Fig. 6. Neutron images of the normal sample at dry and wet states.](image)

![Fig. 4. Procedure of the cyclic corrosion test.](image)
the fully wet and dry states. These images were constructed by merging raw images to enhance the contrast for the regions of corrosion and water. The wet and dry images were obtained with equivalent exposure time of 20 min and 55 min, respectively. The contrast in the images was adjusted to enhance differences between the states.

The image of the dry sample appears to show regions of corrosion, and that of the wet samples indicate regions of corrosions and water. The difference in the neutron transmission ratio between the fully wet sample and the dry sample is a few percent. The transmission ratio for the 6 mm-thick steel is 54%.

There were no sample regions in Fig. 6 images. The imaging sensor on these regions was exposed to the neutron beams directly. Thus these regions were used for estimating the intensity of the exposed neutrons. The two black square boxes with a circular hole in the images are plastic markers with 10 mm thickness, which were used to superimpose photograph and blister shape information.

3. Image Analysis Procedure

The intensity of neutrons transmitted through the dry sample is described as

\[ I^D = I_0^D \cdot e^{-t_D/L_D}, \]

where \( t_D \) and \( L_D \) are the thickness and neutron attenuation length of the dry sample comprising the steel, the painted film, and the corrosion. \( I_0^D \) is the intensity of illuminated neutrons. For the wet sample, water is incorporated in the formula for the dry sample. Thus, the intensity of the transmitted neutrons for the wet sample is

\[ I^W = I_0^W \cdot e^{-t^W/L^W}, \]

where index “W” denotes the wet sample and index “a” denotes the water. Equation (2) is divided by Eq. (1) and the result is solved to obtain the water thickness

\[ t_a = -L_a \cdot \log \frac{I^W}{I^D} / \frac{I_0^W}{I_0^D}. \]

The time at which the sample was considered to be dry, was defined as 150 min from its removal from the water.

4. Results and Discussion

4.1. Water Distribution Images

Figure 7 presents the time dependence of the water distribution for both samples. The pixel size is 0.8 × 0.8 mm². The most of water is distributed at the center of the sample. The distribution of the water is in good agreement with the position of the blister in the under-film corrosion. The normal steel has a larger area of water than the alloy. Most of the water had disappeared after 1 hour of air-drying for the alloy steel while considerable amount of water remained in the normal steel.

![Water Distribution Images](image)

Fig. 7. Time dependence of the water distributions. The colors indicate the estimated water thickness at each pixel.
4.2. Total Amount of Water in the Samples

The total amount of water in the samples was estimated by integrating over the sample shown in Fig. 7. The data points with error bars in Fig. 8 indicate the total amount of water in the samples over time, which were obtained by analyzing the corresponding neutron images. The lines in the Fig. 8 indicate the total amounts of water measured by monitoring the weight. The results of the neutron measurements and weight monitoring are in good agreement for both the alloy and normal samples. Hence, quantity of water in the samples estimated by neutron imaging is validated.

It is clear from Fig. 8 that the amount of water in the alloy sample was about 70% of that in the normal when the samples were removed from the water. Thus, the alloy sample includes less water, which is a direct factor causing corrosion. In addition, the water in the alloy sample evaporates more rapidly than that in the normal sample, suggesting that the samples with film coating have different corrosion-resistance characteristics.

4.3. Analysis by Regions

4.3.1. Definition of the Regions

To determine the movement of the water in more detail, the time variation of the water distribution was analyzed region by region. The scratch and blister regions were identified visually by comparing the optical images in Fig. 5. As shown on Fig. 9, the scratches were identified by the dark lines at the center of the samples, where corrosion could be directly observed owing to the luck of the coated film. The blisters were defined by the regions surrounded by the dotted curves in the Fig. 9. Note that the blisters include the scratches. The region in the sample excluding the blisters, markers and edges of the sample are defined as flat regions.

4.3.2. Blister Shape

Three-dimensional (3D) shapes of the sample surface, as shown in Fig. 10, were measured by a laser triangulation method to obtain volumes of the blister regions. The Fig. 10 indicates the blisters and the scratched on the center of the sample. The 3D shape images and the photographs were superimposed on the water distribution images in the Fig. 7 by utilizing the edges of the samples and the plastic markers. Table 1 shows the surface area, average height, and volume of each region in the samples. The areas of the blister and scratch are projected onto the flat region of the samples. The height is defined as the vertical distance from the flat regions of the samples. The blister region of the normal sample has a large area and volume than that of the alloy sample.

![Fig. 8. Time dependence of the total amount of water in the samples.](image)

![Fig. 9. Definition of the blister regions.](image)

![Fig. 10. Surface shape of the samples. The two squares with circles are the plastic markers. Concentric circles are markers, which were not utilized in this study. During the neutron exposure, concentric circles were removed.](image)

| Table 1. Surface area, average height, and volume of each region in the samples. |
|---|---|---|---|
| Sample | Variable | Scratch | Blister | Blister-Scratch |
| Normal | Area [mm²] | 176 | 1,573 | 1,397 |
|        | Height [mm] | 0.903 | 0.662 | 0.636 |
|        | volume [mm³] | 159 | 1,042 | 888 |
| Alloy  | Area [mm²] | 155 | 1,184 | 1,029 |
|        | Height [mm] | 1.22 | 0.616 | 0.541 |
|        | volume [mm³] | 189 | 729 | 557 |
4.3.3. Amount of Water in Each Region

It is considered that the flat region might include some water, which penetrates pinhole defects and/or unavoidable scratches in the film, and reaches the corrosion regions generated by the penetrating water and/or is contained in the film. However, amounts of water in the flat region observed in the flat region were under the measurement error. Therefore, we assume most of the water exists in the blister region.

The time dependences of the amount of water in each region estimated by the neutron imaging method are shown in Fig. 11. Most of the water is distributed in the blister region. The blister region in the normal sample contains more water than that in the alloy, and tends to accumulate water. This is due to the difference in the corrosion resistance between the samples. Because the normal sample has a tendency to contain more water than the alloy, it is anticipated that there is a longer contact time between the bare steel and the water, resulting in promoting corrosions under the film.

The scratches of both samples have similar time dependences in terms of the amount of water and the rate of change, because each scratch has a concave shape, incised by the sharp knife, one may consider that similar amounts of water accumulated, when the sample was removed from the water, and remained there. But the blister portion of the normal has more water than that of the alloy.

4.3.4. Water Content Ratio

Figure 12 shows the water content ratio (WCR) for the each region, which is defined as $WCR = \frac{\text{[amount of water]}}{\text{[volume]}}$. The amount of water by neutron imaging method is shown in the Fig. 11 and converted to the water volume, since water density is $1 000 \text{ mg/mm}^3$. The volume is defined in the section 4.3.2 and is shown in the Table 1. Thus, the WCR is treated as the non-dimension ratio.

In the scratch regions, there is no coated film, whose thickness is $240 \mu\text{m}$. To treat the scratch regions in the same manner as the other regions when considering the thickness of the water containing layer, thickness of the coated film is added to the height of the scratch. The volumes of the scratches are corrected in the same manner.

One can conclude the following from Fig. 12.

1. Overall, the two samples have little difference in the WCR in all regions. Owing to the formation of corrosion layers in all regions, that contain water, the amount of water per volume is expected to be similar in all regions of both samples.

2. However, the scratch region of the both samples tends to have a slightly higher initial WCR. This may indicate presumably that water accumulates and remains in the incised concave scratch regions as described when discussing Fig. 11.

3. The scratch regions of both samples have slightly lower WCR at all time. This suggests that the movement of water from the other regions to the scratch can be caused
by the gradient of the WCR. The water may evaporate into the air through the scratch, where there is no film, reducing the WCR at the scratch. Subsequently, the water in the adjacent region, where has a slightly higher WCR, may move to the scratch.

(4) The alloy sample has a higher rate of decrease in the WCR than the normal sample, suggesting that water is removed from the alloy sample more rapidly than from the normal sample. As discussed earlier, a difference in the rate of decrease in the WCR, estimated by the neutron imaging method results the different characteristics of the steel and the different properties of the corrosion layers in different steels. Thus, the normal sample has a lower rate of decrease in the WCR, resulting in water remaining for longer time. The normal sample may have more defects and voids in corrosion layer, at which water accumulates, causing the capillary action of the water, in addition to having a larger blister region. In general, it is regarded that a steel in which more water accumulates for a longer time, will exhibit more under-film corrosion and a lower anti-corrosion performance when painted, because the corrosion is caused by contact between the water and the bare steel. In fact, Nakayama et al. experimentally demonstrated that an alloy steel has denser corrosion layers containing fewer defects and voids than a normal steel, resulting in better corrosion resistance.3) We showed that the alloy sample has a higher rate of decrease in the WCR and accumulates less water by the neutron imaging method. It is indicated that the performance of the corrosion resistance of the steel is related to the water detention period in addition to the amount of water.

5. Conclusion

Time-dependent water images of painted steel samples with under-film corrosion were obtained by neutron imaging while the samples were dried. The behaviors of water in a normal steel and a corrosion-resistant alloy steel were compared. The alloy sample contained less water than the normal sample and the water in the alloy escaped more rapidly than that in the normal sample. As a result, it was demonstrated the alloy steel had better corrosion resistance. A compact neutron source is useful, when the observed object has sufficient sensitivity at the available neutron intensity, time resolution, and spatial resolution. In particular, as demonstrated in this study, the water in corroded steel samples was clearly observed. It is suggested that the range of applications of compact neutron sources will be increase further because of their flexibility and availability.

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