Cold Working Effect on Stress Corrosion Cracking Behavior of 316L Stainless Steel in Chloride-contained Primary Water Environment

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1. Introduction

Austenitic stainless steel has been used widely in pressurized water reactor (PWR) primary circuit because it is corrosion-resistive material to primary water environment. Especially, heater sleeve material of pressurizer, which is exposed to very high temperature, consists of 316L stainless steel. Heater sleeve of pressurizer should not be cracked during the operation theoretically though, however, some issues related with stress corrosion cracking (SCC) on heater sleeve has been reported. To maintain the integrity and the economic feasibility of nuclear power plant, SCC phenomenon on 316L stainless steel heater sleeve material should be investigated.

There are several possible causes for SCC on heater sleeve of pressurizer, such as microstructural effect and water-chemical effect. To fix heater sleeve tightly to spacer grid of pressurizer, 'swaging' process is used to be conducted which is a kind of cold working. Corrosion resistance of swaged material might get worse because cold working process can change phase distribution and, furthermore, grain properties.

The other effect, in point of water chemistry, is abnormal ion inflow. According to the PWR primary water chemistry guidelines reported by the Electric Power Research Institute (EPRI) [1], the amount of abnormal ion such as chloride, fluoride, and sulfate is strictly controlled periodically. One of the abnormal ions, chloride, might be a nominee for SCC cause of heater sleeve since chloride can be concentrated in crevice region between spacer grid and heater sleeve.

Even though several preceding research have been conducted to figure out the cold working effect and the chloride influence on SCC behavior of stainless steel, their combined effect has not been investigated so far. Some studies dealt with their effect together, however, it is hard to note that they represented SCC behavior of heater sleeve because they increased dissolved oxygen level as well [2]. Therefore, in this study, chloride induced stress corrosion cracking (CISCC) behavior in primary water environment has been investigated using solution annealed and cold worked 316L stainless steel samples.

2. Experimental

This section describes the experimental setup for SCC experiment in chloride-contained primary water environment using solution annealed and cold worked 316L stainless steel U-bend samples.

2.1 Abnormal primary water environment

Test solution that can simulate normal primary water environment nearby the heater sleeve of pressurizer was set as following the PWR primary water chemistry guideline [1].

Chloride ion might be flowed into the primary circuit by two different ways. The one is sea breeze exposure during plant construction period. And the other one is seawater inflow through condenser from tertiary circuit of power plant during the operation period. The point is that these possible sources start from seawater. Therefore, it can be noted that sodium chloride (NaCl), the major constituents of seawater according to the standard practice for preparation of substitute ocean water ASTM D1141-98 [3], is appropriate to simulate real occasion.

Table I: Chemical Composition of Substitute Ocean Water ASTM D1141-98 [3]

Compound	Concentration [g/L]	Compound	Concentration [g/L]
$NaCl$	24.53	$SrCl_2$	0.025
$MgCl_2$	5.2	NaF	0.003
Na_2SO_4	4.09	$Ba(NO_3)_2$	0.0000994
$CaCl_2$	1.16	$Mn(NO_2)_2$	0.000034
KCl	0.695	$Cu(NO_3)_2$	0.0000308
$NaHCO_3$	0.201	$Zn(NO_3)_2$	0.0000096
KBr	0.101	$Pb(NO_3)_2$	0.0000066
H_3BO_3	0.027	$AgNO_3$	0.00000049

As aforementioned, the concentration of chloride ion is strictly controlled not to exceed 1.5 ppm during the normal operation period following guidelines [1]. But, when some abnormal occasion occurs such as seawater inflow through tertiary circuit, the impurities might come into the primary circuit eventually. So that, the measured data of chloride concentration in secondary circuit, especially inside of steam generator, could be a good reference to set the chloride concentration of abnormal primary water environment. According to the preceding research, the average chloride concentration in Surry 2 steam generator was measured about 5.28 ppm [4]. In conclusion, chloride ion injection into the test solution was done by using 5 ppm NaCl in this study. The detailed experimental conditions are listed as below table.

Table II: Experimental conditions for normal primary water environment except dissolved hydrogen concentration

Pressure [bar]	Temperature [℃]	B [ppm]	Li [ppm]	DO [ppb]	NaCl [ppm]
155	360	1200	2.2	< 5	5

2.2 Material

316L stainless steel mock-up samples were prepared for SCC experiment. Below table shows the chemical composition of the raw material.

Table III: Chemical composition of 316L stainless steel [wt%]

Fe	Cr	Ni	C	Mn
Bal.	16.57	9.83	0.028	1.26
Mo	**Si**	**P**	**S**	**W**
2.04	0.53	0.031	0.001	0.064

Swaging can change microstructure of material, and this affects mechanical property of the material as well such as hardening. Therefore, yield stress might be a valid criterion to identify the level of cold working. To simulate swaging effect of the heater sleeve, mock-up samples were cold rolled with various reduction rate from 13.3 % to 21 %. Tensile specimen fabrication and yield stress measurements were done by following ASTM E8/E8M respectively [5]. According to the data, the yield stress of swaged heater sleeve is about 690 MPa which is similar with the yield stress of cold-worked sample whose reduction rate is 21 %. The yield stress of simulated material is about 705 MPa.

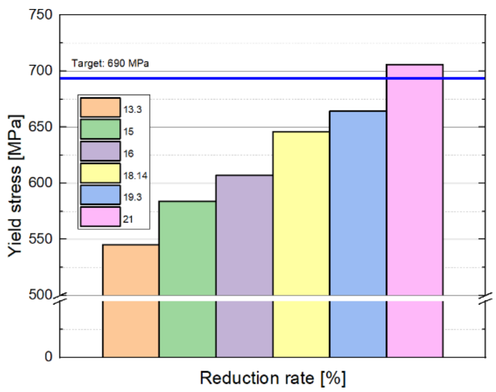

Fig. 1. Yield stress measurement of cold worked samples in various reduction rate

Yield stress of solution annealed heater sleeve and solution annealed raw material was compared as well for the data of control group. The yield stress of solution annealed heater sleeve is about 256 MPa and that of solution annealed raw material is about 263 MPa respectively.

2.3 Sample

U-bend type samples were fabricated for this study using cold worked material whose reduction rate is 21 %, and solution annealed material. The dimension of bar sample is 7 mm width, 70 mm length, and 2 mm thickness and the radius of U-bend is 7.65 mm, thus, the strain on the outer surface of U-bend is about 13 %. The outer surface of every U-bend sample was polished up to 1 μm before bending.

2.4 Experimental facility

Austenite stainless steel is known as vulnerable to corrosion when it is exposed to chloride-contained primary water. So that, experimental facility should be designed to endure the test conditions. To overcome this problem, not only autoclave but every component of static cell was fabricated with Incoloy 800H material which has better corrosion resistance than stainless steel. Some parts which can not be made with nickel-based alloy were coated with nickel to minimize contact area of stainless steel to test solution.

2.5 Analysis

Microstructure of cold worked and solution annealed raw material was observed by using scanning electron microscope (SEM). The phase distribution and the grain boundary characteristic of raw material were analyzed by using electron backscatter diffraction (EBSD). U-bend sample surface was observed with stereoscope every 100 hours of SCC experiment.

3. Result

3.1 Loop data

U-bend samples were exposed to the test solution for 100 hours and then put them out from the autoclave to check whether crack initiated on the surface or not. This process has been repeated up to 1,200 hours so far and the test will be continued until 2,000 hours. Below graph shows the loop data of a set of 100 hours experiment. According to the data it can be noted that test environment had been maintained stably for 100 hours.

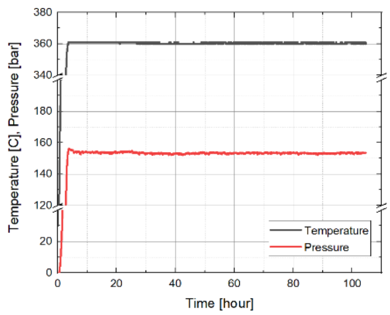

Fig. 2. Loop data of experiment conducted for 100 hours

3.2 Microstructure of raw material

Microstructure of raw materials was observed after polishing their surface up to 1 μm level using diamond suspension. Microetching was done in accordance with ASTM E407-07 [6]. As the below figures show that the average grain size of cold worked sample decreases from about 45.5 μm to 33.3 μm compared to solution annealed sample. Furthermore, twin boundaries which are weak to corrosion were observed on cold worked sample surface, but not from solution annealed sample. These changes, grain size decrease and twin boundaries formation, might affect the corrosion resistance of the material.

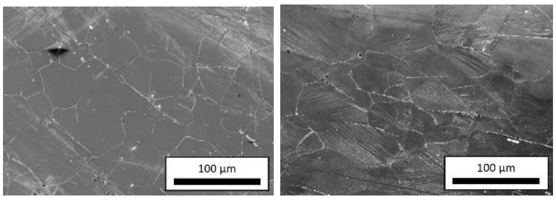

Fig. 3. Microstructure observation for (left) solution annealed, (right) cold worked raw material

EBSD observation was done to figure out the phase distribution, the coincident site lattice (CSL) boundary especially Σ3 boundary (or twin boundary), and kernel average misorientation (KAM) of each material. From the result of phase distribution measurement, portion of austenite phase decreases from about 82.3 % to 69.8 % when the sample undergoes cold working, in other words, martensite phase increases from 17.7 % to 30.2 %. This might be caused by cold working process, and this could affect corrosion resistance of the material. The CSL boundary fraction measurement shows that the fraction of twin boundary increases about 1.36 times when the sample cold rolled. KAM level which can represent the amount of residual strain of material also increases from 2.20 to 2.89 when sample cold worked. This change obviously affected by deformation might increase residual stress of material as well, so that it can be concluded that cold working makes material weak to corrosion. According to those results, cold working could make material susceptible to SCC.

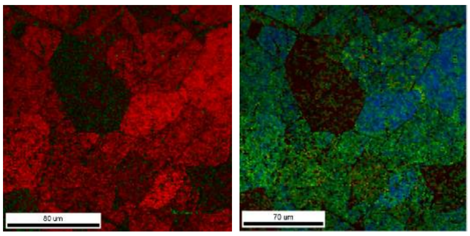

Fig. 4. EBSD observation for solution annealed sample (left) phase distribution, (right) KAM measurement

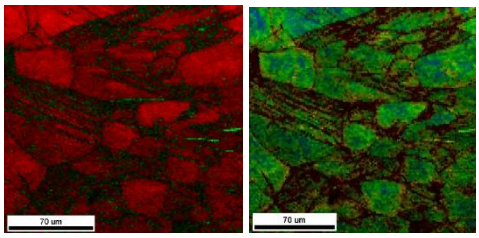

Fig. 5. EBSD observation for cold worked sample (left) phase distribution, (right) KAM measurement

Table IV: Average data from EBSD observation

	Solution annealed	Cold worked
Austenite	0.823	0.698
Martensite	0.177	0.302
Σ3 boundary	0.0275	0.0375
KAM	2.20	2.89

3.3 Microstructure of U-bend sample

Surface observation on apex area of U-bend samples after SCC experiment for 1,200 hours was conducted by using stereoscope. Observation has been done every 100 hours, but any crack did not occur so far. Therefore, the experiment will be continued until 2,000 hours and whether crack occurs or not will be observed repeatedly every 100 hours.

Although any crack did not occur, it is expected that oxide formation on cold worked sample seems have different tendency compared with solution annealed sample because of its color. If oxide layer formation such as chromium oxide, inner oxide which has great passivity for corrosion, was disturbed by combination of cold working and chloride environment, SCC behavior might be affected significantly on the material. Exact chemical composition of oxide will be measured in further study.

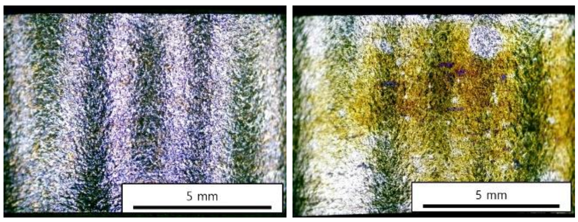

Fig. 6. U-bend surface observation on apex area of (left) solution annealed, (right) cold worked sample

4. Conclusion

Cold working effect on stress corrosion cracking behavior of 316L stainless steel in chloride-contained primary water environment was investigated in this research. Samples were prepared to simulate swaged heater sleeve material of pressurizer in primary circuit of pressurized water reactor by conducting cold rolling.

Cold working affects material properties in point of mechanical and microstructural aspects.

The hardening effect occurs when the material undergoes cold rolling process. The yield stress of material increases about 2.68 times higher than solution annealed material. This might be caused by reduction of grain size, in other words increase of grain boundary fraction, since grain boundary can do a role as barrier to deformation such as slip. According to the results of electron backscatter diffraction (EBSD) observation, cold working changes phase distribution of the material and increase the portion of twin boundary and raise the level of residual stress as well. This increase in residual stress results in volume expansion and compression stress acting as a result of austenite phase transformation into martensite. Therefore, since martensite affects the residual stress, a result of the presence of a greater residual stress appears in the cold-rolled specimen in which martensite is more present. In addition, the increase in the deformation zone and twin structure due to cold rolling causes local hardening and promotes intergranular oxidation near the grain boundaries of the material. Since the twin structure serves to promote the diffusion of oxygen, it affects SCC. Therefore, the cold rolled specimen expected that will be more vulnerable to SCC.

U-bend surface observation after stress corrosion cracking experiment for 1,200 hours did not show any crack on the apex of sample surface, however, the oxide formation on the sample seems to be affected by the combination of cold working and chloride environment. The martensite produced by cold rolling has higher electrochemical reactivity and may corrode at a lower electrochemical potential than the corresponding austenite when exposed to sulfuric acid/hydrochloric acid solution. Therefore, cold rolled specimens with a higher martensite ratio than solution annealed specimens are expected to be vulnerable to SCC.

However, the exact chemical composition measurement will be done in further study to support the correlation between cold working and chloride effects.

ACKNOWLEDGEMENT

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