

## IGSCC GROWTH RATE OF SENSITIZED TYPE 304 STAINLESS STEEL IN SIMULATED BWR ENVIRONMENT

E. Kikuchi<sup>1</sup>, M. Itow<sup>2</sup>, H. Sakamoto<sup>2</sup>, J. Kujiya<sup>1</sup>, M. Kitamura<sup>3</sup>

<sup>1</sup>Hitachi Ltd.

<sup>2</sup>Toshiba Corporation

<sup>3</sup>Tokyo Electric Power Company

### 1. Introduction

Recently, reactor water improvement, such as reducing dissolved oxygen concentration in reactor water, has been considered to be a good SCC countermeasure for structural materials in BWR plants. Hydrogen addition to reactor feedwater, known as hydrogen water chemistry (HWC), has been largely applied to the primary stainless steel piping systems of commercial BWR plants outside Japan.

On the other hand, in one study on intergranular stress corrosion cracking (IGSCC) of sensitized Type 304 stainless steel carried out from the viewpoint of dissolved oxygen concentration and conductivity in a simulated BWR environment, a critical potential was found below which SCC did not occur and this value depended on both conductivity and dissolved oxygen concentration. That is, the critical corrosion potential was lower when the conductivity was high over a period of time (such as during startup) and was higher when the conductivity was low. Therefore, it is expected that reducing dissolved oxygen and conductivity should be suitable SCC countermeasures from the view point of water chemistry. In order to establish the water chemistry guidelines for HWC application, it is important to clarify the effects of corrosion potential and conductivity on the crack growth rate in BWR environments.

Thus far, there have been few reports on the relation of crack growth rates and environments that simulated content of hydrogen peroxide, dissolved oxygen, dissolved hydrogen, and radiolytic species at various locations in BWR plants.

The aim of the present work was to study the effects of corrosion potential and low conductivity on the SCC behavior of sensitized Type 304 stainless steel. Results are summarized on the effect of reducing corrosion potential and conductivity on SCC growth rates of sensitized Type 304 stainless steel under test conditions which simulated the respective steady-state concentrations of radiolytic species at various locations in normal water chemistry (NWC) and HWC.

### 2. Experimental methods

#### 2.1 SCC test

A cold-rolled alloy plate of Type 304 stainless steel was used. Composition is given in Table 1. The alloy initially was furnace sensitized at 620°C for 24 h. After completion of the heat treatment, the plate was machined into a standard compact tension (CT) specimen. Sensitization

levels were measured using the electrochemical -potentiodynamic reactivation technique (EPR:JIS G 0580). The EPR value for the sensitized specimens was 39.2 %. Immediately before the tests, the specimen was polished with emery paper, and finally degreased with acetone.

The test facility is shown schematically in Figure 1. The water feed consisted of a preheated stream of pure, degassed water to which were added small flows of water containing oxygen, hydrogen and impurities to be tested. The dissolved oxygen concentration adjustment was made in the mixing tank. An automatic control system was employed there to switch the solenoid valve in synchronization with the dissolved oxygen concentration monitoring system and to bubble in alternatively nitrogen gas and oxygen gas. The hydrogen peroxide solution was fed directly into the autoclave through an injection nozzle without preheating. Concentration adjustment of the hydrogen peroxide was made by changing the delivery ratio between the mixing water tank and chemical solution tank.

The experiments were performed to determine crack growth rates under constant loading in 288°C water containing dissolved oxygen, dissolved hydrogen and hydrogen peroxide. The stress intensity factor was  $K=100\text{kgf}/\text{mm}^{1.5}$ . Crack lengths and their growth rates were determined by the reversing DC potential drop method. The crack lengths obtained from these measurements were compared with those measured on fracture surfaces. The test environments were high-purity deionized water with <10 to 440 ppb dissolved oxygen, 0 to 570 ppb hydrogen peroxide and 14 to 150 ppb dissolved hydrogen. The hydrogen peroxide concentration was determined colorimetrically, using phenolphthalein as indicator. About 100 ml aliquots were withdrawn for analysis from the reaction solution both at the loop inlet and outlet. The conductivity was controlled at 0.1 $\mu\text{S}/\text{cm}$  or 0.3 $\mu\text{S}/\text{cm}$  by sodium sulfate addition. The flow rate through the test section was 0.0354-0.233 cm/s.

### *2.2 Corrosion potential measurement*

An electrode made of Type 304 stainless steel was used which was heated the same as the material described in Section 2.1. The plate was cut to 18mm w  $\times$  25mm l  $\times$  2mm t and sensitized (620°C, 24 h).

To measure the electrochemical potential, an silver-silver chloride internal electrode or silver-silver chloride external electrode was used. A Teflon tube was used to insulate the specimen and autoclave. The solution inside the reference electrode was 0.1 kmol/m<sup>3</sup> KCl. The reference electrode was used for each experiment as described in Section 2.1 and the potential values were converted to the normal hydrogen scale.

The effect of corrosion potential on the crack growth rates of the same heat(as described in Section 2.1) was evaluated in the same test environment.

## **3. Results and discussion**

The experiments described in this paper were performed under a constant loading SCC test in the simulated NWC condition with <200 to 440ppb dissolved oxygen, 100 to 150 ppb hydrogen peroxide and 20 to 150 ppb dissolved hydrogen and in the simulated HWC condition with  $\leq$ 100 dissolved oxygen, and 20 to 50 ppb dissolved hydrogen.

A plot of crack length vs. time for the specimen tested under constant loading using the DC potential drop method at conditions which gave changes from NWC to HWC is shown in Figure 2. These data were converted into hydrogen peroxide concentration in the SCC test section based on hydrogen peroxide decomposition. In NWC with 440ppb dissolved oxygen, 150 ppb hydrogen peroxide and 50 ppb dissolved hydrogen, the crack length increased with passage of time, but in HWC with <1ppb dissolved oxygen and 150 ppb dissolved hydrogen, SCC growth did not occur during the entire 350 hours. The appearance and scanning electron micrographs of a CT specimen slit apart mechanically after the test are shown in Figure 3. The crack length was measured on the cross section of the samples by optical microscopy and scanning electron microscopy. The fracture mode observed under the NWC condition indicated typical intergranular cracking. In this case, the crack length and the crack growth rate for IGSCC were determined as 0.68 mm and  $1.9 \times 10^{-7}$  mm/s, respectively.

The crack growth rates of sensitized Type 304 stainless steel performed by the test method mentioned above in simulated NWC and HWC environments for various combinations of hydrogen peroxide, dissolved oxygen, dissolved hydrogen and conductivity are shown in Table 2. It was

found that the crack growth rates were  $4.9 \times 10^{-8}$  to  $3.0 \times 10^{-7}$  mm/s at initial the stress intensity  $K=100\text{kgf/mm}^{1.5}$  in the simulated NWC. However, in situ reversing DC potential drop measurements and observed fractography of the CT specimens tested by the constant load method indicated no apparent crack growth during the entire 350 hours of loading in the hydrogen modified high temperature aqueous environment. The crack growth rate was found to be less than  $1 \times 10^{-9}$  mm/s in the simulated HWC condition containing  $<1$  ppb dissolved oxygen and 150 ppb dissolved hydrogen. Similarly, for water containing  $<100$  ppb dissolved oxygen and 50 ppb dissolved hydrogen, SCC growth did not occur during the entire 500 hours of loading in the hydrogen modified high temperature aqueous environment. The corrosion potentials of sensitized Type 304 stainless steel measured under the SCC test conditions are also included in Table 2. The corrosion potential was higher when the content of hydrogen peroxide and dissolved oxygen were high and was lower when the content of hydrogen peroxide and dissolved oxygen were low. Figure 4 shows relationships between crack growth rates of sensitized Type 304 stainless steel and the water quality in  $288^\circ\text{C}$  water. It was found that the crack growth rates correlate extremely with dissolved oxygen concentration and hydrogen peroxide concentration. Figure 5 plots relationships between crack growth rates, corrosion potential and conductivity. The crack growth rates decreased with decreasing corrosion potential and a critical potential below which SCC growth did not occur was less than about  $-200\text{mV}_{\text{SHE}}$ . Increasing the conductivity level from  $0.1\mu\text{S/cm}$  to  $0.3\mu\text{S/cm}$  increased crack growth rates somewhat. From the above, the alternative water chemistry known as hydrogen water chemistry that involves suppression of reactor water dissolved oxygen  $\leq 100$  ppb via hydrogen injection to the feedwater in conjunction with control of conductivity to  $\leq 0.1\mu\text{S/cm}$ , was found to be generally beneficial.

#### 4. Conclusions

The effects of corrosion potential and conductivity on the stress corrosion cracking (SCC) of Type 304 stainless steel have been studied by using fracture mechanics type standard CT specimens in simulated boiling water reactor environments at  $288^\circ\text{C}$ . Tests were performed under constant loading. Crack lengths and crack growth rates were determined by the reversing DC potential drop method. Results are summarized as follows.

1. It was found that the crack growth rates were  $4.9 \times 10^{-8}$  to  $3.0 \times 10^{-7}$  mm/s at the initial stress intensity  $K=100\text{kgf/mm}^{1.5}$  in simulated normal water chemistry. However, the crack growth rate was less than  $1 \times 10^{-9}$  mm/s in the simulated hydrogen water chemistry.
2. The crack growth rates decreased with decreasing corrosion potential and a critical potential below which SCC growth did not occur was less than about  $-200\text{mV}_{\text{SHE}}$ .
3. Increasing the conductivity level from  $0.1\mu\text{S/cm}$  to  $0.3\mu\text{S/cm}$  increased crack growth rates.
4. It was confirmed that hydrogen water chemistry gave the benefits in terms of prevention of stress corrosion cracking and found that the lowering the conductivity from  $0.3\mu\text{S/cm}$  to  $0.1\mu\text{S/cm}$  was more effective in terms of prevention of crack growth rates .

#### 5. Acknowledgment

This study was carried out in a joint study program of six Japanese BWR utility companies, two BWR plant vendors and 2 reactor component suppliers.

#### 6. References

- 1) W.J. Shack, et al.: Nuclear Engineering and Design 86,57(1985)
- 2) T.F. Kassner, et al.: Proceedings, Seminar on BWR Corrosion, Chemistry and Radiation Control, Oct.8-10, Palo Alto California, EPRI(1984)
- 3) L.G. Ljungberg: Proceedings, Seminar on BWR Corrosion, Chemistry and Radiation Control, Nov. 10-12, Palo Alto California, EPRI(1986)

Table 1 The chemical composition of Type 304 stainless steel in weight percent

Material	C	Si	Mn	P	S	Ni	Cr
Type 304	0.06	0.42	0.83	0.028	0.005	8.41	18.32

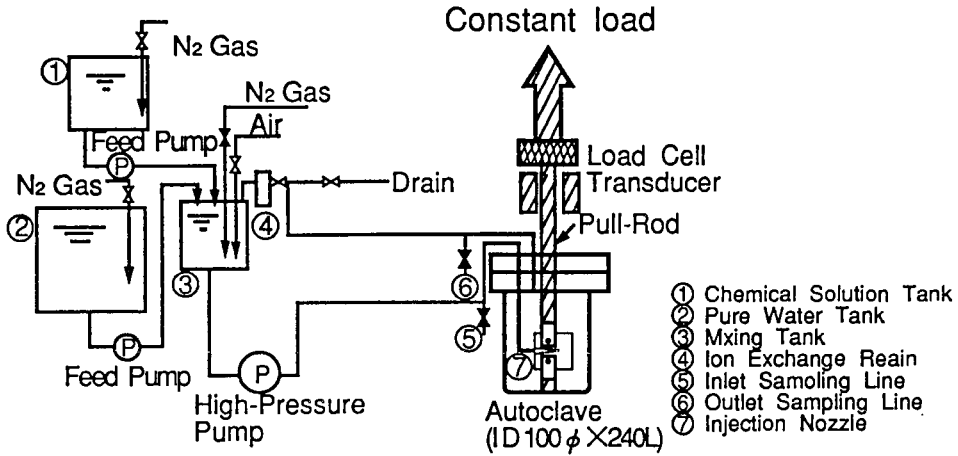


Figure 1 The experimental apparatus used for SCC test

Table 2 Effects of corrosion potential and conductivity on the crack growth rates of sensitized Type 304 stainless steel performed under constant loading at 288 °C in simulated normal water chemistry and hydrogen water chemistry environments containing hydrogen peroxide, dissolved oxygen and dissolved hydrogen

	Test condition				Crack growth rate (mm/sec)	Corrosion potential (mV <sub>SHE</sub> )
	O <sub>2</sub> (ppb)	H <sub>2</sub> O <sub>2</sub> (ppb)	H <sub>2</sub> (ppb)	Conductivity (μS/cm)		
HWC	<1	0	150	0.1	No SCC growth*	-630
				0.3	No SCC growth*	-650
	100				No SCC growth*	-210
NWC	50	20	50	0.1	1.2 × 10 <sup>-8</sup>	-90 ~ -80
				0.3	2.9 × 10 <sup>-8</sup>	-140 ~ -120
	0.1	1.3 × 10 <sup>-8</sup>		-50 ~ -40		
	0.3	No SCC growth**		-180		
	200	100	20	0.3	4.9-7.4 × 10 <sup>-8</sup>	10 ~ 20
					3.2 × 10 <sup>-8</sup>	-60
	0.1	5.4 × 10 <sup>-8</sup>		20 ~ 30		
	240	570		14	0.3	1.4 × 10 <sup>-7</sup>
440	150	50	0.1	1.9 × 10 <sup>-7</sup>	50	
			0.3	3.0 × 10 <sup>-7</sup>	10	

HWC:Hydrogen water chemistry \* : <1.0 × 10<sup>-9</sup> mm/sec Stress intensity: 100kg/mm<sup>1.5</sup>  
 NWC:Normal water chemistry \*\* : <5.6 × 10<sup>-9</sup> mm/sec

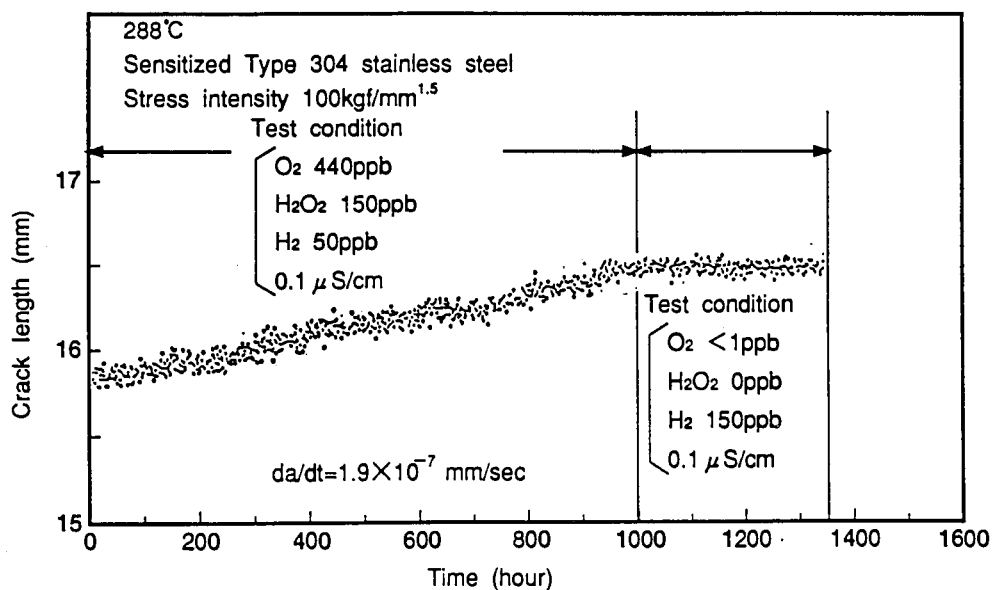


Figure 2 Crack length vs time for specimen tested under constant loading using DC potential drop method at condition which gave changes from normal water chemistry to hydrogen water chemistry

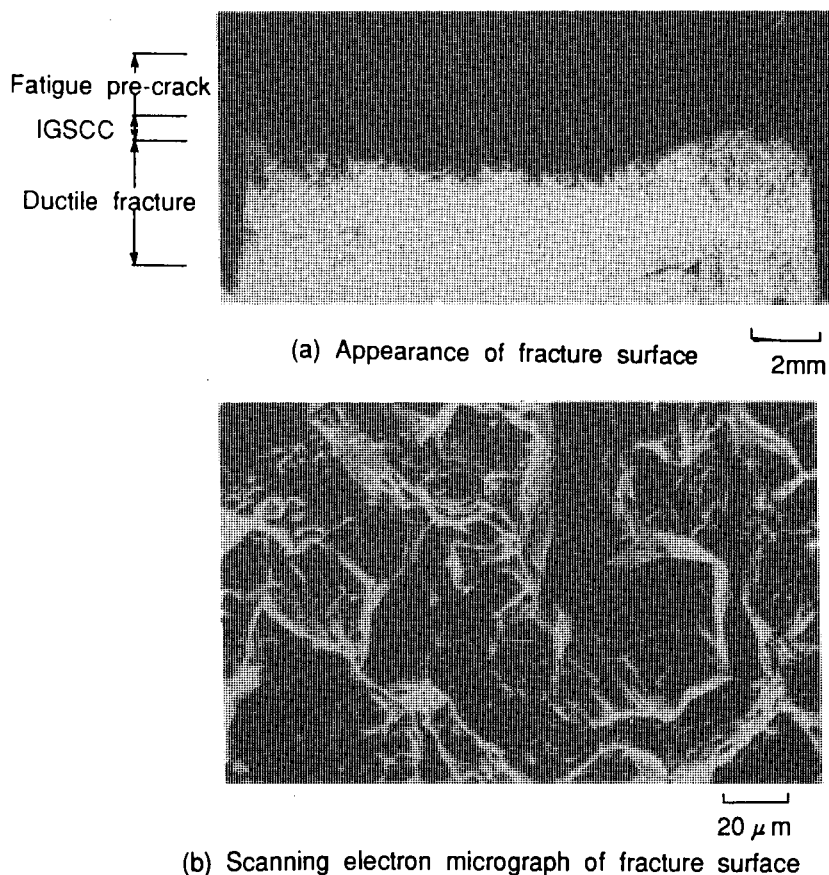


Figure 3 Appearance and scanning electron micrograph of CT specimen slitting apart mechanically

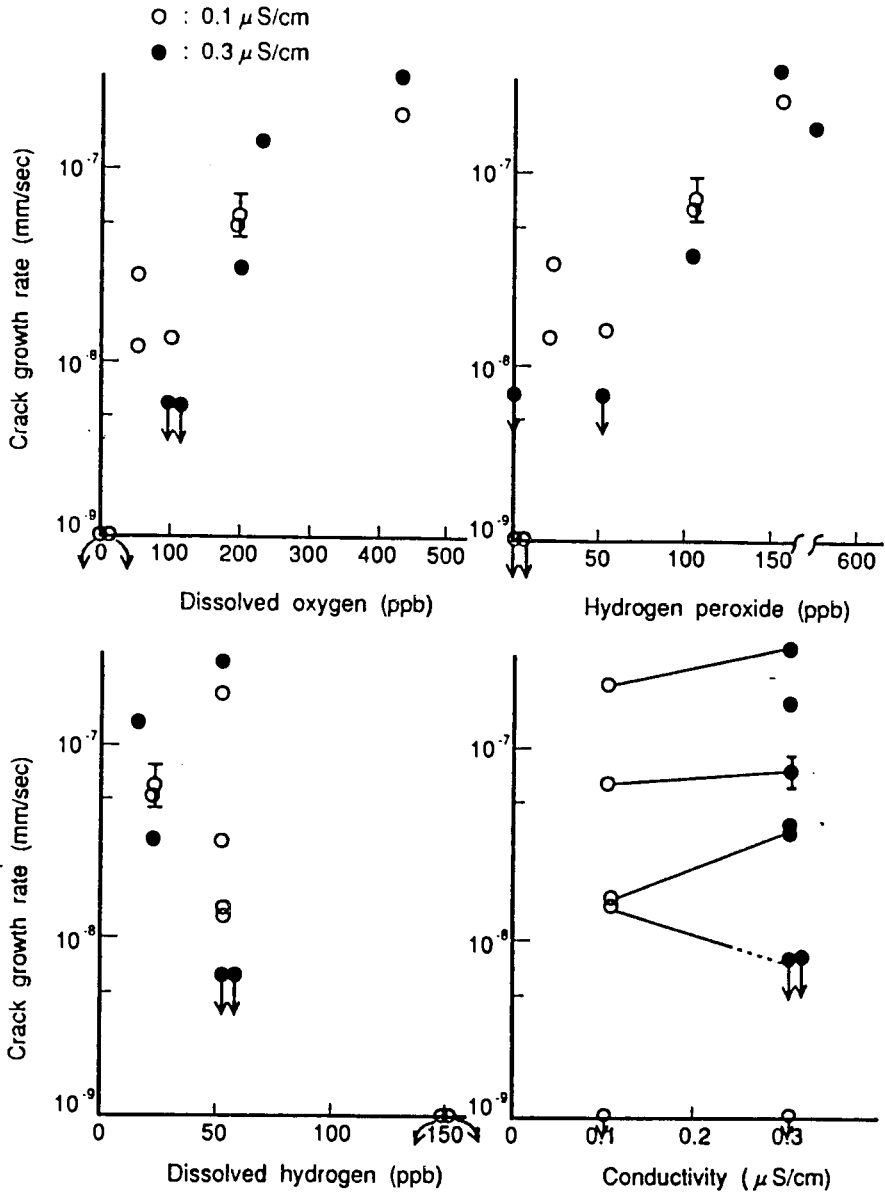


Figure 4 Effects of dissolved oxygen, dissolved hydrogen, hydrogen peroxide and conductivity on the crack growth rates of sensitized Type 304 stainless steel

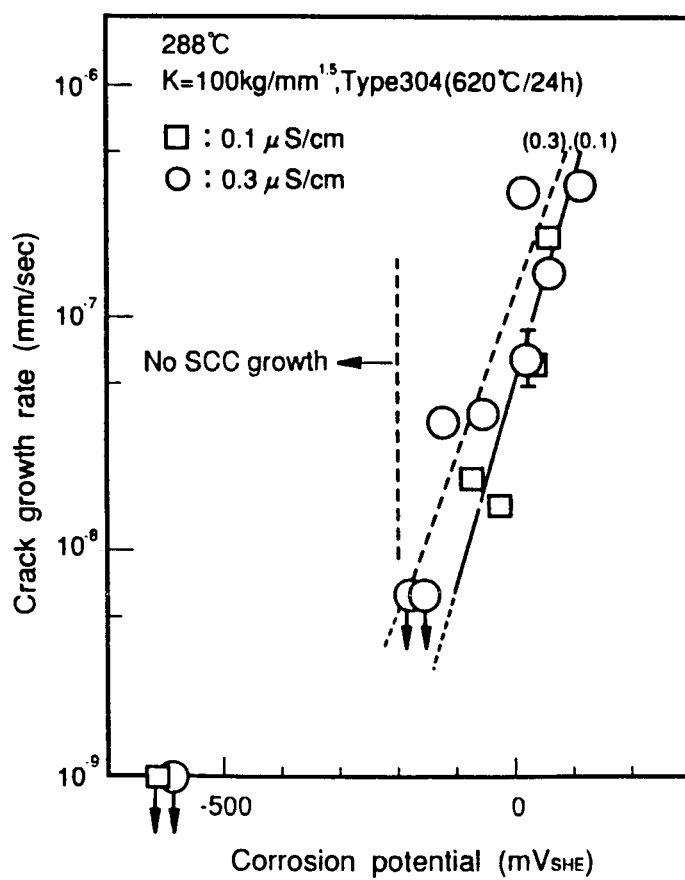


Figure 5 Effect of corrosion potential and conductivity on crack growth rates of sensitized Type 304 stainless steel

