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Corrosion Behavior of Ni-base Alloys in Aqueous Sulfur Solutions at 340℃

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1. Introduction

Intergranular attack (IGA) and stress corrosion cracking (SCC) of steam generator (SG) tubing materials, mainly nickel-base alloys, have been observed in SG crevices. For PWR plants, lower-valence sulfur species has been identified as the cause of SCC [1,2]. These sulfur species are detrimental to metals and are found inside advancing SCC from the pulled tubes [1,2]. In the present work, effects of environmental (sulfur valence and sulfur concentration) and metallurgical (alloy composition and heat treatment) factors on SCC of nickel-base alloys were investigated. Susceptibilities of the alloys to SCC were assessed by using reverse U-bend specimens in the static autoclave system at 340℃.

2. Methods and Results

2.1 Experimental

Compositions of commercial alloys used for this study and the shape and geometry of the specimen for SCC tests are shown in our previous work [3]. We prepared the test solutions immediately before each test using distilled water (>17 ㏁·㎝) with sodium sulfate (Na_2SO_4), sodium tetrathionate ($Na_2S_4O_6$), sodium thiosulfate ($Na_2S_2O_3$), and sodium hydrosulfide (NaHS). The solution pH was not controlled and no reducing agents were added. The SCC tests were conducted using a static-autoclave system at 340℃ and at corrosion potentials. Before heating, solutions were deaerated with a high-purity (>99.999%) nitrogen gas for 3 h. The test specimens exposed in the autoclave system were inspected every 240 h or 480 h with a stereomicroscope to find cracks. Cracked specimens were removed from the environment and then analyzed by a SEM and an EDS. Deposits of the test specimens were analyzed by an XRD.

2.2 Results of test

The SCC susceptibilities of the alloys increased as follows: $S_2O_3^{2-}$ (+2) < SO_4^{2-} (+6) < HS^- (-2) < $S_4O_6^{2-}$ (+2.5), and Alloy 690 TT < Alloy 600 TT < Alloy 600 HTMA < Alloy 600 MA.

In the 0.01 M SO_4^{2-} solutions, IGSCC was observed for the specimens of Alloy 600 MA [3], but not for Alloy 600 TT and Alloy 690 TT. The surfaces of the test specimens were clean; as a result, XRD analyses were not possible because of a small amount of deposits. After long tests in the 0.1 M SO_4^{2-} solutions, the characteristic odor of sulfur species was not identified. However, Le Canut et al. observed H_2S through its characteristic odor after long tests (500 h) in 5000 and 57000 ppm SO_4^{2-} solutions [4]. The odor of H_2S indicates that the reduction of SO_4^{2-} into low-valence sulfur species such as $S_2O_3^{2-}$ (+2), S^{2-} (-2), and other kinds of sulfur occurred. In our previous work, the oxide films that formed on the test specimen of Alloy 600 MA showed a double layer: an inner Cr-rich oxide layer and outer thick porous-nickel-sulfide layer [3]. This result indicates that the SO_4^{2-} ions reduce to S^{2-} without reducing agents in high-temperature water after adsorption on the surfaces of the specimen.

Intergranular stress corrosion cracking (IGSCC) was observed for the specimens of Alloy 600 MA and Alloy 600 TT, and not Alloy 690 TT in the 0.01 M $S_4O_6^{2-}$ solution [5].

In the 0.005 M and 0.01 M $S_2O_3^{2-}$ solutions, the SCC was observed for the Alloys 600 MA and HTMA, and not for the Alloys 600 TT and 690 TT. After testing, the characteristic odor of H_2S was identified for all tests. The surfaces of the test specimens were covered with thick black deposits mainly composed of Ni_3S_2. For 0.1 M $S_2O_3^{2-}$ solutions, no SCC was observed, and a significant general corrosion occurred in the Alloys 600 HTMA and 600 TT. Fig. 1 shows a weight change of the test specimens of Alloys 600 HTMA, 600 TT, and 690 TT as a function of exposure time. In case of the test specimen of Alloy 600 HTMA, the test was impossible after 3840 h. The effect of alloy Cr content is not clear on the SCC of the Alloys 600 MA, 600 HTMA, and 600 TT, except the Alloy 690 TT. However, the Alloy 600 TT showed higher SCC resistance than Alloy 600 MA and 600 HTMA. This is because semi-continuously spaced grain boundary carbides contribute to the increase of SCC resistance.

In the 0.01 M HS^- solution, the test specimens of Alloys 600 MA and 600 HTMA showed SCC after 960 h and 5760 h. For the test specimens of Alloy 600 HTMA, the cracks were observed through the cross-section specimens by SEM analyses after finishing the tests completely for 5760 h, as shown in Fig. 2. The micrograph of surface morphology analyzed by the SEM indicates IGSCC. No SCC was observed in the test specimens of Alloys 600 TT and 690 TT. After the testing, the characteristic order of H_2S was identified for all tests. The surfaces of the test samples were covered with deposits composed mainly of NiS, Ni_3S_2, and FeS. It is clear from the results of the EDS analysis, the HS^- ions decomposes rapidly to S^{2-} ions in the high-temperature water although the HS^- ions have a low dissociation constant at an ambient temperature. From present results it is confirmed that the S^{2-} ions accelerates the degradation of the alloys.

The results of the EDS analysis and the EDS profiles of cross-section specimens confirmed that the SO_4^{2-}, $S_4O_6^{2-}$, and $S_2O_3^{2-}$ ions reduce into lower-valence sulfur species such as S, S^{2-}, and polymeric S at high-temperature without reducing agents, and the HS^- ions decompose into S^{2-} ions. The results also imply that each sulfur species shows a different SCC mechanism in the alloys.

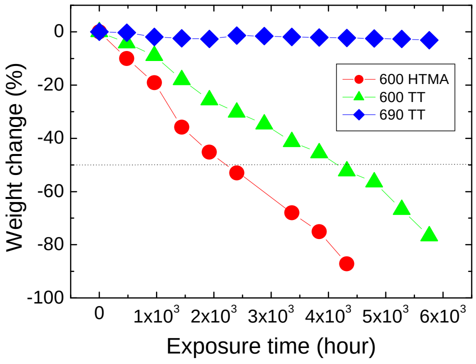

Fig. 1. Weight change of the test specimens exposed in 0.1 M $Na_2S_2O_3$ solution at 340℃.

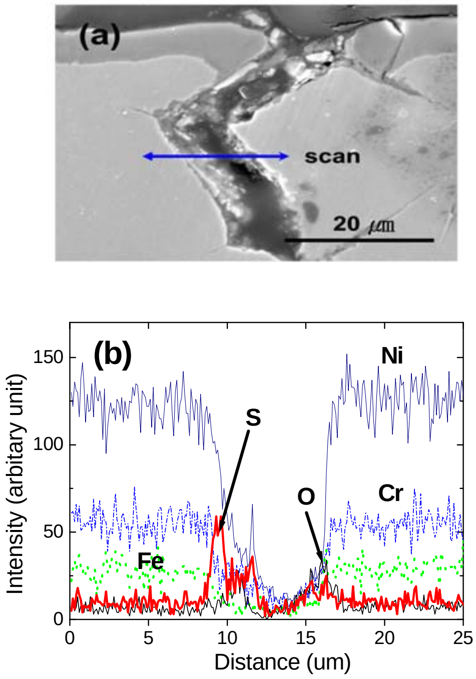

Fig. 5. SEM micrograph (a) and EDS profiles (b) for the cross-section specimen of Alloy 600 HTMA in 0.01 M HS^{2-} solution.

3. Conclusions

The SCC susceptibilities of the alloys in the sulfur-containing solutions increased as follows: $S_2O_3^{2-}$ (+2) < SO_4^{2-} (+6) < HS^- (-2) < $S_4O_6^{2-}$ (+2.5), and Alloy 690 TT < Alloy 600 TT < Alloy 600 HTMA < Alloy 600 MA. The sulfur oxyanions, SO_4^{2-}, $S_4O_6^{2-}$, and $S_2O_3^{2-}$, reduced to lower-valence sulfur without reducing agents; and HS^- ions decomposed into S^{2-} ions. By increasing the concentration of $S_2O_3^{2-}$, the severe general corrosion occurred. The SCC resistance increased with increasing Cr content. The Alloy 690 TT appeared the most SCC resistant, regardless of the sulfur species and concentrations. A Cr oxide layers were built up on the test specimen surfaces in the presence of sulfur.

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