Stress Corrosion Cracking of Alloys 600, 690, and 800 in a Tetrathionate Solution at 340℃

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Abstract

The stress corrosion cracking (SCC) susceptibility of Alloy 600 MA, Alloy 600 TT, Alloy 800, and Alloy 690 TT were investigated in a deaerated 0.01 M solution of sodium tetrathionate using reverse u-bend test samples at 340 ℃. The results showed that SCC occurred in all alloys, excluding Alloy 690 TT. The SCC susceptibility decreased with an increase in the chromium content of the alloys. The results of the deposits and spectra taken from an energy dispersive X-ray system confirmed the existence of a reduced sulfur causing SCC.

Keywords : stress corrosion cracking, Ni-base alloy, sulfur

1. Introduction

Intergranular attacks (IGA) and stress corrosion cracking (SCC) of steam generator (SG) tubing materials have been observed in SG crevices in pressurized water reactor (PWR) plants [1]. Under the SG operating conditions, sulfates, the most common sulfur species introduced into the SG bulk water, are reduced by hydrazine to a lower-valence sulfur species, such as tetrathionate ($S_4O_6^{2-}$), thiosulfate, or sulfide. These lower-valence sulfur species are known to cause SCC and are found inside advancing SCC from the pulled tubes [2]. In the present study, we investigate the effect of sulfur on the SCC susceptibility of SG tubing materials in a $S_4O_6^{2-}$ solution.

2. Experimental and Results

The material used was commercial alloys. We prepared 0.01 M of $Na_2S_4O_6$ solution. The reverse u-bend (RUB) test samples were made with tubular tensile test samples with 20% pre-strained by a tensile testing machine [3]. The test samples then altered to produce parallel branches by bending each tube into a u-shape using a 3-point bending tool. We conducted the SCC tests using a static-autoclave system at 340℃ at corrosion potential. We inspected the test samples with a stereomicroscope to identify cracks every 240 hours and every 480 hours: subsequently, we examined the cracked test samples using SEM and EDS. The deposits were analyzed with XRD. A scent of H_2S was identified after testing. The surface of the test samples was covered with thick, black deposits primarily composed of Ni_7S_6. Two Alloy 600 MA and Alloy 600 TT test samples showed SCC after 240 hours. For Alloy 800, one test sample showed SCC after 3120 hours and the other after

3600 hours. Alloy 690 TT showed no SCC after 6000 hours. The surface morphology of the cracked Alloy 600 MA, Alloy 600 TT, and Alloy 800 test samples was intergranular SCC (IGSCC) formed along the grain boundaries. The Alloy 600 TT was heat treated by Alloy 600 MA for 12 hours at 715 ℃. As a result, the Cr depleted regions along the grain boundaries recovered and this increased the resistance of SCC [4]. Thus, the Alloy 600 MA test sample might have shown more SCC susceptibility than the Alloy 600 TT test sample if the inspection time was more frequent than every 240 hours. The Alloy 800 test samples were less susceptible to SCC because of a higher Cr content. The highest SCC resistance of the Alloy 690 TT test samples was due to them having the highest Cr content in the matrix. Figure 1 shows the spectra taken from an EDS of the Alloy 600 MA test samples after SCC testing: the outer loosely bonded Ni_7S_6 layer was completely removed by sonication: a Cr oxide layer with varying thickness was observed: and the existence of a sulfur peak below this layer was noted. Figure 2 shows the spectra taken from an EDS of the Alloy 600 TT test samples after SCC testing: a very thin Cr oxide layer was present and the deposits of Ni_7S_6 were also removed by sonication. For the Alloy 800 test samples, as shown in Fig. 3, the spectra taken from the EDS is comprised of a double layer consisting of a thin inner Cr-rich oxide layer and a thick outer Cr-rich oxide layer. In addition, the Fe peak is below the outer layer and the S peak is between inner and outer layers. The magnetite which was mixed with Cr oxide probably rendered this layer non-protective [5]. Although a passive film was built up on the alloy surface in the tested solution, this layer is more porous and probably less protective than a Cr oxide layer formed without sulfur [6]. Thus, if a reduced sulfur species were introduced into the cracked Cr oxide, this could

potentially advance any SCC. From these experimental results, the high SCC susceptibility of Alloy 600 MA and Alloy 600 TT in the $S_4O_6^{2-}$ solution appears to indicate that Ni reacts with the sulfur species extremely rapidly. Therefore, the formation of a thick and even Cr oxide layer will be hindered, even though Cr reacts preferentially with OH^- [7]. SCC occurred in Alloy 800, even though it has a higher Cr content than the Alloy 600s. This is because Alloy 800 has a high Fe content. For Alloy 690 TT, the high resistance to SCC is due to a high Cr content, a low Fe content and the heat treatment.
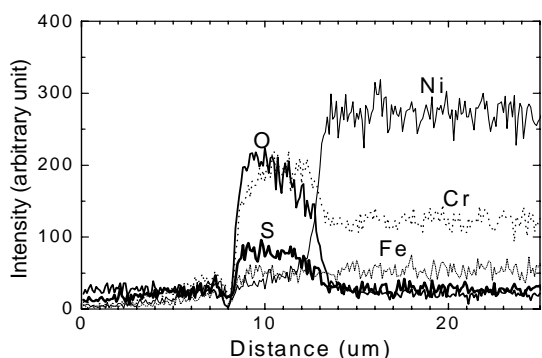

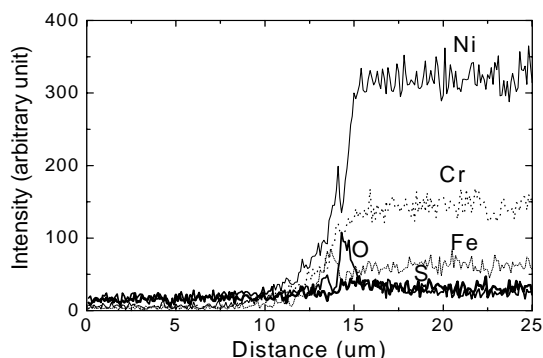**Fig. 1. The EDS spectra of the oxide layer on the Alloy 600 MA test sample surface.**

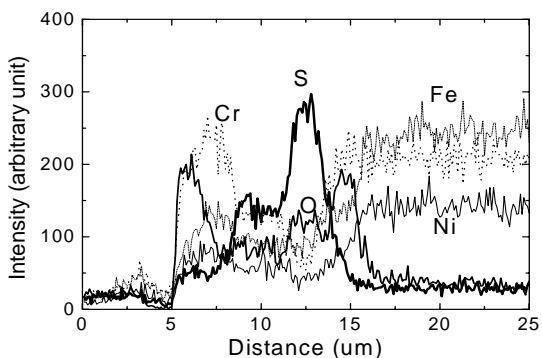**Fig. 2. The EDS spectra of the oxide layer on the Alloy 600 TT test sample surface.**

Fig. 3. The EDS spectra of the oxide layer on the Alloy 800 test sample surface.

3. Summary

In the $S_4O_6^{2-}$ solution, the SCC susceptibility of the SG tubing materials increased in the following order: Alloy 690 TT, Alloy 800, Alloy 600 TT, and Alloy 600 MA. The observed cracks were IGSCCs. A Cr oxide layer was built up on the alloy surface, even in the presence of a reduced sulfur species. However, this layer seemed more porous and less protective than a Cr oxide layer formed without sulfur. The SCC susceptibility of the SG tubing materials was related to the oxide film formed on the alloy surface, heat treatment, and the Cr and Fe content of the alloys.

4. References

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