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PbSCC of Ni-base Alloys in PbO-added Pure Water

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Field experiences and laboratory tests have demonstrated that Alloy 600 steam generator (SG) tubing material is susceptible to stress corrosion cracking (SCC) in caustic sodium hydroxide (NaOH) solutions containing lead oxide (PbO). Since the Alloy 600 is susceptibleto SCC in the caustic solutions alone, it is not easy to separately assess the individual role of PbO from that of NaOH using tests in the solutions where NaOH and PbO coexist. To investigate the effect of PbO on the susceptibility of Alloy 600, SCC tests were performed in leaded or unleaded pure water without NaOH using the slow strain rate test (SSRT) method at 315°C. No SCC was observed for Alloy 600 tested in the unleaded pure water. In the leaded pure water containing PbO, Alloy 600 showed a mixed mode cracking of TGSCC and IGSCC, but IGSCC was observed only at the surface to a very shallow depth. The SCC mode was not changed by adding nickel boride(NiB) as a lead stress corrosion cracking(PbSCC) inhibitor in the leaded pure water, while the susceptibility to PbSCC decreased in the solution with NiB. In addition, The surface films formed on the fracture surface at crack tip for the SSRT specimens were examined using the Auger and the energy dispersive X-ray spectroscope(EDX) after the tests. Cr-depletion in the outer layer of the film was observed from the specimens tested in the pure water with PbO. The thickness and Cr-depleted depth of the oxide film became thinner by adding NiB into the leaded pure water at 315°C

Keywords : *alloy 600, transgranular stress corrosion cracking(TGSCC), intergranular stress corrosion cracking (IGSCC), lead-induced stress corrosion cracking(PbSCC), inhibitor, steam generator, nuclear power plant*

1. Introduction

Alloy 600 has been used for the last four decades for steam generator (SG) tubing in pressurized water reactor (PWR) nuclear power plants, because of its good mechanical and corrosion properties. A number of corrosion and stress corrosion related incidents however have been reported in the SG tubes of the operating nuclear power plants (NPP). Due to the tube degradation, many SG's have been replaced around the world,[1)] resulting in increased maintenance and thus electric generation unit costs. The causes of a SG tube plugging have evolved with time. In the recent years, outer-diameter stress corrosion cracking (ODSCC) has become a predominant identifiable cause that lead to plugging of steam generator tubes.[2)]

It is reported that Pb contaminated in the secondary side cooling water, and thus accumulated in the sludge piled on the top of tube sheet (TTS) accelerates SCC in the SG tubes in nuclear power plants.[3)] The mechanism of the accelerated stress corrosion cracking by Pb, however, has not been clarified, yet. The susceptibility to the PbSCC of Ni-base alloys, such as Alloy 600 and 690 is known to be dependent on environments. Many laboratory SCC experiments have been performed for Alloy 600 in caustic NaOH solutions to examine the effect of PbO,[4)] It was reported that Pb in the solutions significantly accelerates SCC and changes the mode of cracking from intergranular (IG) to transgranular (TG) for Alloy 600. However, it is not easy to separately assess the individual role of PbO from that of NaOH using tests in the solutions where NaOH and PbO coexist, because the Alloy 600 is susceptible to SCC in the caustic solutions alone. To examine the effect of Pb on SCC, it is thus needed to perform tests in solutions where SCC would not occur without Pb.

In the present study, SCC tests were carried out for an Alloy 600 high temperature mill annealed (HTMA) tubing material in pure water at 315°C where SCC is known not to occur. Pure water and pure water containing PbO were used to evaluate the effect of Pb only on the suscepti-

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bility of the Alloy 600 to SCC by using the SSRT method. Nickel boride (NiB) was previously developed as an SCC inhibitor by the authors at KAERI.[5] Effectiveness of the NiB inhibitor was also evaluated in the present investigation.

2. Experimental

A 19.05 mm OD Alloy 600 HTMA SG tubing material was used for the investigation (19.05mm inner diameter and 1.09 mm wall Inco/Valinox heat number NX8524). The chemical composition is given in Table 1.

The SSRT's were performed in pure water and pure water containing PbO at 315˚C. The SSRT test is known to take a relatively shorter time and show a better reproducibility than the other test methods.[6] The SSRT test was carried out using a 0.5 gallon Ni autoclave at 315˚C and the equilibrium pressure without an impressed potential to the specimens, i.e. at the open circuit potential (OCP). Fig. 1 shows the design of the SSRT test specimen. The strain rate of the SSRT tests was $2 \times 10^{-7}\ s^{-1}$

A pure water with a conductivity of 18 MΩ· was used as a reference solution. To prepare the leaded pure water test solution, 10,000 ppm PbO was added to the reference solution. The maximum solubility of PbO in pure water is reported to be about 350 ppm at room temperature.[7] The solubility would increase at higher temperature, yet the added amount of 10,000 ppm is expected to be much more than the saturation value at the test temperature. To evaluate the performance of the SCC inhibitor, 2 or 4 g/l of NiB was added into the leaded test solution. All the solutions were purged with a high purity nitrogen gas to remove the dissolved oxygen for 24 hours before the tests started.

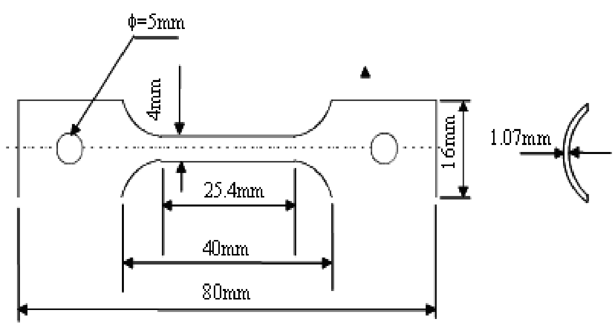


Fig. 1. Design of SSRT specimens.

Surfaces in the gage section and the fracture surfaces after the SSRT tests were examined with an scanning electron microscope(SEM). From the observations with SEM, the morphology and the cracked areas were determined. The SCC behavior and the susceptibility were compared between the specimens tested under different conditions.

3. Results and discussion

3.1 SCC in pure water

Fig. 2 shows the stress-strain curves of the Alloy 600 HTMA SSRT specimens tested in the high purity reference solution, and the solutions containing PbO with/without the NiB inhibitor. As shown in this fig., PbO added into the pure water deteriorate the tensile properties of Alloy 600 HTMA significantly. The elongation and ultimate tensile strength (UTS) of Alloy 600 HTMA tested in the water containing 10,000 ppm PbO was about 30% and 300 MPa, respectively, whereas those obtained in the pure water without PbO was about 55% and 450 MPa, respectively. This means that PbO, itself acts as a species which causes stress corrosion cracking without any other aggressive chemical reagent such as NaOH. When the SCC inhibitor, NiB was added into the water solution containing PbO, there is not much reduction of the UTS but a noticeable increase in its elongation. This indicates that NiB decreases the susceptibility of Alloy 600 HTMA to PbSCC. The effectiveness of the NiB inhibitor increased with the amount of NiB in the solution.

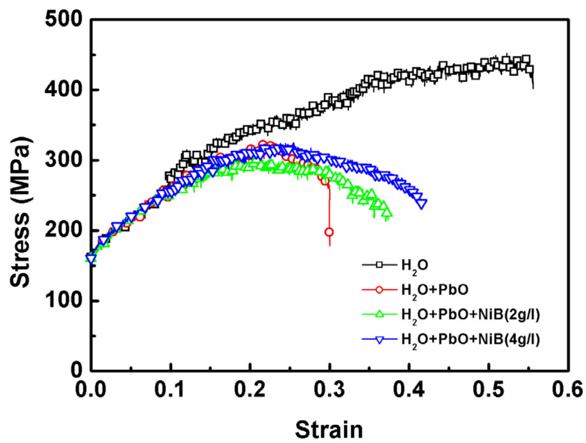
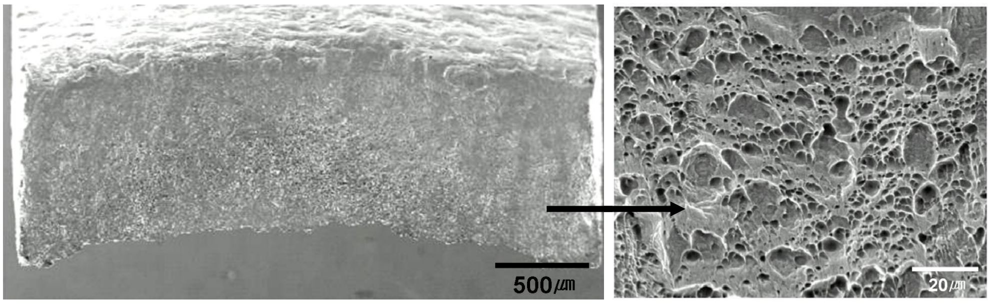


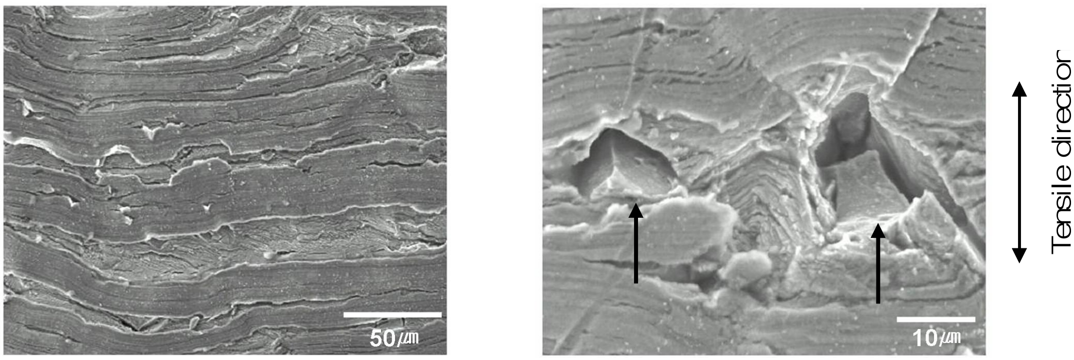
Fig. 2. Stress-strain curves of Alloy 600 HTMA obtained from the SSRT tests in pure water with/without additives.

Table 1. Chemical composition of the Alloy 600 HTMA(NX8524)

Material	C	Si	Mn	P	Cr	Ni	Fe	Co	Ti	Cu	Al	B	S	N
600HTMA	0.025	0.05	0.22	0.07	15.67	75.21	8.24	0.005	0.39	0.011	0.15	0.0014	0.001	0.0103



(a)



(b)

Fig. 3. SEM micrograph of a sample strained in distilled water at 315℃. (a) fracture surface, (b) side surface of the gauge section.

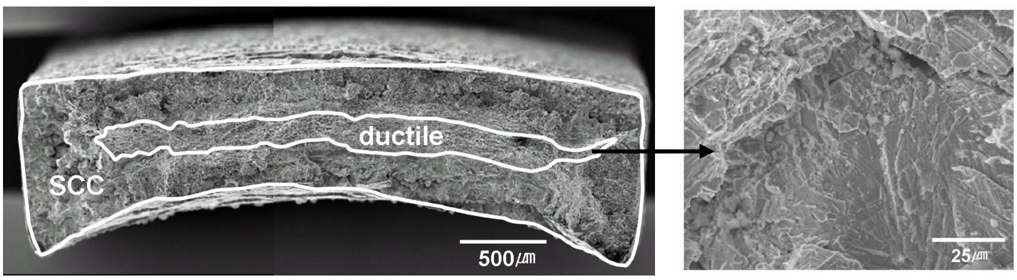


Fig. 4. SEM micrographs of the gauge surface of Alloy 600 HTMA strained in H_2O+10,000ppm PbO.

Fig. 3 is the SEM images of the fractured and the un-fractured gage surface of the SSRT specimens tested in the pure water. The fractured surface shows the ductile fracture features; a dimples mode in fracture surface without evidence of IG- or TG-SCC (Fig. 3a). The un-fractured surface in the gauge section also showed no noticeable cracking except for very rarely observed tiny (about 10㎛) IG crack-like defects (Fig. 3b).

On the other hand, quite different morphologies were obtained from the specimens tested in the water solution containing 10,000 ppm PbO as shown in Fig. 4. Severe stress corrosion cracking occurred, which should cause a significant decrease in the ultimate tensile strength and elongation as described above. The cracking mode in this case was a typically transgranular stress corrosion cracking (TGSCC), whereas in the pure water without PbO, very rarely observed crack-like defects formed on the specimen surface were an intergranular-like as shown in Fig. 3b. TGSCC ratio (A_{SCC}/A_{total}),[6] the fraction of SCC area to the total fracture surface which is used to quantify the degree of TGSCC, was about 83%, while that for the specimen tested in the pure water without PbO was 0%. It has been reported[8] that Alloy 600 LTMA (low temperature mill annealed) tested in a liquid lead at 350°C under a strain rate of 10^{-7} s^{-1} cracked in the IG mode, while in pure water TGSCC occurred with intergranular attack(IGA) formed on the side surface of the specimen. The average crack growth rate(CGR) was estimated to be 1.7×10^{-9} m/sec. from the TG cracked surface area shown in Fig. 4 and by using the following equation (1).[9]

$$\text{Average Crack Growth Rate} = \frac{\text{SCC area} \div \text{Specimen thickness}}{\text{Exposure time}} \quad (1)$$

Fig. 5 shows the specimen surface in the gage section observed from the specimen tested in the water containing PbO. Many deep surface cracks were formed under this test condition. Deposits were seen to precipitate on the specimen surface, which was not observed on the specimen tested in the pure water without PbO. The composition of the precipitates was 41.5 and 58.5 atomic % of Pb and O, respectively. This is close to the composition of PbO, The observation is consistent with the reported results which state that the precipitated Pb on an Alloy 600 surface mostly consists of metal Pb or/and PbO.[4),10)]

Fig. 6 is an optical micrograph for the cracks formed on the Alloy 600 HTMA specimen. The cracks are predominantly TG except IG for some small cracks limited in the area near the specimen surface, as observed by M. Helie[9]) from Alloy 600 LTMA tested in the water containing PbO of 10g/l at 320˚C. As seen in this fig., the primary crack was ramified during propagation into many secondary cracks with a transgranular mode.

In order to evaluate the performance of the SCC inhibitor, NiB, SSRT tests were performed with the Alloy 600 HTMA specimens in a 10,000 ppm PbO-containing water solution with NiB of 2 g/l or 4 g/l at 315˚C. As shown in Fig. 1, elongations of the test specimens increased from 37.0% to 41.8% with an increase of the added NiB from 2 g/l to 4 g/l, while the UTS showed not much difference when compared with the specimen tested in the water containing PbO without NiB. Stress corrosion cracking mode observed with SEM was the same as that obtained in the test condition without NiB, which is mostly TGSCC(IGSCC in minority). However, the SCC area ratio (A_{SCC}/A_{total}) in this case was measured to decrease to 71% for 2 g/l of NiB and 62% for 4 g/l of NiB, which is comparable with 83% for the test condition without NiB as mentioned above. The CGR calculated by using the equation (1) was 1.4×10^{-9} m/sec(78% of CGR for no NiB) for 2 g/l of NiB and 1.0×10^{-9} m/sec(60% of CGR for no NiB) for 4g/l of NiB. The number of surface cracks formed on the specimen surface under this condition was observed to decrease.

The precipitated PbO on the specimen surface was also noticeably decreased by adding NiB in the leaded water solution. From these observations, it can be concluded that NiB acts as an inhibitor for PbSCC of Alloy 600 HTMA in the water containing 10,000 ppm PbO. The SSRT test results obtained in the pure water with/without additives for Alloy 600 HTMA are summarized in Table 2.

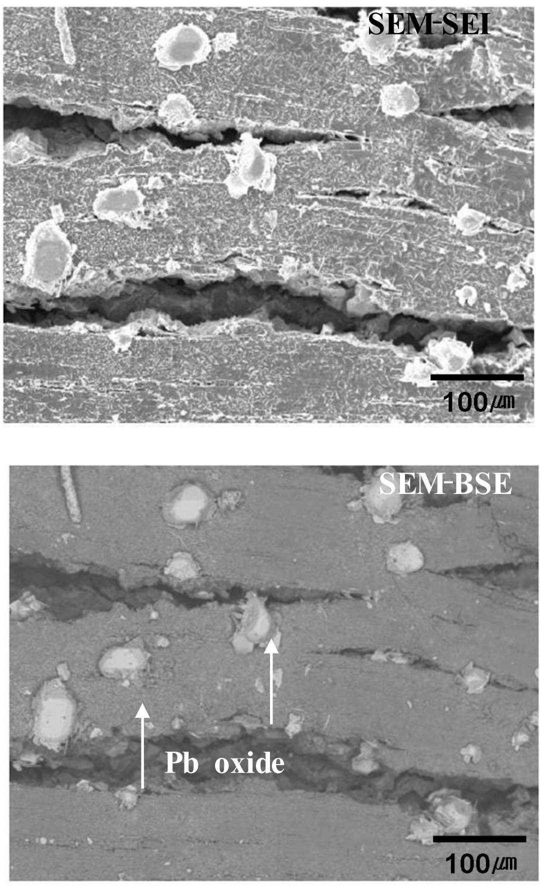


Fig. 5. SEM micrograph of the gauge surface of Alloy 600 HTMA strained in H_2O+10,000ppm PbO.

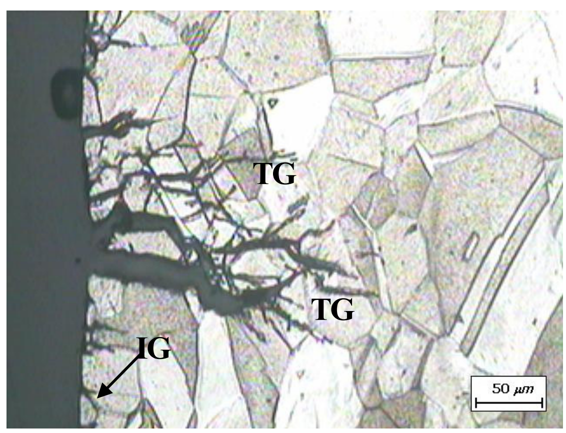


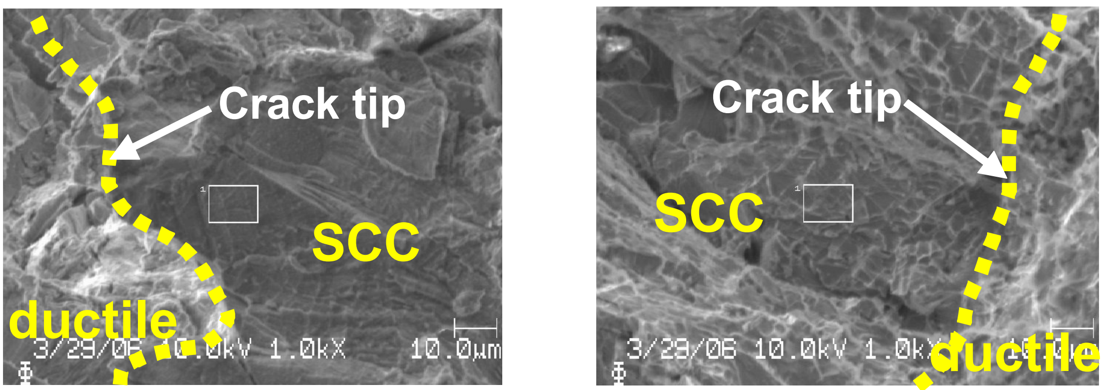
Fig. 6. Optical micrograph of SCC occurring in Alloy 600 HTMA strained in H_2O+10,000ppm PbO.

Table 2. Summary of the SSRT Results for Alloy 600 HTMA.

Condition	EL(%)	Time to failure (hr)	SCC ratio (%)	CGR (m/sec)	Crack mode
H_2O	55.6	826	Neg.	〈$1x10^{-12}$	IGSCC-like
H_2O+PbO(10,000ppm)	30.0	371	83	1.7×10^{-9}	Mostly TGSCC
H_2O+PbO(10,000ppm)+NiB(2g/l)	37.0	445	71	1.4×10^{-9}	Mostly TGSCC
H_2O+PbO(10,000ppm)+NiB(4g/l)	41.8	516	62	1.0×10^{-9}	Mostly TGSCC

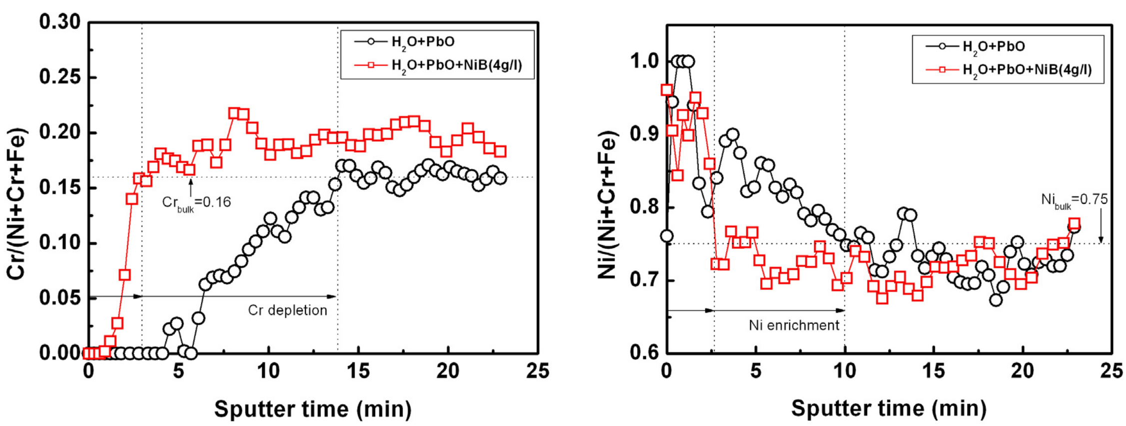
3.2 Analysis of oxide films formed at crack Tip.

Oxide film formed on the fracture surface at crack tip(see Fig. 7) was analyzed using an Auger electron spectroscope(AES) in order to see the effect of PbO and NiB dissolved in pure water on the oxide film property which should change the susceptibility to stress corrosion cracking of Alloy 600. The regions where oxide films around the crack tip were analyzed using AES are represented with rectangles on the fracture surfaces shown in Fig. 7. The depth profiles of Cr and Ni obtained from the regions by successive sputtering of the oxide films on the fracture surfaces are shown in Fig. 8. Severe Cr-depletion was detected from the oxide film formed in the water with PbO and the film thickness was determined to be approximately



(a) (b)

Fig. 7. Fracture surfaces showing the crack tips of Alloy 600 specimens tested in (a) H_2O+PbO and H_2O+PbO+NiB(4g/l) at 315°C. AES analysis done in the rectangular regions with white boundary on the fracture surfaces



(a) (b)

Fig. 8. Depth profile of oxide film compositions formed on the fracture surface at crack tip. Depth profiles of (a) Cr and (b) Ni.

14 μm. In the leaded water solution added with NiB, however, the oxide film thickness was reduced to be about 3 μm and the Cr-depleted depth was much thinner when compared with that in the leaded water solution without NiB. Even though the oxide film thickness formed in the solution with NiB becomes thinner than that in the solution without NiB, the resistance to PbSCC of Alloy 600 was turned out to become higher by adding NiB in the leaded water solution. This means that the oxide film property should be much denser, more compact, and stable by NiB added in the leaded water solution. In other words, these results may suggest that the improved resistance to PbSCC by adding NiB into the H_2O+PbO solution is attributed to the high stability and compactness of the oxide film formed at crack tip during the crack propagates.

Additional investigations are, however, needed to elucidate the inhibition process and the stress corrosion cracking mechanism of Ni-base Cr-Fe alloys. It would be very useful to analyze the film characteristics, such as compactness, electronic and electrochemical properties, structural components, etc..

4. Summary

The PbSCC of Alloy 600 HTMA tubing material was investigated in pure water and water containing PbO. In addition, the performance of an SCC inhibitor, NiB was evaluated in the Pb-containing pure water. From the experimental observations and analyses, the followings are concluded;

1) SCC of Alloy 600 HTMA did not occur in the pure water at 315˚C in the SSRT tests .

2) PbO in the pure water at 315˚C accelerated the SCC of Alloy 600 HTMA. The cracking mode in this condition was a mixture of intergranular and transgranular, but mostly transgranular.

3) The susceptibility of Alloy 600 HTMA to PbSCC in the pure water containing 10,000 ppm PbO could be reduced (inhibited partially) by adding NiB into the solution. The addition of NiB into the solutions did not change the cracking mode.

4) The thickness of oxide film formed near the crack tip became thinner by adding NiB into water with PbO at 315˚C

5) Severe Cr-depletion occurred in the outer layer of the oxide film, which may be the main cause of PbSCC.

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References

1. J. Benson, Steam Generator Progress Report, Rev. 14, EPRI Report TE-106365-R14 (Palo Alto, CA, EPRI, 1999)
2. D.R. Diercks, W.J. Shack, and J. Muscara, *Nuclear Engineering and Design*, **194**, 19 (1999).
3. R,W, Staehle, *Proc. of 11th International Symposium on Environmental Degradation of Metals in Nuclear Power Systems-Water Reactors*, p. 381, Stevenson, (2003).
4. H. Takamatsu, T. Matsunaga, B.P. Miglin, J.M. Saver, P.A. Sherburne, K. Aoki, and T. Sakai, *Proc. of 8th International Symposium on Environmental Degradation of Metals in Nuclear Power Systems-Water Reactors*, **1**, 216 (1997)
5. Y. S. Yi et al, Journal of Nuclear Materials, **347**, 151 (2005).
6. Seizaburo Abe, Masao Kojima and Yuzo Hosoi, "Stress Corrosion Cracking the Slow Strain Rate Technique", p. 294, ASTM STP-665, 1977.
7. D. Feron, I. Lambert, *Proceeding of 12th International Conference on Properties of Water and Steam*, Orlando, (1994).
8. M. Helie, *Proceeding of Sixth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors*, p. 179, San Diego (1993).
9. T. Yonezawa, *ECG-EAC meeting*, Toronto (1996).
10. T. Sakai, K. Aoki, T. Shigemitsu, and Y. Kishi, *Corrosion*, **48**, 734 (1992).