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Study on the Performance of Inhibitors for a SCC of SG Tube Materials

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1. Introduction

Steam generator (SG) tube materials have severe problems of a stress corrosion cracking (SCC) in nuclear power plants. Most of SCCs have occurred near the top of a sludge pile on a tubesheet and within a tube support plate crevice in which it is thought to be caustic. Some inhibitors have been studied to reduce the SCC problems for a SG tube. Laboratory tests using C-ring and constant extension rate specimens have shown that some chemical compounds may inhibit a SCC of a SG tube [1-4]. Several titanium compounds have been applied at PWR type nuclear power plants. While they have reported some beneficial effects, there is insufficient evidence as yet that would convince us of its positive effects as an inhibitor [5]. The objectives of this research are to investigate the inhibition effects of a SCC with a variation of SG tube materials and the penetration property in a crevice of the inhibitors

2. Experimental and Results

The test materials in this study are Alloy 600 MA, TT, HTMA and Alloy 800, Alloy 690 TT. Alloy 600 MA was meal annealed at 960^{o}C. TT and HTMA indicate the thermally treated and high temperature meal annealed. The solution used in the SCC tests was pure 10% NaOH for a reference solution. The additives for an inhibitor were TiO_2 (Degussa co., P25), TyzorLA (DuPont) and CeB_6 (CERAC) with an amount at 1g/L. SCC tests were carried out with a modified RUB (reverse U-bend) specimen. The specimen was insulated by using zirconia parts, and it was preloaded by a 20% tensile strain gauge length before being bent.

During the SCC test, the RUB specimens were checked by an optical stereomicroscope. In order to investigate the property of an inhibitor's penetration into crevices, gaps of different sizes were machined on the sheets of Alloy 600. The penetration test was performed in a solution of 1% NaOH at 150^{o}C for 72 hours with or without a crevice flushing process. The titanium concentration in an oxide layer was analyzed using Auger Electron Spectroscopy (AES).

The SCC test was performed by using modified RUB specimens of several SG tube materials. The chemicals for an inhibitor were added into a 10% NaOH solution and the time to a crack initiation is summarized in Figure 1. Compared with the results of the 10% NaOH without any additives, TiO_2 increased the time to a crack initiation (Figure 1(b)). All the specimens were cracked after 50, 90, 50 and 80 days for Alloy 600 MA, TT, HTMA and Alloy 800 respectively, instead of 40 days for Alloy 600 and 60 days for Alloy 800 in the reference solution test (Figure 1(a)). Addition of CeB_6 showed more resistance to a SCC for Alloy 600 type specimens (Figure 1(c)). However, Alloy 800 was cracked before 30 days, and similar results could be observed for the repeated tests. When TyzorLA was added, Alloy 600 type specimens showed a cracking after 50 days, but it was not effective as TiO_2 or CeB_6 as a SCC inhibitor.

The crack morphology of Alloy 600 MA after TiO_2 addition tests showed an intergranular stress corrosion cracking (IGSCC) and lots of deposits or precipitates were observed. Lumsden [2] suggested that the Ti additives improved the SCC resistance of Alloy 600 due to a change in the composition and the structure of the duplex oxide film, and a passive layer plays a critical role in a SCC resistance.

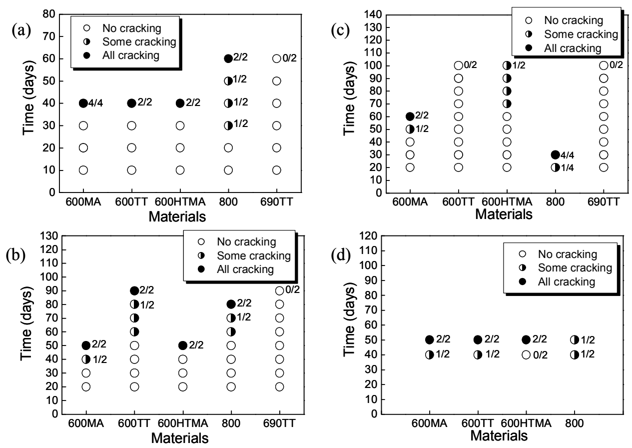
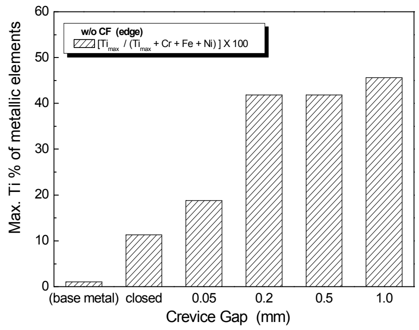
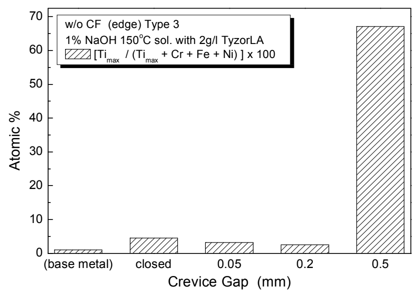


Figure 1. Results of the SCC tests with RUB specimens in the condition of a 10% NaOH solution at 315℃ with (a) no inhibitor (b) TiO_2 1g/L (c) CeB_6 1g/L (d) TyzorLA 1g/L.

Our previous research showed that an addition of TiO_2 changed the electrochemical property in the oxide layer of Alloy 600 [6]. The active current density peak and the current density in the active/passive transition are decreased, and the passive range is extended by TiO_2. A change of the active peak current density and the passive current density might improve the resistance to a stress corrosion cracking and it could be associated with the formation of a passive layer including Ti on the surface of Alloy 600. Model boiler testing showed a positive effect of Ti compounds in an open crevice, but negligible effects have been observed in packed crevices [1]. In this study, the penetration properties of a titanium compound were investigated with different gap sizes by simulating a crevice. The specimens were immersed for 3 days at 150^{o}C and the atomic ratios were measured by AES. Figure 2 shows the results and this indicates that the TiO_2 considerably penetrated the crevice of the 0.05 mm gap and even into the closed gap by a bolting (Figure 2(a)). But in the case of a TyzorLA addition, the concentration of Ti was lower than that of TiO_2 as shown in Figure 2(b). In another test, a pressure drop was performed by 1 bar for 15 seconds or 18 minutes for 4 times for the crevice flushing process. We observed that the penetration of Ti was increased by a crevice flushing and its amount was affected by the pressure drop intervals.



(a)TiO_2 addition



(b)TyzorLA addition

Figure 2. The effect of crevice gap sizes on the maximum Ti concentration in an oxide layer.

3. Conclusion

TiO_2 showed a beneficial effect on a SCC of SG tube materials (600MA, 600TT, 600HTMA and Alloy 800) in a caustic solution (10% NaOH) at 315℃. CeB_6 inhibited the SCC of Alloy 600MA, 600TT and 600HTMA more effectively than TiO_2, at the same conditions. However, CeB_6 addition should be avoided for Alloy 800 due to its negative effect. RUB specimens of Alloy 800 showed a more rapid SCC occurrence with an addition of CeB_6. The effect of TyzorLA on a SCC is less than the other inhibitors. Addition of TiO_2 could affect a SCC by producing some deposits on the crack surface and changing the electrochemical properties on the oxide layer. TiO_2 powder penetrated into a crevice more than TyzporLA, and its penetration was affected by the crevice flushing process.

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