

Dissolved Hydrogen Effect on Crack Initiation Behavior and Oxide Formation of Sensitized 304L Stainless Steel

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1. Introduction

Austenitic stainless steel has been widely used in primary circuits of pressurized water reactor. Especially type 304 and 316 stainless steels are the major materials of the reactor internal structures supporting the reactor core. According to the screening criteria of MRP-227 [1], reactor internals composed of stainless steel have a good resistance to stress corrosion cracking (SCC) except welds. However, when the material exposed to neutron irradiation it becomes susceptible to irradiation assisted stress corrosion cracking (IASCC) [2].

IASCC, a special case of intergranular SCC, referred as intergranular cracking showing little or no ductility. However, it is hard to handle neutron-irradiated materials due to activation, thus, simulation of neutron-irradiation effect is essential to investigate IASCC. Neutron-irradiation can change microstructure and chemical distribution of material. To simulate these effects without using neutron, various attempts have been made so far; heat treatment for chemical distribution change, warm/cold work for microstructural change, and irradiation with other sources such as proton and heavy ion.

Preceding research have been done to increase corrosion resistance of structural materials by changing dissolved hydrogen (DH) concentration. There is a clear relationship between the DH concentration and SCC behavior of Ni-based alloy in PWR primary water condition. However, the electrochemical potential of austenitic stainless steels is different with that of Ni-based alloy. So that, changing DH may aggravate the hydrogen-induced degradation of stainless steels. DH concentration changes diffusion of iron ion which can affect oxide thickness. But the correlation between DH concentration and corrosion behavior of stainless steel has not been clarified so far. Therefore, it should be deeply studied prior to change DH condition of nuclear power plant.

In this study, SCC susceptibility of sensitized 304L stainless steel which can simulate the irradiation effect in point of chemical change was investigated by conducting slow strain rate test (SSRT) combining with direct current potential drop (DCPD) methodology to with differing DH concentration.

2. Experimental

This section describes the experimental setup for SSRT using sensitized 304L stainless steel samples. The method of sensitization is also described.

2.1 Sensitization

To simulate radiation induced segregation effect on material, sensitizing heat treatment was done. Considering carbon content of prepared 304L stainless steel, according to time-temperature transformation diagram of 304L stainless steel, heat treatment under 550 °C during 200 hours is enough to form carbide along the grain boundary which can simulate irradiation effect. Below table shows the chemical composition of the material that was used for each experiment.

Table I: Chemical composition of 304L stainless steel [wt%]

Fe	C	Si	Mn	P	S	Cr
Bal.	0.024	0.45	1.43	0.033	0.003	18.35
Ni	Mo	N	Co	Cu	Ti	
8.11	0.18	0.044	0.17	0.28	0.002	

2.2 Slow strain rate test & Direct current potential drop

SSRT is a common SCC test methodology which can figure out crack initiation time and crack density by stretching sample very slowly. In this work we focused on crack initiation time to check IASCC resistance of each sample. Strain rate was set as 1×10^{-7} mm/mm/s following ASTM G129 [3].

Suppose that sample is going to be elongated continuously, the electrical resistance of sample will be increased uniformly. However, when some crack occurs on the sample surface the electrical resistance will be changed shortly. So that, detecting this moment by measuring potential drop through the sample gauge section, crack initiation time of sample can be measured. This kind of method is called DCPD. Below figure shows that the sample engaged into the test facility and platinum wires; the first set which is welded at both edge side supplies direct current about 5 A uniformly, and the second set which is welded at the middle side measures potential drop through the gauge section of the sample



Fig. 1. Platinum probe which supplies direct current and measures potential drop

2.3 Primary water environment

The experimental facility was filled with simulated primary water [4]. Temperature and pressure were set as following real plant conditions, and chemical ion such as boron and lithium were put into the test solution. Dissolved oxygen concentration was controlled strictly by injecting hydrogen gas. To investigate DH effect on IASCC, two different DH concentrations were adapted. Below table shows the test conditions that we developed in this study.

Table II: Experimental conditions

Pressure [MPa]	Temperature [°C]	B [ppm]	Li [ppm]	DO [ppb]	DH [cm ³ /kg]
15.5	325	1200	2.2	< 5	25 50

2.4 Test matrix

Sensitized 304L stainless steel samples were used in this research with differing DH concentration 25, 50 cm³/kg respectively. The detailed test matrix is listed in the below table.

Table III: Test matrix

Sample type	DH [cm ³ /kg]	Notation
Sensitized 304L stainless steel	25	2S
Sensitized 304L stainless steel	50	5S

3. Result

3.1 Experimental facility operating data

Experiments had been conducted up to 450 hours which was the longest case. During each experiment, operating data such as pressure and temperature inside of test section had been measured and conductivity of test solution had been monitored as well. As below figure shows, test environment had been uniformly maintained during the experiment.

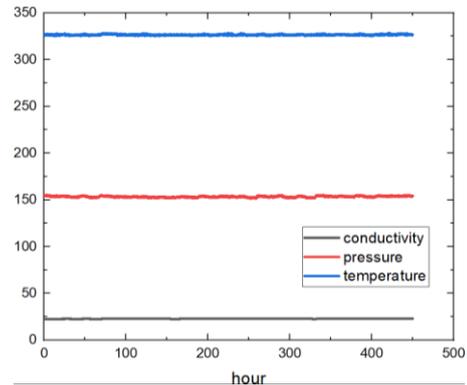


Fig. 2. Experimental facility operating data during the experiment which had been conducted about 450 hours

3.2 Crack initiation behavior

Considering the sample dimension especially gauge section, the electrical resistance of sample will be increased uniformly. But this tendency is going to be changed when crack initiated. The micro crack can decrease cross sectional area of sample which causes rapid increase of electrical resistance, in other words potential drop increase since current maintains as 5 A during experiments. Below plot is DCPD data of one of 2S experiments (black colored line) and fitting curve (red colored line). As it shows, the fitting curve fits almost 99% with measured DCPD data until crack occurs; approximately 320 hours elapsed. After that, the DCPD data fluctuates compared to fitting curve. That means crack increases potential drop and after crack initiation the crack becomes being filled with oxide that can decrease the electrical resistance by increasing cross sectional area.

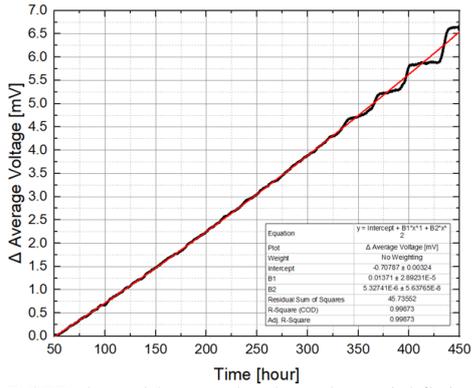


Fig. 3. DCPD data with second order polynomial fitting curve for 2S experiment

To point out the exact crack initiation time from the data, normalizing process was done between measured data and fitting curve. According to the below graph, the signal starts to fluctuate near 330 hours elapsed. And this trend becomes greater. So that it can be noted that crack was initiated and grew continuously.

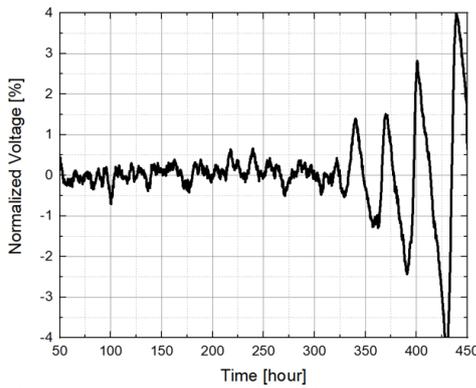


Fig. 4. Normalized DCPD data for 2S experiment

SSRT experiments using 50 cm³/kg concentration of DH were done following the same manner with 2S experiments. From the DCPD results, the data followed quadratic function well and it fluctuated after 230 hours.

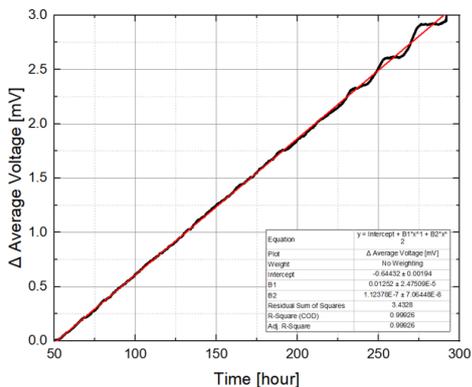


Fig. 5. DCPD data with second order polynomial fitting curve for 5S experiment

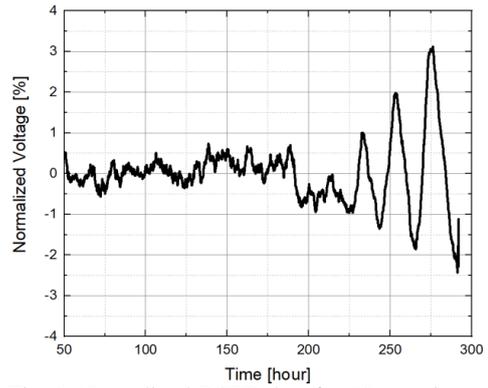


Fig. 6. Normalized DCPD data for 5S experiment

Gathering data from several repeated experiments 2S and 5S respectively, crack initiation time affected by dissolved hydrogen concentration can be summarized as below chart. When the DH concentration set as 25 cm³/kg the average crack initiation time was about 361 hours and that of 50 cm³/kg DH was 261 hours. In conclusion when DH concentration increases the crack initiation time was shortened.

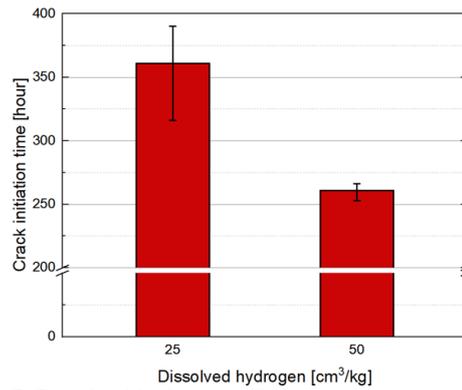


Fig. 7. Dissolved hydrogen effect on crack initiation time

3.3 Oxide formation on crack tip

Chemical composition of oxide on crack tip from experiments 2S and 5S were measured by using transmission electron microscope (TEM) combining with energy dispersive X-ray spectroscopy (EDS) respectively.

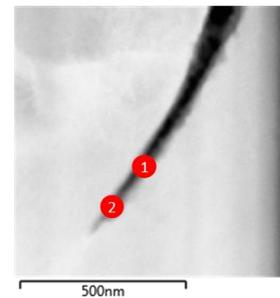


Fig. 8. TEM EDS measured points for oxide on crack tip from 2S sample

Table IV: TEM EDS results for oxide on crack tip from 2S sample [at%]

Element	Point 1	Point 2
C	0.00	0.00
O	47.86	46.34
Si	1.56	0.97
Cr	12.93	13.64
Mn	0.80	0.97
Fe	32.26	34.40
Ni	4.59	3.68

According to the TEM EDS results of oxide on crack tip of 2S experiment show that the oxide consists of iron oxide and chromium oxide mainly. This kind of oxide chemical composition follows common oxide of stainless steel, iron oxide as outer and chromium oxide as inner oxide.

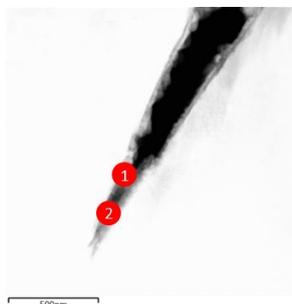


Fig. 9. TEM EDS measured points for oxide on crack tip from 5S sample

Table V: TEM EDS results for oxide on crack tip from 5S sample [at%]

Element	Point 1	Point 2
C	6.58	5.81
O	42.58	39.71
Si	13.75	21.36
Cr	7.72	9.12
Mn	0.60	0.61
Fe	27.02	21.40
Ni	1.76	1.99

However, the chemical composition of oxide on crack tip from 5S experiment is different with that of 2S experiment. The amount of major elements such as iron and chromium decreases compared to that of 2S sample, furthermore, the amount of silicon increases up to about 21 at%. Increasing DH concentration can change the diffusion rate of cation interstitial such as iron ion (Fe^{2+} , Fe^{3+}) and that also might change the diffusion rate of silicon ion as well, which may cause the shortening the crack initiation time.

4. Conclusion

To figure out dissolved hydrogen concentration effect on stress corrosion cracking resistance of sensitized 304L stainless steel, slow strain rate tests combining with direct current potential drop methodology were conducted. Each experiment was done in the simulated primary water chemistry condition changing dissolved hydrogen concentration; 25 cm^3/kg and 50 cm^3/kg respectively.

Comparing between measured potential drop and second order polynomial fitting curve, every case fits well with theoretical approach, and they show fluctuated potential drop after certain elapsed hours as well. To find the exact moment when crack initiated, normalizing process was done.

When the dissolved hydrogen concentration increases from 25 cm^3/kg to 50 cm^3/kg , crack initiated faster than before; 361 hours to 261 hours. This crack initiation time change might be caused by diffusion rate of ion depending on the dissolved hydrogen concentration. According to the results of chemical composition measurement, the oxide loses iron and chromium portion and gets more silicon inside when the dissolved hydrogen concentration increases. This might affect the stress corrosion crack initiating mechanism on sensitized 304L stainless steel.

ACKNOWLEDGEMENT

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