

Effect of Sulfur on a Stress Corrosion Cracking of Steam Generator Tubing Materials

E. H. Lee, Zhao Shuan, B. S. Choi, and W. Y. Maeng
Nuclear Materials Research Division, Korea Atomic Energy Research Institute,
1045 Daedeok Street, Yuseong, Daejeon 305-353, Korea
ehlee@kaeri.re.kr

1. Introduction

Sulfur has been identified as one of the major impurities introduced into the secondary water of pressurized water-reactors (PWRs) [1]. Under steam generator (SG) operating conditions, sulfate (SO_4^{2-} , +6) reduces to lower-valence sulfur species, such as tetrathionate ($\text{S}_4\text{O}_6^{2-}$, +2.5), thiosulfate ($\text{S}_2\text{O}_3^{2-}$, +2), or sulfide (S^{2-} , -2). These lower-valence sulfur species are more detrimental than SO_4^{2-} and have been found inside an advancing stress corrosion cracking (SCC) from pulled tubes [2]. Many researchers have investigated the effects of reduced sulfur species in wide pH ranges with or without additives [2,3]. In the present work, we investigated the effects of sulfur valences on the SCC susceptibility of SG tubing materials, alloys 600, 690, and 800, in various sulfur solutions at 340 °C. From this work, the relationship of the sulfur valence to the susceptibility of SCC was discussed.

2. Methods and Results

The material used was commercial Alloy 600 MA, 600 HTMA, 600 TT, 690 TT, and 800. We prepared test solutions using distilled water with addition of reagent-grade sodium sulfate (Na_2SO_4 , +6), sodium tetrathionate ($\text{Na}_2\text{S}_4\text{O}_6$, +2.5), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, +2), and sodium hydrosulfide (NaHS , -2). The solution pH was not adjusted. For the SCC test, the shape and geometry of the test specimen are presented in Figure 1 [4]. We made reverse u-bend (RUB) test specimens with tubular tensile test specimens, 20 % pre-strained by a tensile testing machine, and then altered the test specimens to produce parallel branches by bending each tube into a u-shape using a 3-point bending tool.

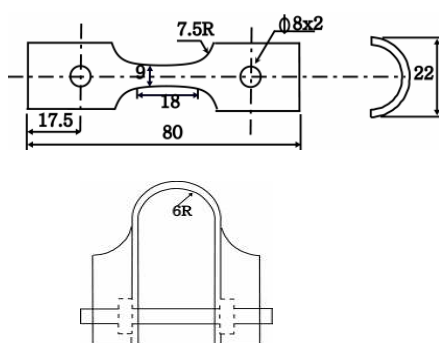


Figure 1. Test specimen of 20 % pre-strained reverse U-bend.

The SCC tests were conducted in deaerated 0.005 M, 0.01 M, and 0.1 M sulfur solutions using a static-autoclave system at 340 °C and a corrosion potential. SCC test specimens were inspected every 480 hours with a stereoscopic microscope to observe cracks. The cracked test specimens were examined with a scanning electron microscopy (SEM) and an energy dispersive X-ray system (EDS). The deposits were analyzed with a low angle X-ray diffractometer (XRD).

The SCC susceptibilities of the test samples increased in the following order: Alloy 690 TT, Alloy 800, Alloy 600 TT, Alloy 600 HTMA, and Alloy 600 MA. The Alloy 600 MA showed SCC in all tested solutions; however the Alloy 690 TT showed no SCC. Increased SCC susceptibilities of the Alloy 600 MA corresponded with the following order: $\text{Na}_2\text{S}_2\text{O}_3$, Na_2SO_4 , NaHS, and $\text{Na}_2\text{S}_4\text{O}_6$. The surface morphologies of the cracked test samples were intergranular SCC (IGSCC).

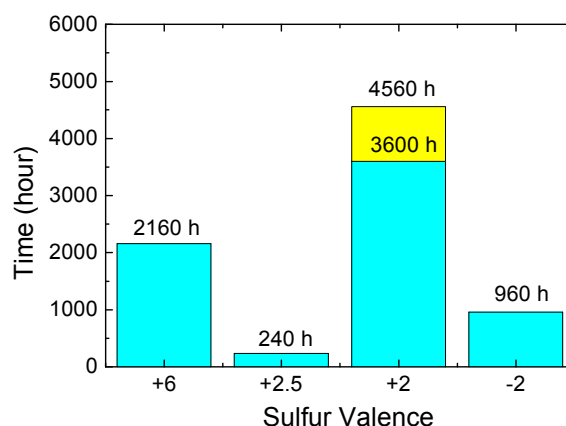


Figure 2. The effects of sulfur valences on the SCC of the Alloy 600 MA in 0.01 M sulfur solutions.

Figure 2 shows the results for the SCC of Alloy 600 MA in 0.01 M Na_2SO_4 , $\text{Na}_2\text{S}_4\text{O}_6$, $\text{Na}_2\text{S}_2\text{O}_3$, and NaHS solutions. We couldn't observe the effects of sulfur valences on the SCC. Sakai et al., has reported that reduced sulfur accelerates corrosion of sensitized Alloy 600 MA and Alloy 600 TT [3]. In this work, the Alloy

600 MA might be similar microstructure to sensitized alloys. In the $\text{Na}_2\text{S}_4\text{O}_6$ solution, the test sample cracks were deep and penetrating. This trend was not observed in Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, and NaHS solutions. In the $\text{Na}_2\text{S}_4\text{O}_6$, $\text{Na}_2\text{S}_2\text{O}_3$, and NaHS solutions, a scent of H_2S was identified after testing. The surfaces of the test specimens were covered with thick, black deposits composed of mainly Ni_7S_6 for $\text{Na}_2\text{S}_4\text{O}_6$ solution, Ni_3S_2 for $\text{Na}_2\text{S}_2\text{O}_3$ solution, NiS, Ni_3S_2 , FeS, and ZrO_2 for NaHS solution.

Figure 3 shows the SEM and EDS spectrum micrograph of the surface morphology for the cracked Alloy 600 MA test specimen in the NaHS solution. The cracks were an IGSCC formed along the grain boundaries. The fractured surface in Figure 3 (a) was covered with many impurities. The particle, as indicated by an arrow in Figure 3 (a), on the fractured surface, contained sulfur, as shown in Figure 3 (b). This sulfur peak consisted of mainly Ni_3S_2 , NiS, and FeS as confirmed by the XRD analysis. These results confirm that NaHS was dissociated into Na^+ , S^{2-} , and H_2 . And then S^{2-} ions reacted with the Ni^{2+} , Fe^{2+} , and H^+ ions to form Ni_3S_2 , NiS, FeS, H_2 , and H_2S . Marcus et al. suggested that sulfur occupies the adsorption sites of the OH^- ions with a high binding energy [5]. Therefore, this sulfur may react preferentially with the Ni, while the OH^- ions may react with the Cr. The presence of sulfur inhibits the formation of a passive film on the surface of alloy specimens, which leads to a SCC.

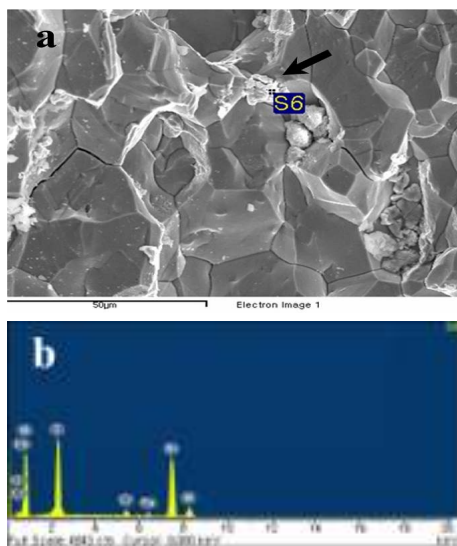


Figure 3. SEM micrograph (a) and EDS spectrum (b) of the cracked surface of Alloy 600 MA specimen in the 0.01 M NaHS solution at 340 °C.

3. Conclusion

In the deaerated 0.005 M, 0.01 M, and 0.1 M sulfur solutions at 340 °C, an IGSCC was observed in the

Alloy 600 MA for all the solutions and the Alloy 600 HTMA for the NaHS solution. It seems that the microstructure of the Alloy 600 MA is similar to that of a sensitized alloy. In the Na_2SO_4 solution, the Alloy 600 MA was more susceptible to a SCC with an increasing solution concentration. The increase of the $\text{Na}_2\text{S}_2\text{O}_3$ concentration accelerated the general corrosion. Reduction of Na_2SO_4 , $\text{Na}_2\text{S}_4\text{O}_6$, and $\text{Na}_2\text{S}_2\text{O}_3$ to species of lower valence, which was confirmed by the EDS and XRD data, was observed. However, there were no effects of sulfur valences on the SCC of the tested alloys in the sulfur solutions. Each sulfur solution showed an obvious difference in the corrosion morphologies. The results obtained in this study can be used to investigate a sulfur induced SCC mechanism of other sulfur compounds with different oxidation states.

REFERENCES

- [1] O. Bouvier, E. M. Pavageau, F. Vaillant, and D. Vermeeren, Influence of High Reducing Conditions on IGA/SCC of Alloy 600 in Neutral Sulfate Environments, 11th Int. Conf. Environmental Degradation of Materials in Nuclear Systems, pp. 467-476, 2003.
- [2] C. Laire, G. Platbrood, and J. Stubbe, Characterization of the Secondary Side Deposits of Pulled Steam Generator Tubes, 7th Int. Conf. Environmental Degradation of Materials in Nuclear Systems, pp. 387-397, 1995.
- [3] T. Sakai, O. Okabayash, K. Aok, K. Matsumoto, F. Nakasyasu, and Y. Kishi, Effect of Reduced Sulfur on High Temperature Aqueous Corrosion for Alloy 600, 4th Int. Conf. Environmental Degradation of Materials in Nuclear Systems, pp. 12_47-12_49, 1989.
- [4] T. Yonesawa, N. Sasaguri, and K. Onimura, Effects of Metallurgical Factors on Stress Corrosion Cracking of Ni-base Alloys in High temperature Water, JAIF Int. Conf. on Water Chemistry in Nuclear Power Plants, Vol. 2, pp. 490-495, 1988.
- [5] P. Marcus and J. M. Grimal, The Antagonistic Roles of Chromium and Sulfur in the Passivation of Ni-Cr-Fe Alloys Studied By XPS and Radiochemical Techniques, Corrosion Science, Vol. 31, pp. 377-382, 1990.