

## Stress Corrosion Cracking of Steam Generator Tubing in a 0.01 M NaHS Solution

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### 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 ( $\text{SO}_4^{2-}$ , +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 ( $\text{S}^{2-}$ , -2). These lower-valence sulfur species are more detrimental than  $\text{SO}_4^{2-}$  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 effect of  $\text{S}^{2-}$  on the SCC susceptibility of SG tubing in a NaHS solution at 340 °C. From this work, we can establish the reducing mechanism of other sulfur compounds.

### 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 0.01 M sodium hydrosulfide (NaHS). The solution pH was not controlled. 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.

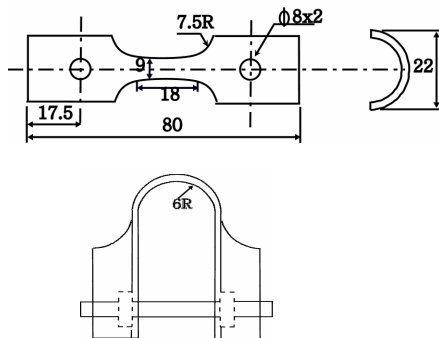


Figure 1. Test specimen of 20 % pre-strained reverse U-bend.

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

Figure 2 shows the variation of the  $\text{SO}_4^{2-}$  concentration during hideout return analyses at the domestic PWR plant from the 9<sup>th</sup> cycle to the 17<sup>th</sup> cycle. After an exchange of the SG tubing material to Alloy 690 TT, the amount of returned  $\text{SO}_4^{2-}$  decreased a little at cycle 17. This is because the crevices of the SG were cleaned during the exchange of the SG tubing, however the concentration of the returned  $\text{SO}_4^{2-}$  is still high.

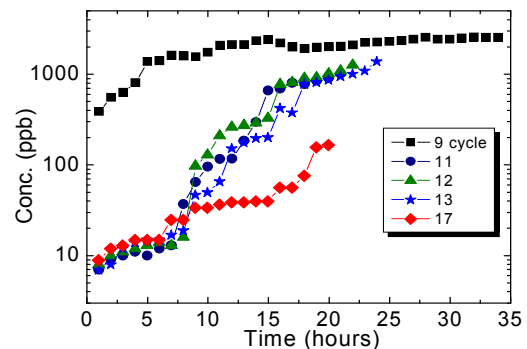


Figure 2. The results of hideout return of  $\text{SO}_4^{2-}$  at domestic plant from 9 cycle to 17 cycle.

For the SCC tests, a scent of  $\text{H}_2\text{S}$  was identified after a testing. The Alloy 600 MA showed the most SCC susceptibility. Two Alloy 600 MA test specimens exhibited a SCC after 960 hours. No SCC was observed on the test specimens except for the Alloy 600 MA after 6000 hours. This is because the microstructure of the tested alloys is very different from each other. In particular, the Alloy 600 MA has a similar microstructure of most alloys which are sensitized. These sensitized alloys have been reported as more susceptible to a SCC [3].

The surfaces of the test specimens were covered with thick, black deposits composed of mainly NiS,  $\text{Ni}_3\text{S}_2$ , and FeS.  $\text{ZrO}_2$  was also observed because Zr oxidized nuts were used for the RUB loading. This indicates that

the Zr nuts are corroded because of the hydrogen evolved during the SCC test.

Figure 3 shows the micrograph of the surface morphology analyzed by the SEM and EDS spectrum for the cracked Alloy 600 MA test specimen. The cracks were an intergranular stress corrosion cracking (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  $\text{Ni}_3\text{S}_2$ ,  $\text{NiS}$ , and  $\text{FeS}$  as confirmed by the XRD analysis. These results confirm that  $\text{NaHS}$  was dissociated into  $\text{Na}^+$ ,  $\text{S}^{2-}$ , and  $\text{H}_2$ . And then  $\text{S}^{2-}$  ions reacted with the  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{H}^+$  ions to form  $\text{Ni}_3\text{S}_2$ ,  $\text{NiS}$ ,  $\text{FeS}$ ,  $\text{H}_2$ , and  $\text{H}_2\text{S}$ . Marcus et al. suggested that sulfur occupies the adsorption sites of the  $\text{OH}^-$  ions with a high binding energy [5]. Therefore, these sulfur may react preferentially with the Ni, while the  $\text{OH}^-$  ions may react with the Cr [5]. The presence of sulfur inhibits the formation of a passive film on the surface of alloy specimens, which leads to a SCC.

## REFERENCES

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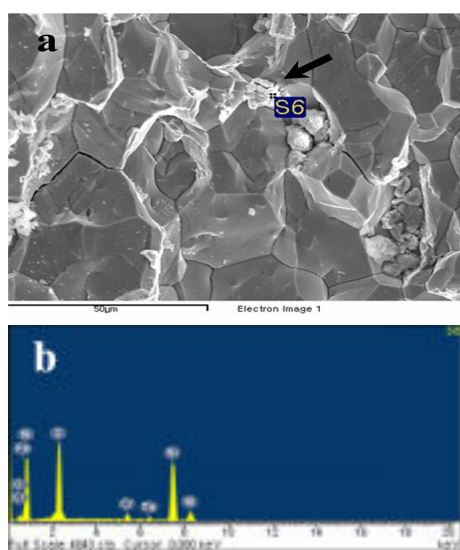


Figure 3. SEM micrograph (a) and EDS spectrum (b) of the cracked surface of Alloy 600 MA specimen in the 0.01 M of NaHS solution at 340 °C.

## 3. Conclusion

In the deaerated 0.01 M of NaHS solution at 340 °C, a IGSCC was observed only in the Alloy 600 MA. It seems that the microstructure of the Alloy 600 MA is similar to that of a sensitized alloy. The deposit of the tested alloys was composed of  $\text{Ni}_3\text{S}_2$ ,  $\text{NiS}$ ,  $\text{FeS}$ , and  $\text{ZrO}_2$ . The results obtained in this study can be used to investigate a sulfur induced SCC mechanism of other sulfur compounds with different oxidation states.