

Stress Corrosion Cracking of Ni-base Alloys in Sulfur Containing Solutions at 340°C

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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]. Sulfur can originate from various sources, such as resin sources, feed water, cooling water in-leakage, and condenser leaks. Under steam generator operating conditions, sulfates (SO_4^{2-} , +6), the most common sulfur species, should be reduced 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) by a reducing additive of hydrazine. Many authors have investigated effects of reduced sulfur in a wide pH range with or without additives [2-6]. The presence of reduced sulfur species on the surfaces of pulled tubes having stress corrosion cracking (SCC) was also identified [2]. In present work, SCC tests were conducted to investigate effects of reduced sulfur species on the SCC behavior of Ni-base Alloys.

2. Methods and Results

2.1 Experimental

The tested material was commercial Alloy 600 MA, 600 TT, and 690 TT. Chemical compositions and heat treatments of the alloys were presented in our previous work [3]. The shape and geometry of the test specimen were also shown in that work [3]. We prepared test solutions using sodium sulfate (Na_2SO_4), sodium tetrathionate ($\text{Na}_2\text{S}_4\text{O}_6$), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), and sodium hydrosulfide (NaHS). The solution pH was not adjusted and no reducing agents were added. The SCC tests were conducted using a static-autoclave system at corrosion potentials and at 340°C. Solutions were deaerated with a high-purity nitrogen gas for 3 h. The specimens exposed to the autoclave system were inspected every 240 h or 480 h with a stereomicroscope to find cracks. Cracked specimens were analyzed by a SEM and an EDS. The deposits were analyzed by an XRD.

2.2 Results and discussion

Table 1 shows results of SCC tests. Intergranular SCC (IGSCC) was observed for the specimens of Alloy 600 MA, but not for Alloy 600 TT and Alloy 690 TT in

0.01 M SO_4^{2-} solution. The oxide films that formed on Alloy 600 MA showed a double layer: an inner Cr-rich oxide layer and outer thick porous-nickel-sulfide layer, indicating that SO_4^{2-} ions reduce to S^{2-} [6]. IGSCC was observed for the specimens of Alloy 600 MA and Alloy 600 TT, and not Alloy 690 TT in 0.01 M $\text{S}_4\text{O}_6^{2-}$ solution [3]. For all tests, the characteristic odor of the sulfur species was identified, indicating that the reduction of $\text{S}_4\text{O}_6^{2-}$ occurred. In 0.01 M $\text{S}_2\text{O}_3^{2-}$ solution, the specimens of Alloy 600 MA showed IGSCC but not for Alloy 600 TT and Alloy 690 TT. In 0.01 M HS^- solution, the specimens of Alloy 600 MA showed SCC after 960 h [6]. No SCC was observed in the specimens of Alloys 600 TT and 690 TT. The characteristic order of H_2S was identified for all tests. The surfaces were covered with deposits composed mainly of NiS, Ni_3S_2 , and FeS. This indicates that the HS^- ions decompose to S^{2-} ions in high-temperature water.

The SCC of Alloy 600 MA occurred in pure sulfur solutions in all tested sulfur solutions. However, no SCC occurred in Alloy 690 TT, which appeared the most SCC resistant regardless of the sulfur species. The Cr content of the alloy increased the SCC resistance significantly. Alloy 600 TT showed IGSCC only in 0.01 M $\text{S}_4\text{O}_6^{2-}$ solution, indicating that the heat treatment of Alloy 600 increased the SCC resistance.

Table 1: SCC results of the alloys

Species	Conc. (M)	Alloys	Exposure (h)	Cracking mode
Na_2SO_4	0.01	600 MA	2160	IGSCC[6]
		600 TT	6000	NOSCC
		690 TT	6000	NOSCC
$\text{Na}_2\text{S}_4\text{O}_6$	0.01	600 MA	240	IGSCC[3,6]
		600 TT	240	IGSCC[3]
		690 TT	6000	NOSCC[3]
$\text{Na}_2\text{S}_2\text{O}_3$	0.01	600 MA	3600/4560	IGSCC[6]
		600 TT	6000	NOSCC
		690 TT	6000	NOSCC
NaHS	0.01	600 MA	960	IGSCC[6]
		600 TT	5760	NOSCC
		690 TT	5760	NOSCC

Fig. 1 shows a SEM image (Fig. 1(a)) and the EDS profiles (Fig. 1(b)) of O, S, Ni, Cr, and Fe from the cross-section specimen of Alloy 600 MA tested in 0.01 M $\text{S}_2\text{O}_3^{2-}$ solution. Significant grain boundary damage appeared and IGSCC occurred along the grain boundaries. The grain boundary damage can have a

major role in IGSCC. Cr, Fe, and oxygen are depleted whereas Ni is a little depleted in the crack. However, S is significantly enriched in the middle of the crack. This suggests that the reduced sulfur formed near the surface of the specimen diffuses reacting with Ni along the grain boundaries.

From present results, it is clear that the sulfur species reduced to lower-valence sulfur species without any reducing agents and these sulfur species accelerate the degradation of the alloys.

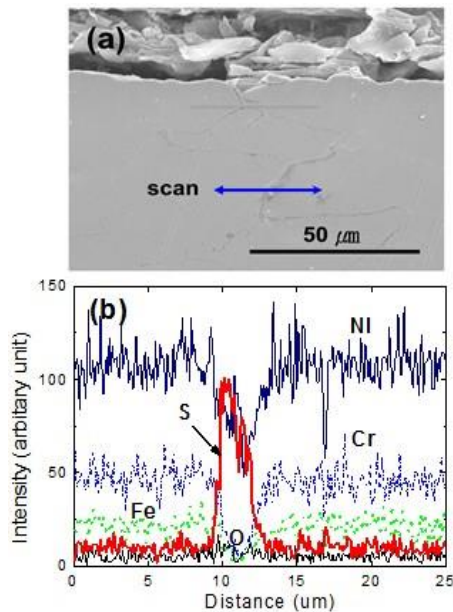


Fig. 1. SEM image (a) and EDS profiles (b) for the cross-section specimen of Alloy 600 MA in 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ solution after 3600 h exposure.

3. Conclusions

The SCC susceptibilities of the alloys in present work increased as follows: $\text{S}_2\text{O}_3^{2-}$ (+2) < SO_4^{2-} (+6) < HS^- (-2) < $\text{S}_4\text{O}_6^{2-}$ (+2.5), and Alloy 690 TT < Alloy 600 TT < Alloy 600 MA. The sulfur species of SO_4^{2-} , $\text{S}_4\text{O}_6^{2-}$, and $\text{S}_2\text{O}_3^{2-}$ reduced to lower-valence sulfur species without reducing agents in high-temperature water, whereas HS^- ions decomposed into S^{2-} ions. The Alloy 690 TT showed the most SCC resistant, regardless of the sulfur species. The Cr content and heat treatments of alloys appeared the increase in the SCC resistance.

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