

Corrosion –Potential Fluctuation and Polarization Resistance Method for Corrosion Monitoring in Subcritical and Supercritical Water Environments

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For developing a corrosion monitoring method applicable to subcritical and supercritical water oxidation (SCWO) environment, the potential fluctuation and the polarization resistance (R_p) of UNS30400 (type-304) stainless steel were measured at subcritical and supercritical temperatures up to 600 °C, in a 1.04×10^{-3} mol/dm³ HCl solution saturated with pure O₂ gas. The corrosion phenomena of the working electrode (WE) immersed in the solution at the high temperatures were also investigated. The shape of the potential fluctuation at 360 °C was random, while RD (rapid drop followed by slow recovery)-type fluctuations were observed at 300°C. The WE immersed at 360 °C was subjected to intense general corrosion. The initial pits and intergranular corrosion defects were formed on the WE immersed at 300°C. The change in R_p with temperature also suggested the WE was subjected to intense general corrosion at around 360 °C. The feature in the polarization curves showed a corrosion rate was controlled by the level of limiting diffusion current for cathodic reaction at the temperatures from 200 to 360 °C. The corrosion rates estimated from the R_p s and the Tafel slopes showed good agreement with those estimated from the limiting diffusion currents of the cathodic polarization curves.

1. Introduction

The use of subcritical and supercritical fluids is considered as a key technology for an earth-friendly disposal process. These fluids, however, are highly corrosive environment for structural materials for chemical plants. Even precious metals as well as nickel-base alloys are not immune from the corrosion damages at some stages in the process [1]. Thus, precise corrosion control is required to avoid serious corrosion damages. To conduct the corrosion control correctly in an actual plant, it is necessary to establish a corrosion monitoring technique that enables us to reliably assess the severity of process environment in real time.

The electrochemical noise measurement (ENM) has received significant attention as a promising on-line monitoring technique, because it has a capability to provide information not only on the general corrosion activity but also about the localized corrosion activity. Among a variety of ENM methods, we have especially focused on the potential fluctuation (potential noise) measurement, because it requires relatively simple measuring system and it scarcely causes electrochemical disturbances to a working electrode (WE) during the measurement. The relations between the form

of the fluctuation and the type of corrosion activity are well established at lower temperatures up to 100 °C. Random potential fluctuations are observed when the electrode is being subjected to general corrosion[2,3], while potential fluctuations with a characteristic changing pattern, rapidly dropping to negative direction and slowly recovering to a original level appear when initial localized corrosion events[4,5] are happening on the electrode (Fig.1). We call this fluctuation pattern as RD-type[8].

In our former study, it was confirmed the above relations between the fluctuation patterns and the corrosion phenomena were also held even at high-subcritical temperatures[7], using UNS10276 alloy for the WE. In this study, the potential fluctuation of UNS30400 (type-304) austenitic stainless steel was measured in an oxidizing hydrochloric acid at subcritical temperatures. The polarization resistance and the polarization curve of the WE were also measured.

2. Experimental Methods

2.1. Electrodes and test solutions A 1.5 mm diameter wire of UNS30400 (type-304) austenitic stainless steel was used for the material of the working electrode (WE). It was used as a purchased condition without applying any heat treatment.

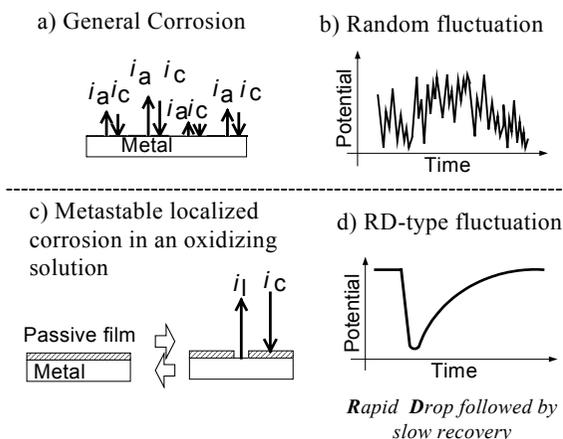


Fig. 1. The relations between the type of corrosion activity and the form of potential fluctuation in an oxidizing solution at low temperature up to the boiling point.

After the polishing up to #2000 and cleaning with acetone, the wire was inserted into an aluminum tube, leaving an exposed area of 15 mm in length at the one end of it. The dimensions of the aluminum tube were a 3.0 mm in outer diameter and a 0.5 mm in thickness. The hydrochloric acid of 1.04×10^{-3} mol/dm³ was used for test solution, which was saturated with pure O₂ gas at ambient temperature and under atmospheric pressure. A pure titanium wire was used for the material of the reference electrode (RE). It was set in lower temperature part inside the reactor where the solution was cooled to ambient temperature. Another pure titanium electrode was prepared and used for a counter electrode (CE) when the polarization resistances were measured and the polarization curves were generated.

2.2. Experimental system A coaxial tube reactor[9] was used for this experiment. The general view of the experimental system with this reactor is schematically shown in Fig. 2. A core tube of pure titanium was coaxially located inside a pressure vessel of type-316 stainless steel. The core acts as an anti-corrosion boundary, and the vessel sustain a high-pressure inside the reactor. The test solution was fed into the core tube, while pure water was injected into the gap between the core and the vessel. The test solution flowed through the core tube merged into the pure water at the end of the reactor and then was drained. This setup served to

balance the internal and the external pressures over the core tube, and allowed us to use pure titanium as a material for the reactor. Although it is inferior in mechanical strength at high temperature, it shows good corrosion resistance in high temperature oxidizing solutions. The test solution was heated by a tubular electric furnace set over the middle of the reactor through the highly purified water, which is considered not an aggressive environment against the stainless steel even at the super-critical temperatures. The dimensions of the vessel were a 9.5 mm outer diameter, 1.2 mm thickness, and 1m length; those of the core tube were 6.4 mm, 1.0 mm, and 1m, respectively. The position of the pressure vessel was offset by 5 to 10 mm relative to the core tube, and fixed there, to provide room for the test solution to flow through the core tube merge into the pure water. The WE was inserted into the core tube from the downstream side, and placed it in a position which corresponds to the edge of the electric furnace. A solution temperature at the working electrode was estimated with reference to a temperature at the surface of the vessel using a calibration curve measured before the experiments. Another sheathed thermocouple with the same dimension as the WE was set in the same position where the WE was positioned. The temperature difference between the both thermocouple was measured at various operating temperatures. The RE was placed at the very end of the downstream side of the reactor. Both end of the reactor were water-cooled, so that the solution temperature at the RE is considered to be kept at ambient. The CE was set at the opposite end of the reactor, where the solution is also considered to be cooled at ambient temperature.

2.3. Electrochemical cell The schematic representation of the electrochemical cell is shown in Fig.3. The test solution and the pure water were fed into the reactor using a high-performance liquid chromatography (HPLC) pump. The feed rates were adjusted to the flow rates being equal in and out of the core tube. The pressure inside the reactor was adjusted to 24 MPa with a back pressure valve. The corrosion potential fluctuation of the WE was measured under open-circuit conditions. It was continuously sampled every 0.5 s using the high input impedance (>10 GΩ) digital voltmeter. The polarization resistance and the polarization curves were measured using a potentiostat.

In the polarization resistance measurement, the overpotential at -5, +5, -10, and +10 mV were

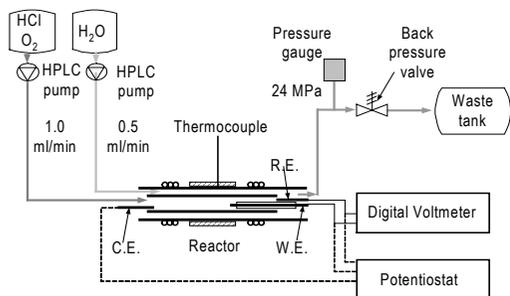


Fig. 2. Schematic representation of the experimental system.

applied to the WE and the changes in electrolysis currents were measured. In the polarization curves measurement, the potential of the WE was stepwise decreased by 25 mV every 120 s from open-circuit potential to the overpotential of -200 mV, and then the potential was increased from the open-circuit potential to the overpotential of +200 mV in the same way. The intensity of current to each potential level was recorded at just before the potential was increased or decreased to the next level. The WE was immersed for 1 h in solution at the measurement temperature prior to starting the measurement.

2.4. Capillary-like liquid junction By placing the RE at ambient temperature, a significant temperature gradient occurred between the WE and the RE. This gradient generates large thermal liquid-junction potential, and this will be the source of potential fluctuations. If the solution existing between these electrodes is significantly stirred by the convection, the fluctuations of the thermal liquid junction potential (TLJP), which do not related to electrochemical process on the WE, would be added to the corrosion potential measured by the RE. To relieve it, a unique design for the gap between the WE's insulator and the core tube was prepared. As mentioned above, the insulator has a 3.0mm outer diameter, and the core tube has about 4.4 mm inner diameter; 6.4 mm in outer diameter and 1.0 mm in thickness, so that the gap between them is as little as 0.7 mm, and the distance between the electrodes is over 0.3 m. It is considered that this narrow and long gap acts as a capillary-like liquid junction. This structure might suppress the potential fluctuation generating by the disturbance in the TLJP. This design also carries the advantage that the junction acts as a Luggin capillary when the polarization resistance of

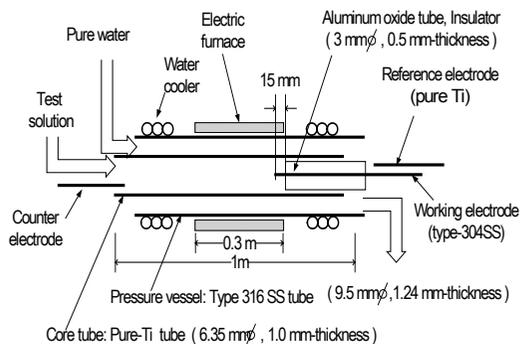


Fig. 3. Schematic representation of the experimental cell.

the WE was to be measured.

3. Results and Discussion

3.1. Potential noise measurement and surface morphology observation

Figure 4 - a) and b) shows typical potential fluctuations measured at 300 and 360 °C, respectively. Any distinct fluctuations were not found at the temperatures lower than 250 °C. The fluctuations shown in Fig.4 - a) seem spike-like signals in the less-noble direction, however, in the further magnified representations, all of the signals show the typical RD-type form indicated in Fig.1. Many pit-embryo traces were found on the WE after it was used for the measurement. Fig.4 - c) is a cross-sectional view of the WE immersed at 300 °C. A trace of pit-embryo is found on the figure. These results suggest that the WE was considered to be subjected localized corrosion activity at temperatures around 300 °C. At 360 °C, random fluctuations with large amplitudes observed (Fig.4 - b)) and thick corrosion films were formed on the WE (Fig.4 - d)). From these results, it could be said that the WE was subjected intense general-corrosion activity at 360 °C.

3.2. Change in the polarization resistance with temperature

The change in the polarization resistance (R_p) of the WE with temperature was measured at the some temperatures from 90 to 600 °C. The results are shown in Fig.5, where the R_p is represented as their inverse values ($1/R_p$), which is roughly proportional to the general corrosion rate. As shown in Fig.5, the $1/R_p$ increased with temperature and reached the maximum at 360 °C. Above the critical temperature, however, the $1/R_p$ dropped to a lower level and kept it over the supercritical temperatures up to 600 °C. This shows the WE was subjected to an intense

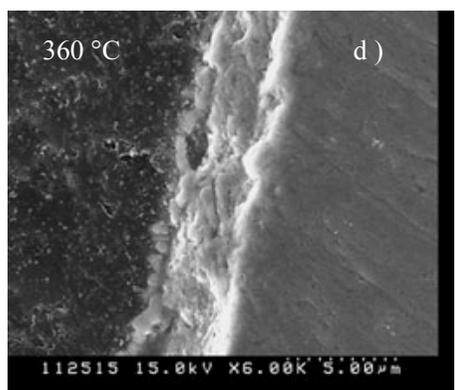
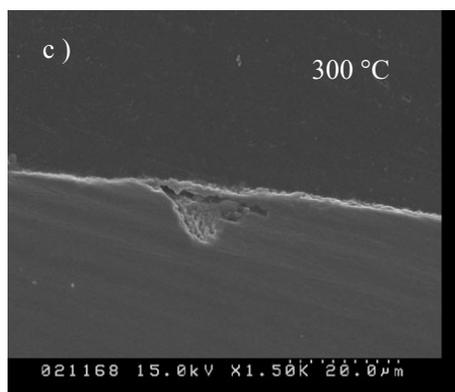
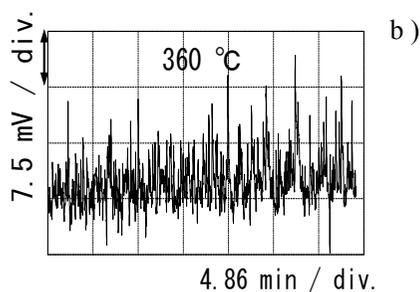
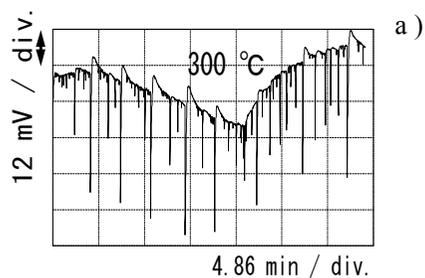


Fig. 4. Typical potential-fluctuation patterns measured at 300 and 360 °C (figure a and b), and the cross-sectional views of the electrode at these temperatures for 7 h (figure c and d).

general corrosion at around 360 °C, and its resistance, or stability of the surface oxide film increased remarkably at the temperature over the critical point. For making a comparison, the $1/R_p$ was also measured in a deaerated solution at the same range of temperatures; its hydrogen chloride concentration was equivalent to that of the solutions mentioned above but it was saturated with pure N_2 gas. The $1/R_p$ in the deaerated solution was lower than that in the O_2 saturated solution, and kept almost constant value over the examined temperature range.

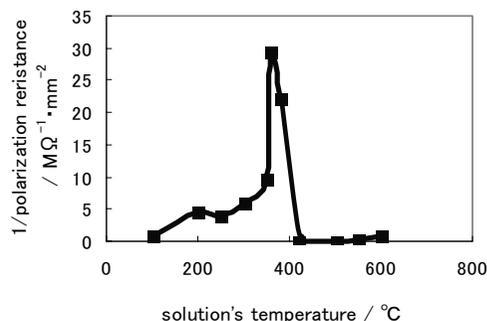


Fig. 5. The changes in the polarization resistance of the WE with temperature. It was measured in O_2 gas saturated 1.04×10^{-3} mol/dm³ HCl solutions.

3.3 Polarization curves at various temperature

Figure 6 shows change in the anodic and cathodic polarization curves of the WE with solution temperature from 90 to 360 °C. In this figure, the potentials are plotted as a function of overpotential with respect to corrosion potentials under each condition. The polarization curves a slightly changed at the temperature range from 200 to 300 °C, however, at 360 °C, it shift to almost 10 times higher current-density region in comparison with the curves at the lower temperatures. This shift is regarded as showing good agreement with the results on potential fluctuation and the polarization resistance measurement. The potential fluctuation shows random potential fluctuation at the temperature of 360 °C, and the inverse of the polarization resistance also reached a peak value at this temperature. Both of the results suggest the happening of intense general corrosion activity at this temperature. At temperature up to 360 °C, the logarithm of the anodic currents increased proportionally with the intensity of the overpotential; their slope, or anodic Tafel slop were 100 to 150 mV per decade. This suggests that the rate-determining step in an anodic reaction is a

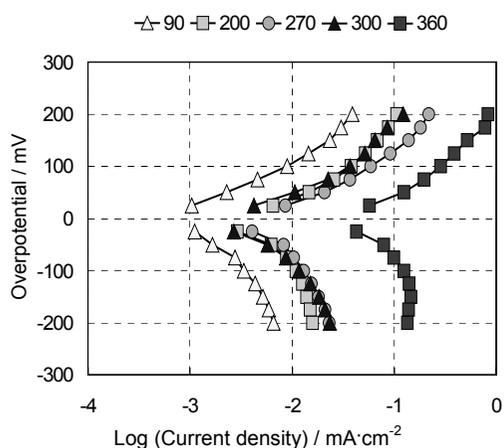


Fig. 6. The change in the anodic and the cathodic polarization curves with solution temperature.

charge-transfer reaction within this temperature region. However, the cathodic polarization curves at the same temperatures show limiting currents at the overpotential of -150 to -200 mV, which might suggest that the rate-determining step in a cathodic reaction is a mass-transfer reaction. In this case, the overall reaction rate must be controlled by the oxygen diffusion rate from bulk solution to the interface of the WE. To check this assumption, the corrosion currents estimated from the polarization resistance and the Tafel slopes of the polarization curves were compared with the intensities of the limiting currents. The estimated currents are shown in Table 1. It could be said that the estimated corrosion currents showed relatively good agreement with the levels of the limiting current at the same temperature, so that the corrosion reaction

Table 1. The summary of the corrosion current estimated from the polarization resistance the Tafel slopes of the polarization curves

Solution Temperature / °C	Corrosion Current / mA·cm ⁻²
90	0.003
200	0.013
240	0.007
270	0.012
300	0.023
330	0.071
360	0.093
380	0.018

rate was regarded as being controlled by the oxygen diffusion rate at these temperatures.

4. Conclusions

Potential fluctuation of UNS30400 (type-304) stainless steel electrode were measured in a 1.04×10^{-3} mol/dm³ HCl solution at temperatures up to 600 °C and the pressure of 24MPa. The polarization resistance (R_p) was also measured under the same conditions. The $1/R_p$ reached a peak value at 360 °C. The potential fluctuation measured at the temperature 360 °C showed the random fluctuation pattern with larger amplitude. The surface morphology of the working electrode (WE) after being used for the measurement suggested it had been subjected to intense general corrosion during the measurement. However, during measurement at the temperature of 300 °C, the RD-type potential fluctuations were measured and the traces of localized corrosion activity were observed on the WE. At the temperatures below 250 °C, no fluctuations were found on corrosion potential, and the surfaces of the WE showed no corrosion traces, too. The features in the polarization curves generated at 90 °C to 360 °C suggested a corrosion rate of the WE was controlled by the level of a limiting diffusion current for cathodic reaction at the temperature from 200 to 360 °C. The corrosion rates estimated from the R_p values and the Tafel slopes of the polarization curves showed good agreement with those estimated from the limiting diffusion currents at these temperatures, too.

Acknowledgements

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