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Effects of chemical compounds on the stress corrosion cracking of steam generator tubing materials in a caustic solution

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Abstract

Some nuclear power plants have degradation problems of their steam generators, associated with caustic SCC or lead-induced SCC in a caustic environment. The electrochemical corrosion potential is measured for a mill-annealed Alloy 600 specimen in a caustic solution with Cu oxide if it is present in the sludge. The effect of the applied potential on SCC is tested using a slow strain rate test unit for the same tube material in a caustic solution containing lead species. All kinds of steam generator tubing materials used for nuclear power plants in operation and under construction in Korea are tested with modified reverse u-bend specimens in a caustic solution containing lead oxide and their crack morphology is investigated. In addition, the effects of the inhibitors such as TiO_2 and CeB_6 on SCC are tested for these tubing materials in a caustic solution.

1. Introduction

Stress corrosion cracking (SCC) has been reported in a number of steam generator tubes of nuclear power plants in a caustic environment with or without lead species in the sludge accumulated on the top of the tube sheets. Laboratory test results indicate that the SCC of steam generator tubing materials is accelerated in the presence of lead species in a caustic environment [1–9]. Since some other chemical compounds besides lead species may accelerate this SCC, the electrochemical potential effect is investigated on the SCC of steam generator tubing materials in this caustic environment. On the other hand, it has been reported that some chemical compounds can enhance the resistance to SCC in this caustic environment, even though available data are limited [10–14].

2. Experimental

Chemical compositions of the steam generator tubing materials are listed in Table 1 for the constant extension rate tests (CERT) and immersion tests with modified reverse u-bent (RUB) specimens. In the case of CERT, the tube had dimensions of a 22.23 mm OD and 1.27 mm wall thickness and it was split into two pieces and machined to have a 6 mm width and 25 mm gauge length as shown elsewhere [2]. The test solution was

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Table 1
Chemical compositions of the steam generator tubing materials

Material	Chemical composition (wt%)																Test method
	C	Si	Mn	P	S	Cr	Ni	Co	Mo	Ti	Cu	Al	Nb	Fe	B	N	
600 MA	0.01	0.1	0.3		0.001	15.4	75.1			0.17	0.2	0.22		8.0			CERT
600 MA	0.02	0.1	0.2		0.001	15.2	74.4				0.1			9.0			RUB
600 TT	0.025	0.15	0.21	0.001	0.001	15.1	74.9	0.02		0.32	0.011	0.21		9.08			
600 HTMA	0.027	0.09	0.21	0.006	0.001	16.26	73.84	0.005		0.32	0.016	0.15		9.07	0.004	0.006	
690 TT	0.017	0.21	0.29	0.006	0.001	29.4	59.4	0.011	0.01	0.29	0.01	0.041	0.01	10.2	0.004	0.024	
800 H	0.06	0.58	1.17		0.001	19.6	30.5	0.07		0.5		0.41		46.9			

prepared to have a pH 10 at RT by adding NaOH and PbO powder. The solution was de-aerated by purging with N_2 gas. Test specimens were extended by $2 \times 10^{-7}\,s^{-1}$. In the case of the immersion tests with modified RUB specimens, split tube specimens were elongated by 20% of the gauge length in order to accelerate the SCC tendency and were deformed to make a shape of RUB as shown in Fig. 1. These specimens were checked by a stereomicroscope to find the cracks after every exposure time. The modified RUB specimens were prepared by etching with nitric acid to investigate the crack morphology after the immersion tests. An Ag/AgCl reference electrode with 0.01 N KCl was used to measure the polarization curves and corrosion potentials (E_{corr}).

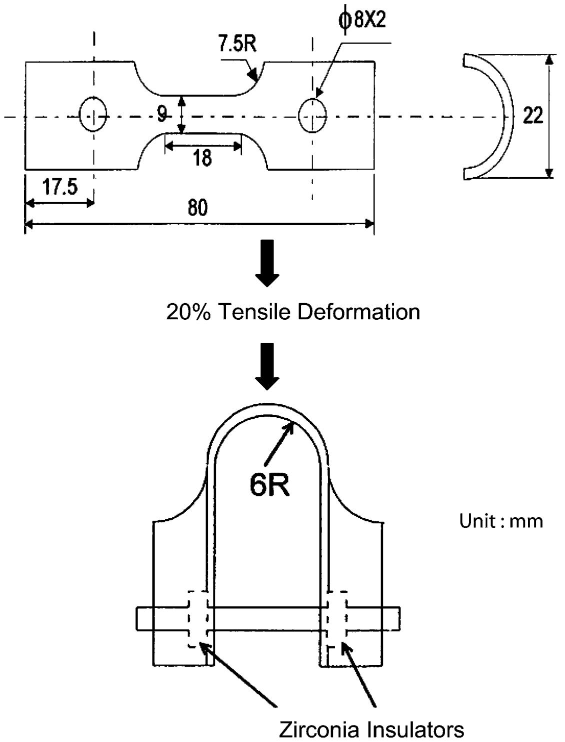

Fig. 1. Schematic drawing and dimensions of the modified reverse U-bent (RUB) specimen.

3. Results and discussion

The mill-annealed (MA) Alloy 600 tubing material was tested to investigate the stress corrosion cracking at different potentials in a solution of pH 10 containing 1000 ppm Pb as PbO at 300 °C, as shown in Fig. 2. An area of SCC was measured by comparing it with the total fractured surface area after each test. It showed the highest SCC susceptibility (42%) at −650 mV versus a 0.01 N Ag/AgCl reference electrode. A considerable amount of SCC was observed by 35% and 25% at −750 mV and −800 mV, respectively. No SCC was found at potentials above −500 mV. When the steam generator tubes are operated with the sludge accumulated on the top of the tube sheet, the chemical compounds of the sludge might change the corrosion potential of the tubes. The effect of CuO on the corrosion potential of the same tube material was tested in a solution of pH 10 at 300 °C as shown in Fig. 3. The CuO increased its corrosion potential to −420 mV with 100 ppm and gave an almost saturated value, −350 mV with the concentration of more than 300 ppm. This indicates that the SCC susceptibility of the Alloy 600MA tubing material might be changed, when it is exposed to a caustic solution with the coexistence of PbO and CuO in the sludge, for an example.

One of the nuclear power plants in Korea had SCC of its steam generator tubes in an environment containing lead species. It had a steam generator tubing of thermally treated (TT) Alloy 600 and its crack morphology was a transgranular (TG) SCC at the crack mouths for several grains and it was changed to an intergranular (IG) SCC to the crack tips. The crack morphology is often used as one of the indicators to determine the SCC in the environment containing lead species. The crack morphology was investigated for all kinds of steam generator tube materials of the operating nuclear power plants in Korea. Modified RUB specimens of these materials were tested in a 10% NaOH solution containing 1000 ppm Pb as PbO at 315 °C. Their crack

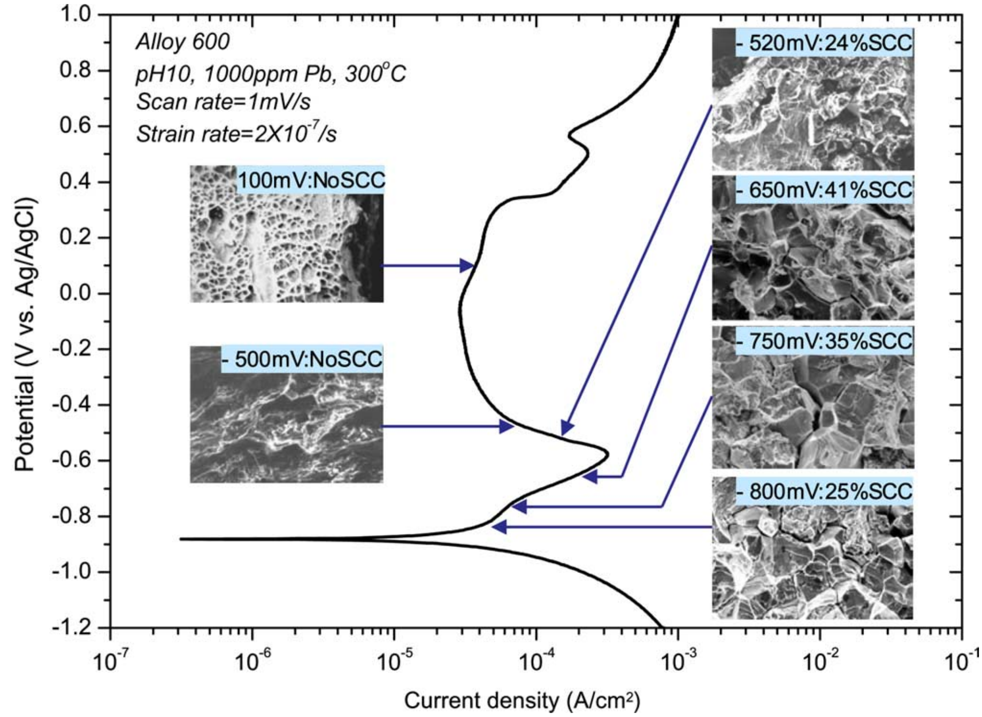

Fig. 2. Potential effect on the SCC of Alloy 600 MA in a pH 10 solution containing 1000 ppm Pb at 300 °C.

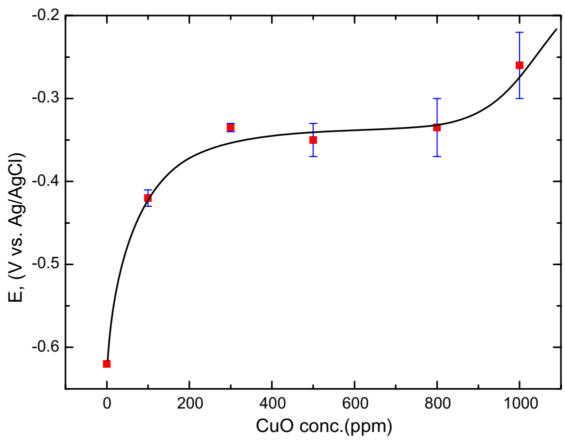

Fig. 3. Effects of the CuO content on the corrosion potential of alloy 600 MA in a pH 10 solution at 300 °C.

morphology after the tests is shown in Fig. 4. The crack morphology of Alloy 600 MA, Alloy 600 HTMA (high temperature mill-annealed) and Alloy 600 TT was IGSCC and the crack morphology of Alloy 690 TT and Alloy 800 was TGSCC. It has been reported that Alloy 600 TT shows TGSCC at a controlled potential in a caustic environment containing PbO [2] and some TGSCC in an all volatile treatment condition containing PbO [7]. Therefore, the crack morphology of the SCC can be IGSCC or TGSCC, depending on the tube materials of the steam generators. The crack morphology of TGSCC is not often revealed, except in a caustic solution with lead species, for Alloy 600 TT, Alloy 690 TT and Alloy 800 tube materials. This TGSCC can be one of the possible indicators for the lead-induced SCC in a caustic environment in the case of Alloy 600 TT, Alloy 690 TT and Alloy 800, but not for Alloy 600 MA and Alloy 600 HTMA.

Modified RUB specimens were tested in a 10% NaOH solution at 315 °C to investigate the time to crack initiation for Alloy 600 MA, Alloy 600 TT, Alloy 600 HTMA, Alloy 800 and Alloy 690 TT as shown in Fig. 5(a). Specimens were examined to find the cracks by a stereomicroscope every ten days during the test. All the specimens of Alloy 600 MA, Alloy 600 TT and Alloy 600 HTMA showed cracks after a 40 days exposure. The crack of one specimen was detected after an exposure of 30 days and another specimen was found to be cracked after a 60 days test for Alloy 800. No crack was shown after an exposure of 60 days for Alloy 690 TT. These tubing materials were tested in a 10% NaOH solution with 1000 ppm Pb as PbO at 315 °C as shown in Fig. 5(b). Two specimens were cracked after a 10 days exposure for Alloy 690 TT which showed the highest resistivity to SCC in a 10% NaOH solution without PbO. Two other specimens of Alloy 690 TT were tested

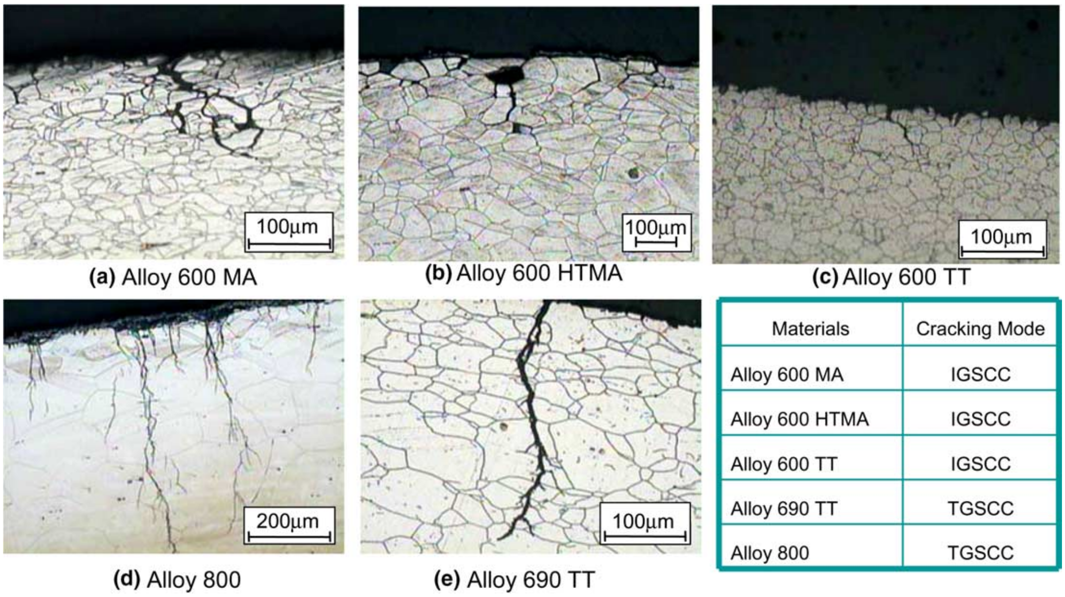

Fig. 4. Crack morphology of the steam generator tube materials tested in a 10% NaOH solution containing 1000 ppm Pb at 315 °C.

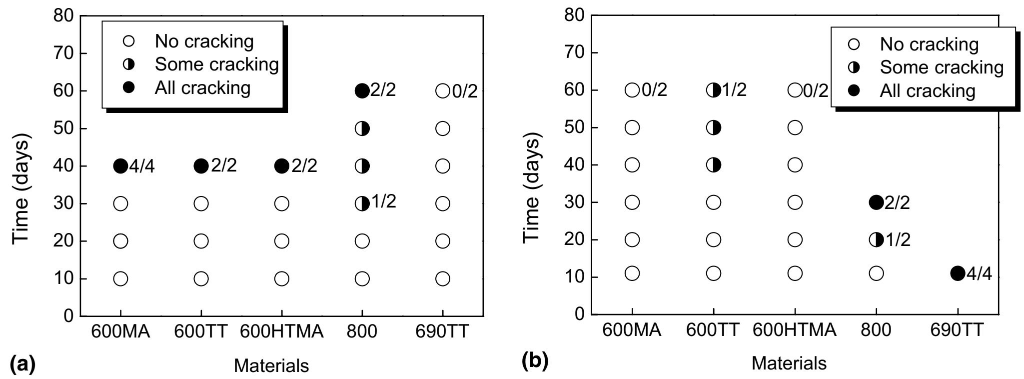

Fig. 5. Results of the SCC tests with the RUB specimens in a 10% NaOH solution with or without Pb at 315 °C. (a) No additives, (b) 1000 ppm Pb.

again to check the reproducibility and these were cracked after a 10 days exposure. One of the specimens of Alloy 800 was cracked after 20 days and another specimen was cracked after 30 days. Alloy 800 specimens showed the low resistivity to SCC in this caustic solution containing PbO, when compared with the value without PbO. Alloy 690 TT was the most affected in lead compared to without lead. However, the specimens of Alloy 600 MA and Alloy 600 HTMA did not reveal any cracks after 60 days and a good explanation is not available at this moment for this unexpected result. Castano-Marin et al. reported the same kind of tendency [7]. C-ring specimens of Alloy 600 MA were not cracked after 500 h in 10% NaOH solution containing 0.1 M or 0.01 M PbO at 350 °C, while the specimens were cracked after 500 h in the same condition without PbO.

A chemical compound, TiO_2 was added into this 10% NaOH solution and the time to crack initiation is summarized in Fig. 6(a). This TiO_2 increases the time to crack initiation by some extent. All the specimens were cracked after 50 days, 90 days, 50 days and 80 days for Alloy 600 MA, 600 TT, 600 HTMA and Alloy 800, respectively, instead of 40 days for Alloy 600 MA, 600 TT and 600 HTMA and 60 days for Alloy 800 without a TiO_2 addition. Another chemical compound, CeB_6 was added to the same solution. Fig. 6(b) shows the SCC tendency for these materials. Some cracks were found after 60 days for two specimens of

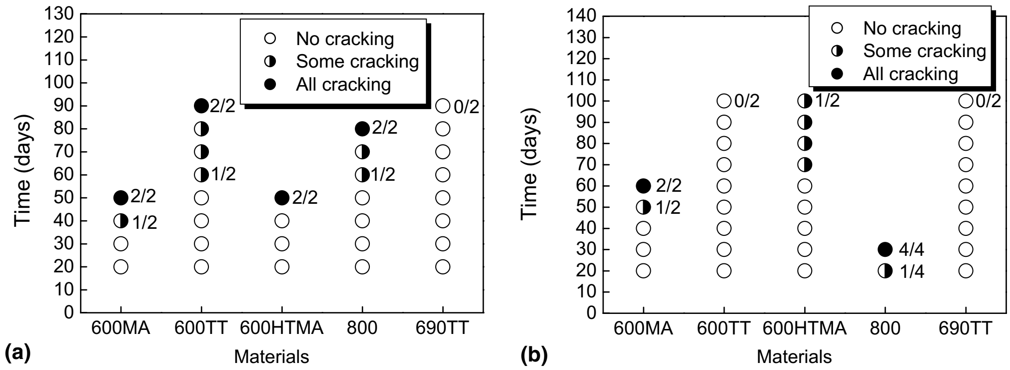

Fig. 6. Results of the SCC tests with the RUB specimens in a 10% NaOH solution with TiO_2 or CeB_6 at 315 °C. (a) 1 g/L TiO_2, (b) 1 g/L CeB_6.

Alloy 600 MA and no cracks could be seen after 100 days for Alloy 600 TT. One of the two specimens did not show cracks after 100 days for Alloy 600 HTMA. However, two specimens of Alloy 800 showed cracks after 30 days and the same results could be observed for the repeated tests with two more specimens. Totally, four specimens showed cracks after a 30 days exposure. Therefore, the chemical compound, CeB_6 highly increased the resistivity to SCC for Alloys 600 MA, 600 TT and 600 HTMA but it decreased the resistivity to SCC for Alloy 800.

Polarization curves were obtained in a 10% NaOH solution at 315 °C for Alloys 600, 690 and 800 as shown in Fig. 7. The solution was de-aerated and the specimens were scanned anodically. The anodic current density peaks are the highest for Alloy 600 and the lowest for Alloy 690. The passive transition current density shows higher values for Alloy 800 than the values for Alloy 600 and Alloy 690. The active to passive current density

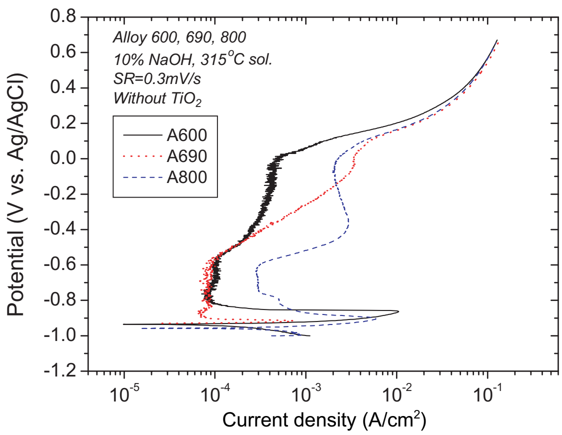

Fig. 7. Polarization curves for Alloy 600, 690, 800 in a 10% NaOH solution at 315 °C.

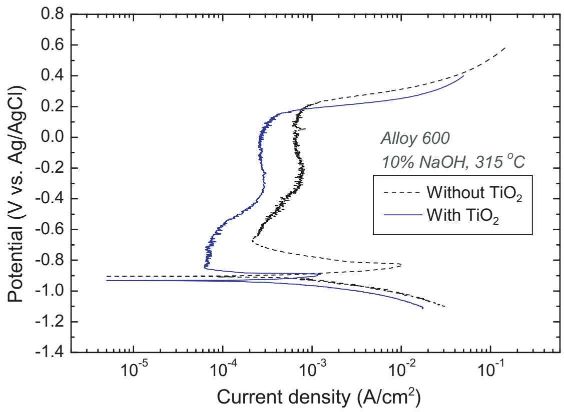

Fig. 8. Polarization curves for Alloy 600 in a 10% NaOH solution at 315 °C with/without TiO_2.

of Alloy 690 is much lower than the values of Alloy 600 and Alloy 800. This polarization curve information can explain why the specimens of Alloy 690 give the highest resistivity to SCC in a 10% NaOH solution. Fig. 8 provides some information on the effect of TiO_2 on the polarization curve in the case of Alloy 600 in a 10% NaOH solution at 315 °C [10]. The active current density peak is decreased and the current density in the active/passive transition and the passive range is decreased by the addition of TiO_2. This polarization curve result is in good agreement with the SCC data in a 10% NaOH solution at 315 °C with or without a TiO_2 addition.

4. Conclusions

- The applied potential effect on SCC by a CERT was investigated for an Alloy 600 MA tubing material in a mildly caustic solution (pH 10) containing PbO at 300 °C. The maximum susceptibility to SCC is observed at a potential of −650 mV and no crack is found at potentials at or above −500 mV.

- The crack morphology was examined for the tubing materials of Alloys 600 MA, 600 HTMA, 600 TT, 690 TT and 800 in a strong caustic solution (10% NaOH) containing PbO at 315 °C. The Alloys 600 MA, 600 HTMA and 600 TT show IGSCC and the Alloy 690 TT and 800 reveal TGSCC.
- The stress corrosion cracking was investigated by an immersion test with modified RUB specimens for these tubing materials in a strong caustic solution (10% NaOH) at 315 °C with or without chemical compounds, PbO, TiO_2, and CeB_6. The PbO addition accelerates the SCC of Alloy 690 TT and Alloy 800. All the specimens of Alloy 690 TT are cracked at a 10 days exposure. This cracking of Alloy 690 TT was confirmed by repeating the test.
- TiO_2 addition decreases SCC of Alloys 600 MA, 600 TT, 600 HTMA and 800 under the same conditions. CeB_6 addition inhibits the SCC of Alloys 600 MA, 600 TT and 600 HTMA more effectively. However, CeB_6 addition should be avoided for Alloy 800, this has been confirmed by an additional test.

Acknowledgement

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