

Abstract

The effectiveness of inhibitors for stress corrosion cracking (SCC) of Alloy 600 steam generator tubes was evaluated in 10% NaOH solution at 315 \cdot . The material was exposed to the test solutions as a specimen type of C-ring and polarized at various potentials above the corrosion potential for five days with and without additives such as TiO₂, TiB₂ and CeB₆. Ti-compounds and cerium boride increased the resistance to SCC. Cerium boride, the most effective, decreased the crack propagation rate more than a factor of three compared with the reference test at 150 mV. Cerium acetate and TiO₂ were also effective to mitigate SCC in lead contaminated caustic solution. Based on the results of the anodic polarization behaviors and the chemical compositions of the films formed on the crack tip in the C-ring specimens being characterized using scanning Auger spectroscopy, it was discussed that the change of the active-passive transition potential and the film profile were related to the resistance of SCC.

Keywords : caustic IGSCC, inhibitor, cerium boride, cerium oxide, Alloy 600, crack tip film, AES analysis

2001

가 Alloy 600 , , 2 1 . . 1999 가 51 , 20 [1]. 가 Alloy 600 가 가 • , P S . , Cr 가 Cr Alloy 600 Alloy 690

가 가 2 가 [2], 가 , 1 [3] 가 . 2 가 2 TiO₂ [4]. TiO_2 가 [5] crevice [6]. TiO₂ 가 315 10% NaOH 가 가 Alloy 600 가 가

가

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2.1

10% NaOH 가 315 . TiO_2 , TiB_2 , CeB_6 , 2 g/l 가 19.05mm, 7 1.10mm Alloy 600 (NX9824) 4 flattening 5 mm 10 mm 가 Table 1 . SiC • 600 grit . Teflon Alloy 600 lead wire . Ni , , Ni-200 5% H₂ - 95% N_2 가 1.38 MPa (200psi) 가 2 , 1 가 350 cc/min cover gas .

1.

5% H ₂ - 95%	N ₂ 7	1.38 MPa	가	가	
	30			(vs. Ni)	20
mV/min					Ni

2-3.

				22.22 mm,	가 1.23 mm	Alloy 6	600 (H602019)
,		Table 1			C-ring		가
, Alloy 6	00			1.5 mm		가	
가						C-ring	가
,	120			3	C-ring		,
10% NaOH	5,000)ppm PbO	가				

Table 1.Chemical composition of Alloy 600 (wt%)

Element Heat No.	Ni	Cr	Fe	С	Si	S	Mn	Cu	Ti	Al	Co	Р	В	N
NX9824	75.28	15.57	8.31	0.026	0.10	<0.001	0. 20	0.01	0.32	0.17	<0.001	0.004	0.004	0.009
H602019	74.8	15.5	8.4	0.02	0. 2	0.001	0.2	0.1						

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2-4.

C-ring			scanning Auger electron				
spectroscopy(AES)	. Cr		Cr				
	. Sputtering	SiO_2	82 Å/min .				

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3-1.

Fig.1	315	10% 1	NaOH							. Reference	
			Alloy	600				가			
	. 가	가					가	가	, Ti	B ₂ , TiO ₂ , CeB ₆	i
	가					TiO ₂ , TiB ₂	С	eB ₆	가	reference	
	11	0 mV		140 mV	, 156 m ^v	V, 192 mV	7	የት			
A	Alloy 600			-							

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Fig. 1 Effect of additives on the potentiodynamic anodic polarization behavior of Alloy 600 in 10% NaOH at 315 .

Fig. 2 Crack depth of Alloy 600 after exposure to 10% NaOH solution with a potential of 150 and 200 mV at 315 .

3-2.

10%	NaOH	C-ring				Fig. 2		. 150 mV
	가	가가기	7}			가 가	-	
	가		가					
						6.35 µm/h	,	, TiO ₂ (rutile),
TiO ₂ (anat	ase), TiB ₂ , CeB ₆	가	5.5 μm	n/h, 3.6 μm	n/h, 2.16 μ	m/h, 1.75 μm/h		
TiO ₂ 7	'ŀ	1/2			, CeB ₆	가		
1/3			,	200 mV	가			
					가			
Fig. 3	10% NaOH	5,000 ppr	n PbO	가	150 mV	가		
				7.11 μ	m/h	cerium acetate	가	4.68 μm/h,

cerium acetate 가 TiO₂ (anatase) 가 3.79 µm/h 가 TiO_2 . CeB₆ 가 Ti-가







(b) Ce acetate

Fig. 3 Optical micrographs showing IGSCC of alloy 600 after exposure to 10% NaOH solution with 5000 ppm PbO at 315 for 5 days.

(a) reference

3-3.

Fig. 4	10%	NaOH	150	mV		가	C-	ring	
					AES			Fig.	5
•					Cr		Ni-Fe		Ni-Cr-
Fe						•	duplex		
IC	GSCC		Alloy 600					5,6	TiO ₂ (anatase)
가				Fi	ig. 6				Cr
				가					
Ti				Fig. 7	CeB ₆	가			Cr
			,	Cr				. CeB ₆	가가 IGSCC
가									
		가			•	Ce	В	AES	
			가						
Fig. 8	200	mV	가		CeB ₆	가			
1	AES		•				Cr		
	CeB ₆	가	150 mV	V		Cr			
			200 m	V			가		

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Fig. 4 SEM morphorogies of the crack tip after exposure to 10% NaOH solution at 315



Fig. 5 AES in –depth composition profiles of alloy 600 in 10% NaOH at 315 for 5 days at 150mV (vs Ni).



Fig. 7 AES in –depth composition profiles of alloy 600 in 10% NaOH + $4g/l CeB_6$ at 315 for 5 days at 150mV (vs Ni).



Fig. 6 AES in –depth composition profiles of alloy 600 in 10% NaOH + $4g/I TiO_2$ at 315 for 5 days at 150mV (vs Ni).



Fig. 8 AES in –depth composition profiles of alloy 600 in 10% NaOH + $4g/l CeB_6$ at 315 for 5 days at 200mV (vs Ni).

가 CeB₆ 가 가 가 가 $80 \ \mathrm{mV}$ 가 가 가 가 NaOH 가 [7] 가 가 가 가 가 110 mV 150 mV , 가 가 가 150 mV pН 11.5, $-1.3 \sim -1.4 V_{SHE}$ [8,9]. Pourbaix diagram[10] [9] Ni, Cr, Fe 300 316 가 -1.15 ~ -1.30 V_{SHE} 150~200 mV Ni NiO CrO_2^{-} Fe , Cr Fe₃O₄ HFeO₂⁻ Cr caustic Fe . CrO_2^{-} Fe • AES depth-profile Fe Cr , NiO 가 Ni Ni 가 porosity • , Cr AES 가 Ti 가 TiO₂ TiB₂ , primary passive 가 Cr Fe Cr Fe . CeB₆ AES Cr . Cr Alloy 600 Cr pН • , 가 2 boric acid 가 가 Na₂B₄O₇ CeB₆ B 가 [11]. 가 가 [12,13] TiB₂ 가 Cr CeB₆ Ce Cr Cr 가 Ce Cr Cr Cr 가 [14] . 가 가 NaOH Alloy 600 가 film rupture/slip dissolution

4.

가 가 5,000 ppm PbO 가 NaOH cerium acetate TiO₂ 가 40~50% 가 가 가 가 가 TiO₂ [4] crevice [6] TiO₂ cerium acetate crevice 가 tubesheet crevice 가 5. Alloy 600 315 10% NaOH 가 가 1) 10% NaOH TiO₂ TiB₂, CeB₆ 가 150 mV 가 가 CeB₆ 1/3 2) TiO₂, TiB₂, CeB₆ 가 가 -•• 가 3) Cr , Ti-가 가 Ti Cr CeB_6

 Cr
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 4) TiO₂
 cerium acetate
 가 PbO 가 5,000 ppm
 10% NaOH

 40~50%
 .
 cerium acetate
 crevice

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 5)
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가 film rupture/slip dissolution

Reference

[1] J. Benson, Steam Generator Progress Report, Rev. 14, EPRI Report TE-106365-R14 (1999).

[2] D.H. Hur, H.S. Chung, U.C. Kim, J. Nuclear Materials, 224, 179 (1995)

[3] R. Pathania, et al, Proc. 7th Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, 163 (1997).

[4] S.G. Sawochka et al, Experience With Inhibitor Injection to Combat IGSCC in PWR Steam Generators, EPRI Report, TR-105003 (1995).

[5] J.B. Lumsden, S.L. Jeanjaquent, J.P.N. Paine and A. Mcllree, Proc. 7th Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, 317 (1997).

[6] J. Daret, J.P.N. Paine, M.J. Partridge, *ibid*, 177 (1997).

[7] N. Pessall, Corr. Sci., 20, 225 (1980).

[8] J.R. Cels, Corrosion, **34**, 198 (1979).

[9] Iuan-Jou Yang, Materials Chemistry and Physics, 49, 50 (1997).

[10] P.L. Daniel, S.L. Harper, EPRI Topical Report, NP-4831 (1986).

[11] Jacques Daret, Thierry Cassagne and Yves Lefèvre, Proc. Eight Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, 100 (1997).

[12] B.P. Miglin, J.P, Paine, Proc. Sixth Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, 303 (1993).

[13] R.S. Pathania, J.P.N. Panie and C.E. Shoemaker, Proc. Third Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, 511 (1987).

[14] D.P. Whittle and J. Stringer, Phil. Trans. Roy. Soc., London A295, 309 (1980).