A direct current potential drop method for evaluating oxide film thickness formed in high-temperature water

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Abstract
To establish an evaluation technique for oxide film thickness in-situ, the applicability of a four-point-probe direct current potential drop method is discussed in this study. Several samples of JIS SUS316L stainless steel with different oxide film thickness were prepared after immersing them in oxygenated pure water at 288°C for different periods. The oxide film thickness was measured by cross sectional observation using a transmission electron microscope. Potential drop on the oxide surface was measured every second during an acquisition period of about 20 s while a constant current was being injected into the sample simultaneously. This kind of measurement was repeatedly carried out at several arbitrary contact positions on the surface of the same sample. The measurement results showed that the potential drop slightly changed during the acquisition period and the tendency varied at the different contact positions. Multiple measurements at different contact positions revealed that the tendency could be categorized into two general types: the decreasing potential drop and the increasing potential drop, defined by the overall trend of the potential drop during the acquisition time. It was found that the ratio of contact positions with a decreasing potential drop tendency to all the contact positions of measurement tended to increase as applied current increased. This tendency depended on the oxide film thickness. The threshold value of applied current was found to correlate well with the oxide film thickness when the occurrence rate of decreasing potential drop ranged from 70 to 90% showing the best correlation at 70%.

Key words: Electrical resistivity, Direct current, Stainless steels, Oxidation, Surface preparation, Stress corrosion cracking, High-purity water

1. Introduction

Since stress corrosion cracking (SCC) was first found in the primary recirculation pipes and core shroud made of low carbon stainless steels at a Japanese boiling water reactor (BWR) plant (a type of light water reactor plant) in 2002, various tests and examinations have been done for elucidating the SCC mechanism and developing methods for predicting the possibility of SCC.

For many material/environment systems of SCC, several researchers have suggested that oxide film plays an important role in SCC initiation, even including the low-carbon stainless steels in a BWR environment. For example, one of the authors and a coworker carried out an accelerated SCC test in a simulated BWR environment and confirmed that SCC initiated under some conditions where the oxide film thickness of the specimen grew over a certain level (Okizaki, 2013).

The thickness of the oxide film affects the property of mass transfer and is one factor influencing the local water
chemistry change when the film is ruptured. If the thickness of the oxide film can be detected quantitatively and in-situ, one may be able to evaluate the possibility of SCC initiation and take preventive maintenance measures.

Ali et al. previously tried to measure the oxide film thickness of carbon steel formed in an atmosphere between room temperature to 292ºC (565K) using a four-point-probe direct current potential drop (DCPD) method (Ali, et al., 2010, 2012). They showed that the measured potential difference decreased in a constant current condition during acquisition time and finally the current became closer to the value of the non-oxide film condition. They explained the phenomenon as a creep deformation of oxide film caused by partial compression stress at the probe tip and proposed a method on the basis of this phenomenon for evaluating the oxide film thickness using the time of saturated potential drop behavior.

Similar potential drop behavior may occur in the oxide film of low-carbon stainless steels in high-temperature pure water. However, the oxide film of low-carbon stainless steel is usually less than 1 μm, much thinner than that of carbon steel. The structure of an oxide film formed in atmosphere is also considered different than that of the carbon steel. Therefore, the method that Ali et al. have suggested might not be applicable, so an alternative method may be required.

In this report, oxide films formed on low-carbon stainless steel in high-temperature pure water were measured by the four-point-probe DCPD method of Ali et al. By comparing the current change behavior with the measured oxide film thickness, a procedure for evaluating the film thickness is discussed and proposed.

2. Experimental
2.1 Test material and method of oxide film formation

The material used for the test is a rolled plate of 19-mm-thick austenitic stainless steel JIS SUS316L purchased with nuclear specifications in Japan. Its chemical composition is shown in Table 1. Rectangular samples of 140×240 mm² were cut out from the plate so that the rolling direction was parallel to the long side.

Considering that the surface state might affect the result of the potential drop measurement, surface grinding or face milling had been applied before the samples were oxidized in high-temperature water. Table 2 details the conditions of each surface processing.

The samples were immersed in an autoclave connected to a high-temperature pressure water loop for oxide film formation. The circulation water was 288 ºC (561 K) with a pressure of 8 MPa at the test section. Dissolved oxygen concentration was controlled at 8 ppm with oxygen gas and nitrogen gas bubbling. Conductivity of the inlet water was maintained by ion-exchange resin at a value lower than 0.1 μS/cm (at normal temperature). The thickness of the oxide film varied during two different immersion durations: 100 h or 500 h. Table 3 shows the process methods, condition of

<table>
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<th>Process method</th>
<th>Conditions</th>
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<tr>
<td>Surface grinding</td>
<td>Finish with a whetstone of the 800-1000 equivalency Grind the same direction as the rolling</td>
</tr>
<tr>
<td>Face milling</td>
<td>Face milling cutter with 6 teeth (160 mm in diameter), Rotating speed: 240 rpm, Forwarding speed: 85 mm/min, Back engagement: 0.05 mm, Feed direction: The same direction as the rolling</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Process method</th>
<th>Condition of water</th>
<th>Immersion duration (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-100</td>
<td>Surface grinding</td>
<td>288 ºC DO 8 ppm</td>
<td>100</td>
</tr>
<tr>
<td>K-500</td>
<td>Face milling</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td>F-500</td>
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water and immersion durations. The test sample with a machined surface was immersed in water for 500 h only. After the immersion, the samples were dried in air and examined.

To characterize the oxide film structures, 10×10 mm\(^2\) coupon specimens were cut out from a sample with the same heat and surface process and immersed simultaneously in the environment. The cutout location of each coupon was at least 10 mm away from the edge of the sample.

2.2 Observation method of the oxide film

The oxidation film samples were taken from the surface processing side of coupon specimens by the focused ion beam (FIB) method. Structure of the oxide film was observed and investigated using a transmission electron microscope (TEM). The thickness of the oxide was measured using a scanning electron microscope (SEM). A small measurement sample 7 mm wide was taken from the middle of the immersed sample by ion milling and three separate locations about 30 \(\mu\text{m}\) in range were measured at 50 000 magnifications. In addition, an X-ray diffraction (XRD) method was also applied to identify chemical compounds of the oxide film.

2.3 A Direct Current Potential Drop Measurement

The DCPD measurement system of Ali et al. (Ali, et al., 2010, 2012) was used to measure the oxide film of the carbon steel. Figure 1 schematically shows the layout of the measurement system. A direct constant current was applied through a needle-shaped outer probe with a 0.75 mm tip diameter every second and the potential drop was measured between inner probes. The measurement was repeated 21 times (acquisition time from the initial measurement was 20 s) at the same contact position. The load applied to the probes was accurately controlled by springs assembled under the actuator.

3. Results
3.1 Characterization of the Oxide Film

Figure 2 shows a typical TEM observation result of the section of oxidation film on a surface ground and immersed in the water for 500 h (K-500). The oxide film consisted of two layers: a minute inner layer with a uniform structure and a blocky outer layer with non-uniform structure. The average oxide film thickness of each surface finish and immersion time obtained by SEM observations was 0.25 \(\mu\text{m}\) for K-100, 0.40 \(\mu\text{m}\) for K-500 and, 0.48 \(\mu\text{m}\) for F-500.
The scatter was small in each case within 0.05 μm of the mean value. The oxide film thicknesses differed slightly among surface finishes, suggesting that manufacturing conditions might have little effect on the thickness of the oxide film.

The results of XRD analysis of oxide film on the sample which was finished by grinding and immersion in high-temperature water for 500 h suggested that FeCr₂O₄ and NiFe₂O₄ might be the main constituents. There were also some small peaks possibly corresponding to Fe₂O₃.

### 3.2 Potential Drop Measurements of Test Samples

The potential drop was measured at an arbitrary position near the center of the test samples. Some typical results obtained from 10 different contact positions of F-500 are shown in Fig. 3(a), where they are summarized in terms of measured potential drop. As shown in the figure, the measured potential drop was not reproducible among different contact positions. This is thought to be due to the uncontrollable conditions of contact between the current probe tip and the rough surface of the outer layer. On the other hand, the measurement scatter of each contact position was not obvious. Slight change of potential drop can be observed at each contact position within the acquisition time. On the basis of behavior of potential drop change described above, the data were summarized in terms of potential drop difference (ΔE) as shown in Fig. 3(b). Here, the results are plotted as ΔE against the smallest value during the acquisition time. Although the tendency within the acquisition time at each contact position was not monotonous, there

![Fig. 2 TEM observation of cross section of oxide film (Sample: K-500, bright field image). It consisted of a minute inner layer and a blocky outer layer: (a) A typical observation (Black area covering the brocky oxide is W coating), (b) Higher magnification of location A.](image)

![Fig. 3 Summary of the potential drop behavior under repeated measurements (F-500; measurement current: 9 A): (a) Potential drop. The potential drop was not reproducible among different contact positions, (b) Potential drop difference. For the potential drop difference, although the tendency within the acquisition time at each contact position was not monotonous, there seemed to be some recognizable patterns.](image)
seemed to be some recognizable patterns. Thus they were divided these patterns as below. Figure 4 shows some typical examples of ΔE among those results. The value of ΔE decreased after having risen once during the acquisition time (Fig. 4 (a)); the ΔE rose after having dropped once during the acquisition time (Fig. 4 (b)); the ΔE rose monotonically with some intermittent small declines (Fig. 4 (c)). As the effect of oxide film on the ΔE change should be more dominant in the earlier stage of the measurement, patterns shown in Fig. 4(a) and (b) can be categorized as decreasing patterns, if their behavior has some relation to the oxide film.

Figure 5 shows the optical microscopy image of the surface trace at a contact position from where the current probe tip was removed after the measurement. In contrast to the dark brown oxide covering on the surface, the spot had a metallic color. Considering that oxide film formed on stainless steel in high-temperature pure water is solid, this result suggests that the oxide might have been removed during the potential drop measurement and that this event might have affected the behavior of potential drop change. As the oxide film is very thin, the potential change may have

Fig. 4 Typical examples of ΔE behavior (F-100, measurement current: 9 A). According to the results of several measurement of the potential drop difference, the behavior could be mostly categorized as the three patterns: (a) continuously decreasing for most of the acquisition duration, (b) decreasing first and then increasing, but not recovering to the original level, (c) continuously increasing with some step wise decreasing.

Fig. 5 Optical microscope observation of the trace of DCPD current probe on oxidized surface (F-500) after measurement of the potential drop.
been interfered with in some cases by some other factors such as oxide film roughness and contact pressure difference, which leads to the data scatter as shown in the Fig. 3(a). Therefore, multiple measurements were conducted by changing the amount of the direct current for comparison.

Figure 6 shows results of multiple measurements of the potential drop change under different applied currents at sample No. F-500. The $\Delta E$ at each contact position showed different behavior, but, stronger tendency for $\Delta E$ to decreasing with acquisition time could be seen. Hereafter, it is set as a decreasing pattern in which the overall tendency of the potential drop decreased within the acquisition time up to about 10 to 15 s like the pattern shown in Fig. 4(b). Figure 7 summarizes the results in terms of the ratio of the contact positions with decreasing potential drop to all contact positions of measurement, which is defined as the occurrence rate of decreasing potential drop (RDPD), in relation to the amount of direct current on the three types of sample in Table 3. In all three samples, the RDPD tended to increase as applied direct current increased. In addition, the RDPD began increasing at a lower applied current of about 4 A.

Threshold values of RDPD were set as 70, 80, and 90% , and the applied direct current corresponding to each threshold from Fig. 7, hereinafter denoted as critical applied current, was estimated. Figure 8 shows the critical applied currents plotted in terms of thickness of the oxidation film. The thickness of the oxide film and the critical applied current correlated well at each RDPD threshold and correlated best at 70% in this study.

4. Discussions

Ali et al. discussed that the potential drop changes during the DCPD measurement is due to creep of the oxide film caused by Joule heat at the contact point (Ali, et al., 2010, 2012). In this study, the same tendencies of potential changes could be obtained in stainless steel, but they were not as clear as those Ali et al. obtained from carbon steel (Ali, et al., 2010, 2012). Two possible factors are considered to explain the difference. One is the difference in chemical compounds of oxide film and the other is the difference in the thickness and structure of the oxide film.

As for the chemical compounds, electrical resistivity may be the key issue, because it affects Joule heat during the
measurements. Ali et al. did not report a detailed investigation of the chemical compounds of the oxides. On the bases of the material and the environment in which the oxides were formed, it can be extrapolated that they were mainly FeOOH with some Fe$_3$O$_4$ for room temperature (Misawa, 2001) and a mixture of Fe$_3$O$_4$ and Fe$_2$O$_3$ for high temperature (Uhlig, 1974). These oxides are considered to have nonconductive property (Misawa, 2001), due to which the electrical resistivity of the oxide film can be elevated. Considering that the main constituents of the oxide film in stainless steel, as mentioned in 3.1, are also M$_3$O$_4$ type (FeCr$_2$O$_4$ and NiFe$_2$O$_4$) with non-conductive property, explaining the two different potential drop behaviors with their chemical compounds turned out to be difficult.

On the other hand, the oxide film in stainless steel was an order of magnitude thinner than the carbon steel investigated by Ali et al. It is also much smaller than the tip radius of the current probe, so the oxide between the current probe tip and base metal may be removed partially during the repeated current application until it is completely removed as shown in Fig.6. Based on those observations the contact condition between the tip and the thin oxide might be different in each case, which possibly leads to different behavior of $\Delta E$ in each measurement set. It is assumed that the removal process of the oxide film lasts between 10 and 15 s till the contact condition stabilizes in most cases, and after that the potential drop difference starts to rise probably due to the Joule heat effect becoming dominant.

As the oxide was so thin and the $\Delta E$ measured so small, several factors may affect the results. The outer blocky oxide may be one important factor. It affects the initial contact condition between the probe tip and oxide film. During the measurement at the same contact point, the contact condition may have changed gradually in each current application. As shown in Fig. 3(a), a deviation of potential drop an order of magnitude larger than $\Delta E$ could be

![Fig. 7](image1)

**Fig. 7** Measurement current dependence of RDPD (10 -12 measurements) in each sample with different oxide thickness. The RDPD increased with the applied current in both cases. Oxide film thickness may affect the behavior.

![Fig. 8](image2)

**Fig. 8** Relationship between oxide film thickness and critical applied current under arbitrarily set critical ratio of occurrence of decreasing potential drop and oxide film thickness. The thickness of the oxide film and the critical applied current correlated well at each RDPD.
observed even after the repeated measurement on the same sample. Based on the results, change of $\Delta E$ during the contact condition change during the measurement set could increase or decrease probabilistically. For higher applied current, the oxide removal process has become more pronounced due to higher Joule heat at the probe tip and thus made decreasing potential drop difference occurrence at a higher rate.

On the basis of the experimental results, the applicability of the DCPD technique to evaluation of the oxide film thickness in stainless steel was discussed. The oxide film thickness measurement using the DCPD technique is expected to possibly become effective tool in an in-situ technique for evaluating and even predicting SCC initiation behavior without majorly damaging the base metal.

5. Conclusions

Applicability of a four-probe direct current potential drop (DCPD) technique to measurements of the oxide film thickness of low carbon austenite stainless steel formed in high-temperature water was discussed, and the following conclusions were obtained.

1. The oxide films formed on the sample were about 0.25 and 0.5 μm thick and consisted of a minute inner layer with a uniform structure and a blocky outer layer with a non-uniform structure.

2. According to the measurement results of the DCPD method, large scatter of the potential drop was observed. On the other hand, no obvious scatter was observed in the potential drop difference within the acquisition time.

3. The tendency of potential drop over acquisition time varied from one contact position to another even on the same sample. These data were categorized into two types: the decreasing potential drop and the increasing potential drop, defined by the overall trend of the potential drop during the acquisition time. The ratio of contact positions with decreasing potential drop tendency to all the contact positions of measurement (RDPD) tended to increase as applied current increased.

4. The increase of RDPD with increasing applied current depends on the oxide film thickness. The threshold value of applied current was found to correlate well with the oxide film thickness when RDPD was 70%, 80% and 90%.

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References


