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316 NG 不锈钢和合金 800 在含有硫酸盐及氯化物的高温水中应力腐蚀破裂

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摘　要

用 SSRT 方法研究秦山 PWR 核电站主管道焊接的 316 不锈钢和蒸汽发生器传热管 Incoloy-800 合金的应力腐蚀破裂行为，应变速率均为 4.2×10^{-6}/s。316 SS 的试验温度为 315℃，介质为模拟离子交换树脂热分解产物的酸性硫酸盐溶液（几个 ppm 至 1000 ppm SO_4^{2-}）；Incoloy-800 的试验温度为 270℃，介质为模拟离子交换树脂的热分解产物的酸性硫酸盐溶液（几个 ppm 至 1000 ppm SO_4^{2-}）以及硫酸盐和氯化物组合的溶液（1000 ppm SO_4^{2-}，2～1000 ppm Cl^-）。结果表明，316 SS 在上述介质中对穿晶应力腐蚀破裂敏感，Incoloy-800 合金在上述介质中对应力腐蚀破裂不敏感。

STRESS CORROSION CRACKING OF 316 SS AND INCOLOY-800 IN HIGH TEMPERATURE AQUEOUS CONTAINING SULFATE AND CHLORIDE

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ABSTRACT

The stress corrosion cracking (SCC) susceptibility of 316 stainless steel (SS) which was welded for primary pipe and Incoloy-800 (shotpeening) for steam generator (SG) tube have been investigated by a slowstrain rate test (SSRT) at a strain rate of 4.2×10^{-6}/s. Tests were conducted at 315℃ for 316 SS and 270℃ for In-800 in the oxygenated simulated resin intrusion environment (acidic sulfate). Tests of the effect of combination of SO_4^{2-} and Cl^- on SCC of Incoloy-800 were also carried out. The results indicate that Incoloy-800 is unsusceptible to SCC either in the environment with SO_4^{2-} (from a few ppm to 1000 ppm, pH 3～4) or in the environment of combination of SO_4^{2-} (1000 ppm) and Cl^- (from 2 to 1000 ppm). The 316 NG SS is susceptible to transgranular stress corrosion cracking (TGSCC) in the resin intrusion environment with SO_4^{2-} in high temperature water.

INTRODUCTION

In recent years, close attention has been paid to decomposition of intruded resins and the impurities added into the coolant of boiling water reactor (BWR) and pressurized water reactor (PWR) nuclear power plants[1~4]. The purpose of these works are to determine the types and concentrations of chemical species resulting from intrusive resin and the effects of the most important chemical species on SCC and other corrosion behavior of SS and Ni base alloy (Inconel-600 and Inconel-690). However, the SCC behavior of welded 316 SS in primary side and Incoloy-800 in secondary side for PWR environment containing sulfate or chloride has not been investigated extensively. In this paper, the authors utilized SSRT method to evaluated SCC behavior of 316 SS and Incoloy-800 in 315℃ and 270℃ aqueous containing sulfate or chloride as final thermal decomposition product of intruded resins. The 316 SS (casting) and Incoloy-800 (O. D. shotpeening) have been used in primary pipe and SG tube of QinShan NPP PWR in China respectively.

1 EXPERIMENTAL PROCEDURE

Materials and Specimens. The test materials are commercially produced as nuclear grade of 316 SS and Incoloy-800. The chemical composition of the materials is presented in Table 1 (actual composition). The specimens of 316 SS for SSRT were fabricated from welded primary pipe sections include heat-affected zone (HAZ). The welded primary pipe sections were prepared from casting pipe (φ850 ×75) and forging as nozzle (φ850×75) welded together used appropriate SS filler rod (ER 316L, E 316). The welded pipe was used for checking welded procedure and evaluation of technology in the field of Qinshan NPP. The test specimens were machined as tensile type piece, with a gauge length of 20 mm and thickness of 2 mm. The Incoloy-800 (φ22×1. 27 mm, OD shotpeening) is from Sandvik Co. The tensile test specimens were fabricated along direction of longitudinal tube, it has a gauge length of 20 mm, width of 4 mm and thickness of 1. 27 mm (equal to the tube wall).

Table 1 Chemical Composition of the Test Alloys

Element wt%	316 SS(forge) SA182F 316 *	316 SS(cast) * SA451CPF8M	Incoloy-800 * *
C	0.030	0.040	0.010~0.020
Mn	1.730	1.500	0.55~0.67
Si	0.550	1.500	0.41~0.57
P	0.020	0.040	0.015
S	0.003	0.010	0.015
Ni	10.73	9.00~12.00	33.30~34.20
Cr	17.12	18.00~21.00	21.66~22.55
Mo	2.300	2.00~3.00	—
Cu	0.060	0.100	0.012~0.038
Co	0.030	0.080	0.016~0.040
Al	—	—	0.15~0.042
Ti	—	—	0.39~0.52
N	—	—	0.010~0.016
Fe	Balance	Balance	Balance

* welding couple, from F. A. M. Co., France

* * cold draw then shotpeening (OD), Sandvik Co.

Apparatus and Methods. The SSRT method has been used to research the susceptibility of metal to SCC. This tester is named SERT-5000 DP 9H made in Toshin Kohyo Co. Ltd in Japan. The experiment conditions are listed in Table 2 and 3.

Most of specimen tests were performed in the environment with certain partial pressure oxygen (0.1 MPa). Each tensile specimen was held by grips in a 1.9 liter autoclave filled with predetermine static solution. The autoclave was heated up to temperature with a approximate speed of 70℃ per hour. After the autoclave reached preset temperature, the specimen was tightened. Tension test was done at sensitive strain rate of 4.2×10^{-6}/s for SCC.

Test Data Acquisition and Processing. Data of SSRT are collected automatically by microcomputer and X-Y recorder at the same time. Data of SSRT are also processed by microcomputer. The susceptibility index of SCC (Ig) is based on normalization treatment of variety of rupture energy in inert nitrogen gas and aggressive solution after SSRT[9]. The rupture energy is expressed by area under stress-elongation curve. Value of Ig is from zero to unity that means susceptibility degree of SCC increasing step by step, Ig is defined was following equation:

$$I_g = 1 - \frac{A_w}{A_n}$$

where

A_w —— area under stress-elongation curve in agressive water

A_n —— area under stress-elongation curve in inert nitrogen

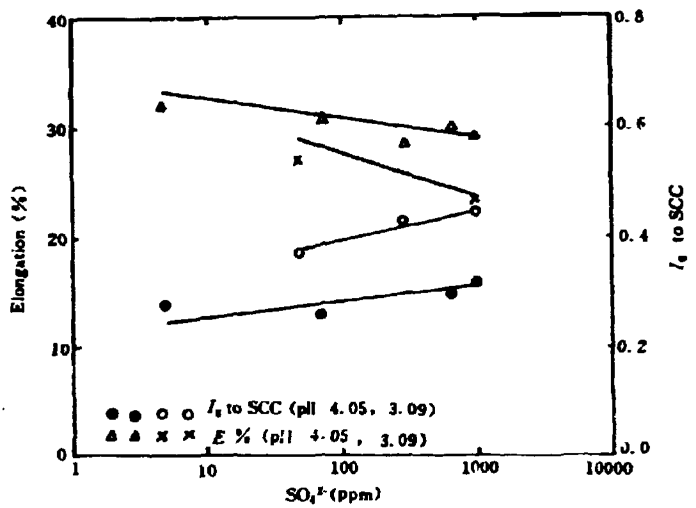

Fig. 1 Effects of SO_4^{2-} on SCC of 316 SS,

315℃; pH 3.09, 4.05; O_2 partial pressure 0.1 MPa; strain rate 4.2×10^{-6}/s

All fractured specimen surface after SSRT are examined by SEM to compare the fractographs of specimens in aggressive water with that in inert nitrogen.

2 RESULTS

Effect of SO_4^{2-} on SCC of 316 SS. The effects of different concentration of SO_4^{2-}(as Na_2SO_4) on SCC of 316 SS are listed in Table 2 and plotted in Fig. 1. The Ig of sensitivity to SCC of 316 SS is obviously increasing as SO_4^{2-} increases. The elongation is obviously reducing as SO_4^{2-} increases in Fig. 1. From Table 1, SCC was observed except the specimens test run in neutral aqueous (pH 6.2, SO_4^{2-} 1000 ppm) and nitrogen. The acid sulfate environment will cause large reduction in the strength, ductility and failure time of the SSRT specimen camparing with the nitrogen and neutral solution containing SO_4^{2-} of 1000 ppm. SEM examination of tested specimens revealed that SCC was initiated along the entire length of the gauge section of most test specimens. The TGSCC on fracture surface was observed as shown Fig. 2. It looks like that welded 316 SS was seriously sensitive to TGSCC at high temperature in slight acidwater containing a few ppm SO_4^{-2}. It is important in the safety aspect that resin intrusion coolant could be crucial role for the environmental degradation of SS as the form of SCC.

Table 2 SSRT Results in Simulated Intrusion Environment for 316 SS at 315℃, $\dot{\varepsilon}=4.2\times10^{-6}$/s

Test Environment			σ max * *	Elongation	Time to	I_g	Type of
SO_4^{2-}	pH	O_2 * (MPa)	(MPa)	(%)	Failure (h)	to SCC	Failure
48	3.09	0.1	452	27.25	18.17	0.369	TGSCC
300	3.09	0.1	445	28.25	18.83	0.426	TGSCC
1000	3.09	0.1	446	23.45	15.63	0.448	TGSCC
1000	3.09	8 ppm	458	24.05	16.03	0.429	TGSCC
4.8	4.05	0.1	438	31.90	21.27	0.294	TGSCC
72.6	4.05	0.1	461	31.30	20.73	0.256	TGSCC
679.8	4.05	0.1	445	29.80	19.87	0.313	TGSCC
1000	4.05	0.1	455	29.15	19.43	0.330	TGSCC
10	5.07	0.1	446	29.80	19.88	0.299	TGSCC
100	5.07	0.1	453	26.75	17.83	0.374	TGSCC
1000	6.20	0.1	479	34.85	23.23	0.140	Ductile
Nitrogen			501	41.28	27.52	—	Ductile

* oxygen partial pressure

* * maximum stress before failure

Effect of pH of sulfate aqueous on SCC of 316 SS. In Fig. 3 and Table 2, Ig values for 316 SS in 315℃ water containing 1000 ppm SO_4^{2-} clearly increased when pH value changed from neutral to acid, enlongation clearly reduced with pH decreasing. Moreover, in test run with neutral aqueous (pH 6.2), even containing 1000 ppm SO_4^{2-}, 316 SS specimens showed that Ig was close to zero. These results mean that there is no SCC of 316 SS in 315℃ neutral aqueous containing sulfate. According to prior works[1,7], the cation resin reacted with high purity water in high temperature to produce primary acid sulfate for the cationic resin. If large amount of resin intruded and then decomposed in occasional case, SCC will occured for SS in stagnant areas.

Effect of O_2 on SCC of 316 SS. Table 2 shows that Ig values for 316 SS slightly increased from 0.43 to 0.443 in 315℃ water containing 1000 ppm SO_4^{2-}, pH 3.09 when oxygen increased from 8 ppm to 0.1 MPa oxygen partial pressure. It seems that there is a very slight effect of oxygen on SCC behavior of 316 SS under this condition.

Effect of SO_4^{2-} on SCC of Incoloy-800. Alloy Incoloy-800 is unsusceptible to SCC in several concentrations of acidic sulfate solution at 270℃. Results of Table 3 and Fig. 4 indicate that values of susceptibility index Ig of Alloy Incoloy-800 in solution with SO_4^{2-} from 4.8 ppm to 1000 ppm and pH from 2 to 4 at 270℃ are close to zero, and elongations in above environment are almost no reduction comparing with the inert environment. There is no cracking on surface along the entire length of the gauge section after SSRT, no evidence of brittle fracture on the surface of all tested specimens after examination by SEM, and the fracture surfaces are entirely ductile.

Fig. 2 SEM Fractographs of 316 SS in environment at 315℃

pH 4.05, O_2 partial pressure 0.1 MPa, strain rate 4.2×10^{-6}/s (A) SO_4^{2-} 11.6 ppm, 40×, and (B) the upper left area, 200× (C) SO_4^{2-} 4.8 ppm, 720×

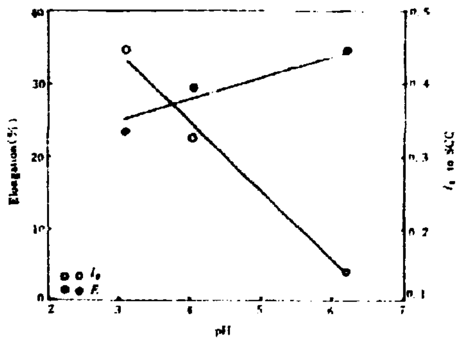

Fig. 3 Effect of pH on Elongation and Susceptibility I_s to SCC of 316 SS

315℃; SO_4^{2-} 1000 ppm; O_2 partial pressure 0.1 MPa; strain rate 4.2×10^{-6}/s

Effect of combination of SO_4^{2-} and Cl^- on SCC of Incoloy-800. Table 3 and Fig. 5 present the results of SSRT run in the environment simulating the secondary side of SG; this test series concentrated on characterizing the effects of combined SO_4^{2-} and Cl^- concentration on SCC of Incoloy-800. The results indicate that the fracture of Incoloy-800 is not sensitive to the concentrations of the combined SO_4^{2-} and Cl^-. All the values of I_s of Incoloy-800 are close to zero and values of maximum stress before fracture are nearly equal that of the stress in inert nitrogen. Examination of the fracture surfaces of failed specimens shows only a ductile failure. In-800 is unsusceptible to SCC in acidic sulfate solution (1000 ppm SO_4^{2-}) with different concentration of Cl^- (from 2 ppm to 1000 ppm) at 270℃. Above results clearly indicate that Alloy Incoloy-800 for SG tube are unsusceptible to SCC either in acidic sulfate environment or in the combined acidic sulfate and chloride. According to the author's prior work[10], Incoloy-800 with shotpeening (OD) appeared SCC in the environment containing 5 ppm Cl^- with 0.1 MPa partial pressure of oxygen at 260℃ by SSRT. It means that Incoloy-800 would be considerably susceptible to SCC caused by the certain combined Cl^- and O_2 at 260℃. At present, however, same Incoloy-800 is not susceptible to SCC even in acidic sulfate solution with Cl^- up to 1000 ppm and 0.1 MPa O_2 at 270℃. It appears that sulfate may take an inhibitory effect on SCC induced by chloride. However, more investigations are needed to confirm this conclusion.

Table 3 SSRT Results in Simulated Intrusion Environment for In-800 at 270℃, $\dot{\varepsilon}=4.2\times10^{-6}$/s

Test Environment				σ max * *	Elongation	Time to	I_s	Type of
SO_4^{2-}	Cl^- (ppm)	O_2 * (MPa)	pH	(MPa)	(%)	Failure (h)	to SCC	Failure
480	—	0.1	2.07	585	31.25	20.83	0.042	Ductile
1000	—	0.1	2.07	580	34.75	23.17	0.000	Ductile
48	—	0.1	3.09	582	34.95	23.30	0.000	Ductile
300	—	0.1	3.09	596	33.50	22.33	0.000	Ductile
1000	—	0.1	3.09	581	33.55	22.37	0.000	Ductile
4.8	—	0.1	4.05	601	33.60	22.40	0.000	Ductile
11.6	—	0.1	4.05	597	33.35	22.23	0.000	Ductile
72.6	—	0.1	4.05	583	33.60	22.40	0.000	Ductile
679.8	—	0.1	4.05	576	34.10	22.73	0.000	Ductile
1000	—	0.1	4.05	588	31.40	20.93	0.036	Ductile
1000	2	0.1	3.13	565	31.95	21.30	0.074	Ductile
1000	5	0.1	3.13	598	32.35	21.50	0.000	Ductile
1000	10	0.1	3.13	551	34.80	23.20	0.031	Ductile
1000	20	0.1	3.13	589	31.75	21.17	0.023	Ductile
1000	50	0.1	3.13	593	33.60	22.40	0.000	Ductile
1000	100	0.1	3.13	575	35.50	23.67	0.000	Ductile
1000	1000	0.1	3.13	597	32.05	21.37	0.000	Dctile
Nitrogen				589	32.55	21.70	—	Ductile

* oxygen partial pressure

* * maximum stress before failure

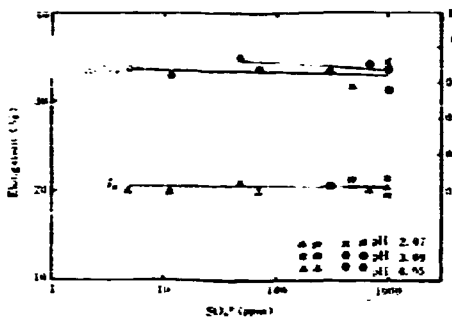

Fig. 4 Effect of SO_4^{2-} on elongation and susceptibility I_s to SCC of Incoloy-800

270℃; O_2 partial pressure 0.1 MPa; pH 2.07, 3.09, and 4.05; strain rate 4.2×10^{-6}/s.

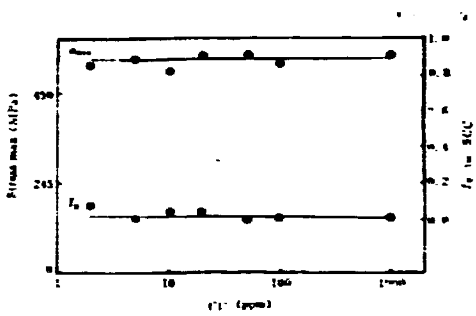

Fig. 5 Effect of Cl^- on stress and susceptibility I_s to SCC of Incoloy-800 270℃

SO_4^{2-} 1000 ppm; pH 3.13; O_2 partial pressure 0.1 MPa; strain rate 4.2×10^{-6}/s.

The secondary water circuits of PWRs may contain of sulfate, chloride and other impurities. Those impurities may arise through slippage from ion exachange beds, thermal decomposition of resin fines carried forward into SG, or from leakage of cooling water containing the impurities. Although the levels of sulfate and chloride can be controlled by an ion exchange plant and by blowdown, the impurities species are concentrated at heat transfer surface very efficiently such as tubesheet and support plate crevices, hence, there is a possibility of concentrating high level impurities in particular at these areas[1]. The SCC or other kind of corrosion behavior of SG tube materials in above faulted environment should be investigated in the future.

3 SUMMARY

In the oxygenated simulated resin intrusion environment (0.1 MPa O_2 partial pressure; pH 3.09, 4.05; SO_4^{2-} 4.8 ppm to 1000 ppm) at 315℃, welded 316 SS exhibits TGSCC at a strain rate of 4.2×10^{-6}/s.

In the oxygenated simulated resin intrusion environment (0.1 MPa O_2 partial pressure; pH3.09, 4.05, 6.20; SO_4^{2-} 1000 ppm) at 315℃, welded 316 SS exhibits TGSCC at a strain rate of 4.2×10^{-6}/s except in the solution with pH 6.2.

In the oxygenated simulated resin intrusion environment (pH 3.09; SO_4^{2-} 1000 ppm; 8 ppm O_2, and 0.1 MPa partal pressure) at 315℃, welded 316 SS exhibits TGSCC at a strain rate of 4.2×10^{-6}/s.

In the oxygenated simulated resin intrusion environment (0.1 MPa O_2, pH 2.07, 3.09, and 4.05; SO_4^{2-} 4.8 ppm to 1000 ppm) at 270℃, Incoloy-800 with shotpeening (OD) is unsusceptible to SCC at a strain rate of 4.2×10^{-6}/s.

In the oxygenated simulated resin and chloride intrusion environment (0.1 MPa O_2; pH 3.13; SO_4^{2-} 1000 ppm; Cl^- 2 ppm to 1000 ppm) at 270℃, Alloy Incoloy-800 with shotpeening (OD) are unsusceptible to SCC at a strain rate of 4.2×10^{-6}/s.

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