LEAD-INDUCED SCC OF ALLOY 600 IN PLAUSIBLE STEAM GENERATOR CREVICE ENVIRONMENTS

M D Wright*, A Manolescu** and M Mirzai***

ABSTRACT

Laboratory stress corrosion cracking (SCC) test environments developed to simulate representative BNGS-A steam generator (SG) crevice chemistries have been used to determine the susceptibility of Alloy 600 to lead-induced SCC under plausible SG conditions. Test environments were based on plant SG hideout return data and analysis of removed tubes and deposits. Deviations from the normal near neutral crevice pH environment were considered to simulate possible faulted excursion crevice chemistry and to bound the postulated crevice pH range of 3-9 (at temperature). The effect of lead contamination up to 1000 ppm, but with an emphasis on the 100 to 500 ppm range, was determined. SCC susceptibility was investigated using constant extension rate tensile (CERT) tests and encapsulated C-ring tests. CERT tests were performed at 305°C on tubing representative of BNGS-A SG U-bends. The C-ring test method allowed a wider test matrix covering three temperatures (280, 304 and 315°C), three strain levels (0.2%, 2% and 4%) and tubing representative of U-bends plus tubing given a simulated stress relief to represent material at the tubesheet.

The results of this test program confirmed that in the absence of lead contamination, cracking does not occur in these concentrated, 3.3 to 8.9 pH range, crevice environments. Also, it appears that the concentrated crevice environments suppress lead-induced cracking relative to that seen in all-volatile-treatment (AVT) water. For the (static) C-ring tests, lead-induced SCC was only produced in the near-neutral crevice environment and was more severe at 500 ppm than 100 ppm PbO. This trend was also observed in CERT tests but some cracking/grain boundary attack occurred in acidic (pH 3.3) and alkaline (pH 8.9) environments. The C-ring tests indicated that a certain amount of resistance to cracking was imparted by simulated stress relief of the tubing. This heat treatment, confirmed to have resulted in sensitization, promoted transgranular cracking in contrast to the intergranular cracking observed in as-received tubing. However, CERT tests on as-received tubing also promoted transgranular cracking, indicating that the cracking mode is dependent on deformation behaviour rather than on grain boundary Cr-depletion.

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INTRODUCTION

Leaking Alloy 600 steam generator (SG) tubes have resulted in significant unavailability of the Bruce-A Units. The major degradation mode has been identified as stress corrosion cracking (SCC) of the tubes at the 40° hot leg U-bend support (HLUBS). The introduction of lead blankets to one of the BNGS-A Unit 2 steam generators in 1986 exacerbated the problem in one bank of steam generators and resulted in shutdown and layup of BNGS-A unit 2 in September 1995. As part of the development of generic CANDU® steam generator fitness-for-service guidelines[1] an experimental program[2] was established and sponsored by the CANDU Owners Group (COG) which included work on lead-induced SCC of Alloy 600.

The possibility of lead-induced SCC occurring in Alloy 600 (76 Ni/16 Cr/8 Fe) steam generator tubing was first established in the 1960's[3], and secondary side SCC attributed to lead contamination has since been widely reported.[4-7] Laboratory studies of lead-induced/lead-assisted SCC have tended to concentrate on comparisons between Alloy 600 and alternative SG tubing materials[5,8,9] and on determining the cracking mechanism[9-13]. These studies suggest that SCC susceptibility is lower in nickel alloys with higher chromium contents e.g.,Alloy 800 (33Ni/22Cr/45Fe) and Alloy 690 (60 Ni/30 Cr/10 Fe)[14] and that cracking can be linked to the selective dissolution of nickel. However, although the relative susceptibilities of the nickel base Alloys 400, 600, 800 and 690 are reasonably well documented, the envelope of environmental, material and mechanical conditions for cracking are still poorly defined. This is especially true for the near-neutral high-temperature pH conditions where most SGs operate and non-lead secondary side SCC is suppressed.[15] With only a few exceptions,[14,16] most testing has been performed with unrealistically high lead levels and/or in highly acidic or alkaline solutions.

The work reported here was intended to more clearly define threshold conditions for lead induced stress corrosion cracking of Alloy 600 under realistic SG crevice conditions. Laboratory SCC test environments were developed to simulate representative BNGS-A SG crevice chemistries[2] and these have been used to determine the susceptibility of Alloy 600 to lead-induced SCC under plausible conditions. A detailed description of the development of the test environments is given in reference 2.

EXPERIMENTAL PROCEDURE

Materials

An important consideration in this program was that testing should be performed on material that was as representative as possible of actual Bruce A tubing, which is mill annealed Alloy 600 with carbon contents as high as 0.05wt%. Tubes were subjected to a final hydrogen furnace anneal at 1093°C (2000°F). During fabrication of the SGs, tube bundles were also heat-treated to relieve the stresses at the carbon steel closure welds. However, heat was only applied to the lower half of the vessel and tube temperature at the U-Bend region did not exceed 538°C (1000°F).

CERT testing was performed on Alloy 600 tubing, supplied to ASME-SB163 from heat number NX8688, considered to be representative of Bruce A material. This tubing has a relatively high carbon content and is high temperature annealed, resulting in a grain size of approximately ASTM 7 (20 to 40 µm grain diameter). The chemical composition is given in Table 1. This table also provides information on two sample lots of archived Bruce B Alloy 600 tubing which were available for SCC tests. These were used for capsule tests at OHT and some preliminary CERT tests at AECL. All the tubing was confirmed to be non-sensitized in the as received condition using ASTM G28 and A262 (C) tests. The relatively low carbon Bruce B material used for capsule tests at OHT was tested as-received and after being sensitized by heat treating at 607°C for 5 hours. This resulted in a corrosion rate of 822 µm/month in a G28 test. In the as-received condition the corrosion rate was 52 µm/month.

Table 1: Chemical Composition of Alloy 600 Tubing Materials

	Chemical Composition wt%							
	C	**Mn**	**S**	**Cu**	**Al**	**Ni**	**Cr**	**Fe**
Example Bruce A*	0.05	0.25	0.007	0.1		76.7	14.7	5.8
Archived** Bruce B (med C)	0.026	0.275	<0.001	0.036	0.26	76.0	15.0	9.2
Archived*** Bruce B (low C)	0.017	0.23	0.004	0.05		75.4	14.8	9.36
NX8688 HTMA	0.04	0.21	0.001	0.11	0.26	75.3	16.0	8.0

* Tube R58-S42 Unit 1 Boiler 3 report ref. OHT 88-20-K, ** archived at AECL, *** archived at OHT

Summary of Test Environments

Laboratory test environments were developed to simulate representative Bruce-A SG crevice environments based on the results of the assessments and analysis described in reference 2. Deviations from the normal near-neutral crevice pH environment were to simulate possible faulted excursion crevice chemistry and to bound the postulated crevice pH range of 4-9 (at temperature). Deaerated conditions were used for the tests. MULTEQ code (Version 2.22, database V 2.77) was used to predict the pH, solution chemistry and precipitate species of the laboratory test environments at both 25°C and 305°C. Table 2 provides a summary of the test environments. The initial laboratory test pH measured at 25°C is also included for comparison.

Table 2: Summary of Simulated Crevice Environments

Crevice Environment Simulated	Composition	MULTEQ Predicted pH: 25/305°C *	Initial Measured Test pH at 25°C
1. Neutral crevice pH with lead BNGS-A normal crevice)	0.15 M Na_2SO_4 0.3 M NaCl 0.05 M KCl 0.15 M $CaCl_2$ ~ 0.5 mole SiO_2 ~ 100 ppm Pb (added as PbO)	8.97/5.60	8.01
2. Alkaline crevice pH with lead	as above in #1 but with addition of 0.4 M NaOH	12.58/8.86	12.89
3. Acidic crevice pH with lead	as above in #1 but with addition of 0.05 M $NaHSO_4$	2.44/3.28	1.5
	as above in #1 but with addition of 0.05 M $NaHSO_4$ and 500 ppm Pb (as PbO)	2.48/3.36	1.7

* -Neutral pH @ 305 °C is 5.18

Stress Corrosion Cracking Tests

CERT Tests

Constant extension rate tensile (CERT) tests were performed using Cortest CERT load frames. These have a maximum load capacity of 2500kN. Single leg CERT specimens of 12.7 mm gauge length were machined from Alloy 600 tubing by electrical discharge. Within the gauge length the cross-sectional area is approximately 3.8 mm^2. In plan view the cross section is a slightly curved rectangle, 3 mm x 1.2 mm (tube wall thickness). Three separate CERT load frames were employed, all with Hastelloy C static autoclaves fitted with 316 stainless steel liners.

A limited number of CERT tests were performed in a lead-free simplified crevice environment before the more complex lead contaminated environments were used. This was to establish whether cracking was likely in the absence of lead at the pH limits proposed. These tests were performed using the medium carbon content archived Bruce B Alloy 600 tubing. Tests in the final crevice environment were all performed on the Alloy 600 representative of Bruce A material (NX8688). The test temperature for all the leaded crevice environment tests tests was 305°C and a relatively low strain rate of 2E-7s^{-1} was employed. Three levels of lead (PbO) contamination were evaluated; 100, 500 and 1000 ppm for each of the crevice environments (acidic, neutral and basic). Each environment was also tested with no lead added. It should be noted that due to contamination of the autoclave these environments could not be considered lead free. Measurements of residual lead levels in previous tests[17] suggest up to 2 ppm should be expected.

Capsule Tests

To simulate the metallurgical condition of SG tubes from BNGS-A U-bends, corrosion coupons were prepared from the low carbon (Table 1) archived Alloy 600 steam generator tubing sections in the as-received condition.

C-ring specimens were prepared from each material (as-received and heat-treated) according to the ASTM Designation G38-73 "Standard Practice for Making and using C-ring Stress-Corrosion Specimens". Three levels of deformations were used, 0.2%, 2% and 4% strain, for each material. Sets of six C-rings were assembled on each loading rod. The main parts of this experimental assembly and most of the capsules used for testing were made of Alloy 600 to prevent galvanic effects. Carbon steel capsules were used in the tests performed in the least aggressive conditions. The testing temperatures were 280, 304 and 315°C . A furnace block was used to expose simultaneously 15 capsules at each testing temperature. Test solutions were the neutral and acid faulted crevice environments described in Table 2. The effect of varying lead contamination was evaluated by testing in solutions containing 0, 100 and 500 ppm PbO. The exposure time was six months for all tests.

Examination Procedure

SCC susceptibility was assessed by examining the cross-sectioned and metallographically-prepared specimens using optical and scanning electron microscopes. Crack depth and crack morphology were noted together with the extent of secondary cracking along the gauge length of CERT specimens. In some cases SEM/EDX and SIMS analyses were used to characterize elemental composition and distribution of contaminants within the corrosion scale and cracks.

RESULTS

CERT Tests

Results of the CERT tests performed in a non-leaded initial crevice environments are given in Table 3. The results show that these simplified concentrated crevice environments with no lead, do not cause cracking.

Table 3: Results of CERT Tests With Archived Bruce B Alloy 600 in the Initial Simplified Concentrated Crevice Environment

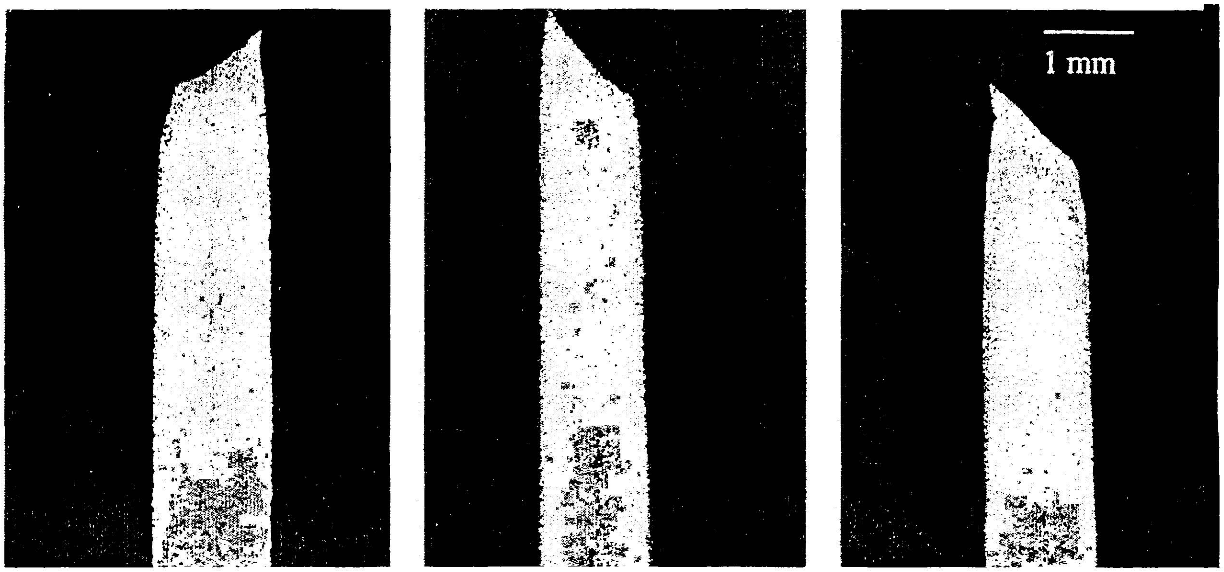
Environment, (all 305°C)		Strain Rate (x10 $^{-7}s^{-1}$)	Total Elongation(%)	Cracks/IGA
0.15M Na_2SO_4	no additions	9.7	72	No
0.3M NaCl	+0.1M NaH SO_4		72	No
0.4M KCl	+0.25M NaOH		77	No
0.01M H_3BO_3	No Boric acid		74	No

Results of the CERT tests performed in the leaded complex crevice environments are given in Table 4 and photomicrographs are shown in Figures 1 to 3. From the results of these tests it appears that the concentrated crevice environments suppress cracking relative to that seen in lead contaminated AVT water. It is not clear from these tests alone whether this is due to inhibition of initiation or reduced crack growth rates. The results in Table 4 and Figures 1 to 3 also indicate that although Pb levels as low as 100 ppm in AVT water result in cracking in CERT[17], this limit increases to ~500 ppm in concentrated crevice environments. It is also noteworthy that only the neutral crevice environment produced cracks with a similar morphology to that seen in an AVT environment and that cracking was most severe in this near neutral environment. This is of particular significance because modifying SG water chemistry to maintain near neutral crevice pH values is thought to prevent cracking in Alloy 600[15] in the absence of lead.

Table 4: Summary of CERT Test Results for Alloy 600 (NX8688) in BNGS-A SG crevice environments with Lead Contamination. Test temperature 305°C, Strain Rate $2x10^{-7}s^{-1}$

Environment		Predicted pH 25C/305°C	Measured pH @ 25°C	Cracking, TG or IG	Crack Depth	Comments
No PbO	Neutral		6.52	pitting	<20 µm	
	Acidic	2.44/3.28	1.58	minor TG intrusions	20 µm	
	Basic		12.26	TG attack /pitting	<20 µm	
100 ppm PbO	Neutral	8.97/5.6	8.2	no cracking		Ductile failure 71% elongation
	Acidic	2.48/3.36	1.51	some TG and IG attack	< 20 µm	Test stopped at 41% elongation
	Basic	12.58/8.86	12.87	some IG attack	< 20 µm	Test stopped at 41% elongation
500 ppm PbO	Neutral		9.52	TG cracking (fine)	~100 µm	Sample failed at 49% elongation
	Acidic		1.67	TG cracking (coarse)	~100 µm	Sample failed at 50% elongation
	Basic		13.03	TG cracking	< 20 µm	Sample failed at 52% elongation
1000 ppm PbO	Neutral		9.75	TG cracking (fine)	~200 µm	Test stopped at 45% elongation
	Acidic		1.58	TG attack (coarse)	< 50 µm	Test stopped at 43%
	Basic		12.7	No Cracks		Test stopped at 49%

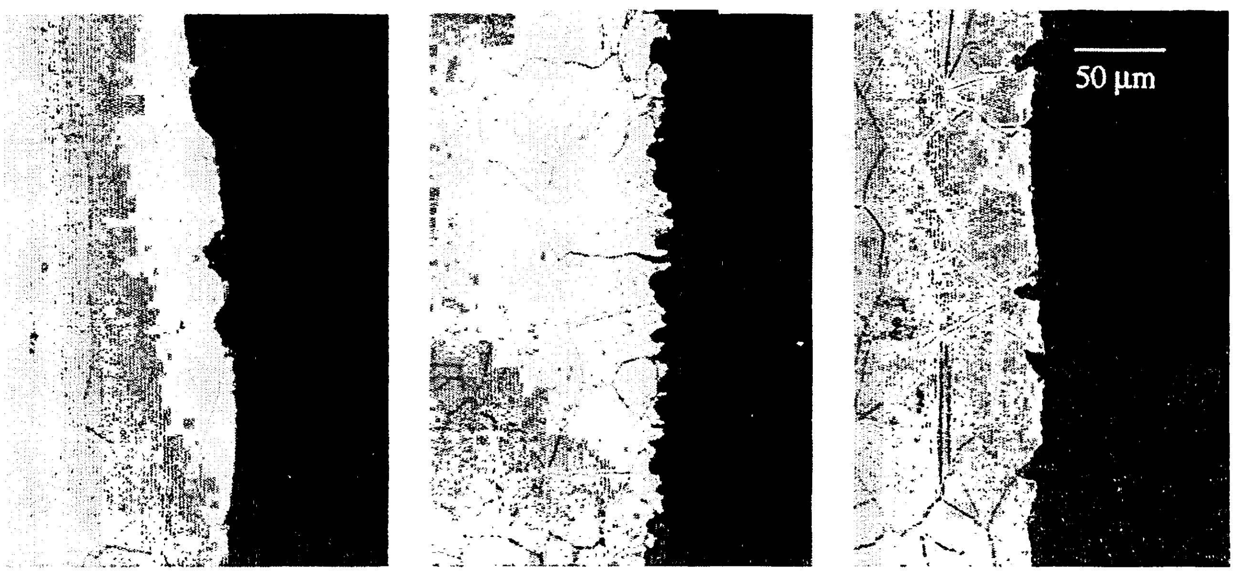
No PbO Added



Neutral Acidic Basic

Figure 1: Micrographs showing ductile failure in CERT specimens tested in the concentrated crevice environments with no PbO added.

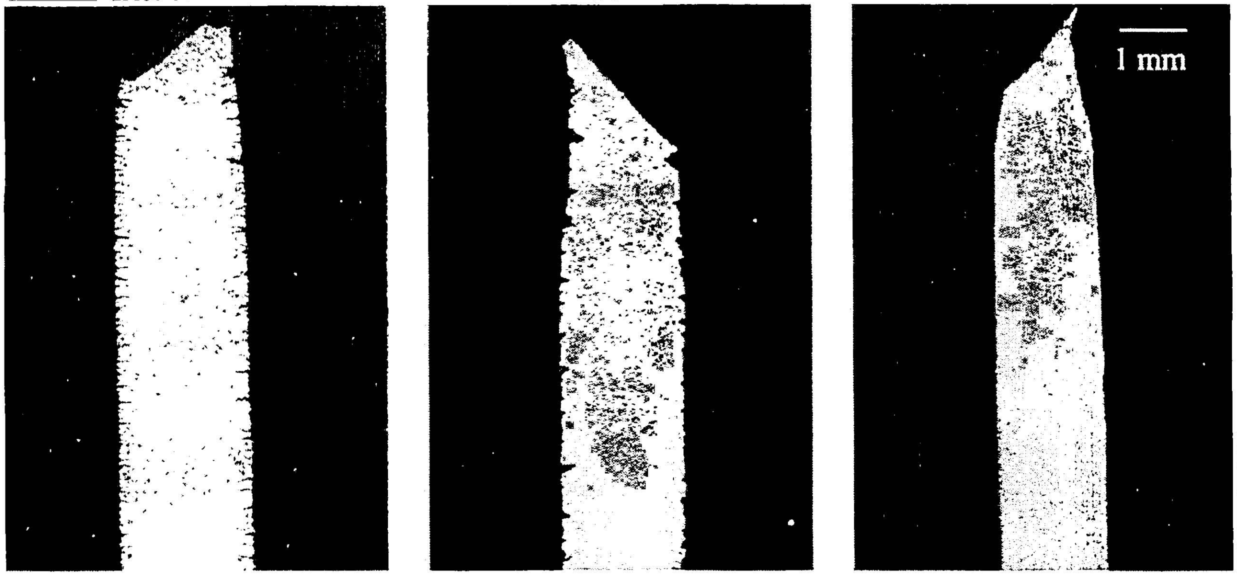
100 ppm PbO



Neutral Acidic Basic

Figure 2: Micrographs showing damage along the gauge length of CERT specimens tested in concentrated crevice environments with 100 ppm PbO. No cracking was observed in any of these tests.

500 ppm PbO



Neutral Acidic Basic

Figure 3: Micrographs showing CERT specimens tested in concentrated crevice environments with 500 ppm PbO. Cracking is most severe in the neutral environment and only very minor cracking is seen in the basic environment.

Capsule Test Results

Table 5 gives a summary of all the tests performed and indicates testing conditions which induced SCC. Details of maximum crack length where cracking occurred are also given. For simplicity the effects of chemistry (amount of PbO and type of crevice), heat treatment of tubing material, stress (level of deformation) and temperature on lead SCC susceptibility of Alloy 600 are summarised as follows:

PbO Concentration: No cracks were observed in tests without PbO; the SCC susceptibility increases with the amount of PbO. After the tests, the lead was found within the oxide scale and cracks; lead appears to influence the incubation time/mechanism for cracking. This observation is consistent with behaviour in AVT environments[17].

Heat Treatment: Archived Bruce-B tubing in the as received condition, simulating Bruce-A U bends, displayed greater SCC susceptibility than heat-treated material simulating Bruce-B tubing; only the higher temperatures (304, 315°C) and the greatest lead concentration (500 ppm PbO) induced cracking in the heat treated material. All non-heat treated samples cracked in an intergranular mode with some minor transgranular cracks, as shown in Figure 4. Conversely for the heat-treated material, cracking was transgranular as shown in Figure 5.

Chemistry: The near-neutral (lead contaminated) crevice environment did induce cracking; no cracking was observed under acidic conditions. However, some very limited cracking was observed in the acidic crevice environment in one test which was performed with no SiO_2 added.

Stress: Lead-induced SCC susceptibility increases with the level of deformation; but under aggressive environmental conditions samples cracked even at the lowest strain level (0.2%).

Temperature: Increasing temperature from 280 to 304/315°C significantly increases SCC susceptibility; however, under all conditions investigated the cracking susceptibility at 304°C was the same as that at 315°C.

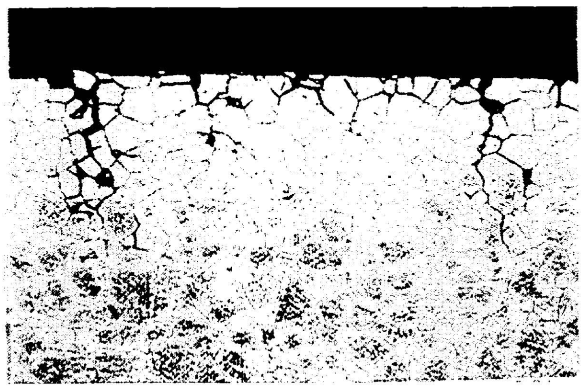


Figure 4: Intergranular cracking in as-received archived Bruce B Alloy 600. C-ring specimen tested at 315°C in neutral crevice environment with 500 ppm PbO.

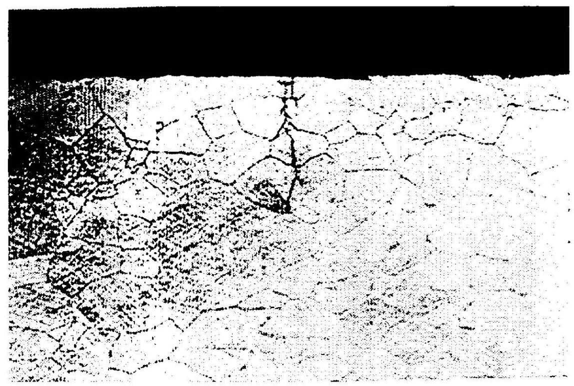


Figure 5: Transgranular cracking in heat treated archived Bruce B Alloy 600. C-ring specimen tested at 315°C in neutral crevice environment with 500 ppm PbO.

Table 5: Pb-Assisted SCC of I600 Maximum Crack Length

Capsule Ident	**Material Condition**	**Stress %Strain**	**Temperature ^0C**	**Chemistry**	**PbO ppm**	**Max. Crack Length Tm**
20	As -Rec	Max	280	NC	500	78
20	As -Rec	Med	280	NC	500	90
3	As -Rec	Max	304	NC	100	87
3	As -Rec	Med	304	NC	100	84
3	As -Rec	Min	304	NC	100	66
5	As -Rec	Max	304	NC	500	205
5	As -Rec	Med	304	NC	500	198
5	As -Rec	Min	304	NC	500	176
15	As -Rec	Max	304	AC	500	24
6	HT	Max	304	NC	500	70
6	HT	Med	304	NC	500	66
33	As -Rec	Max	315	NC	100	75
33	As -Rec	Med	315	NC	100	86
33	As -Rec	Min	315	NC	100	67
35	As -Rec	Max	315	NC	500	210
35	As -Rec	Med	315	NC	500	189
35	As -Rec	Min	315	NC	500	150
45	As -Rec	Max	315	AC	500	27
45	As -Rec	Med	315	AC	500	31
36	HT	Max	315	NC	500	72

Where:
As-Rec.: As-received archive BNGS-B I600 SG Tubing
HT: Heat treated archive tubing
Max.: maximum deformation (4% strain)
Med.: medium deformation (2% strain)
Min.: minimum deformation (0.2% strain)

NC: Neutral crevice
AC: Acidic crevice

DISCUSSION

It was noted in the introduction to this paper that most SCC testing with lead were performed in highly contaminated acidic or alkaline solutions, with pH values significantly higher or lower than used in this work. For these more extreme environments, SCC/intergranular attack is possible even in the absence of lead, and it has been suggested that for Alloys 800 and 690 the role of lead is merely to enhance an existing cracking mechanism.[5,11] The results of this work summarised in Table 3, 4 and 5, show that in the absence of lead the concentrated crevice environments do not produce cracking of Alloy 600 under CERT or C-ring test conditions. Although no cracking was observed, some slight pitting and/or IGA was seen in the CERT in acidic, basic and neutral environments showing all to be relatively corrosive. This tends to confirm that in the absence of lead, even concentrated crevice solutions and acid or base excursion in the pH 4 to 9 range, will not cause cracking of Alloy 600.

If lead contamination is present, this work indicates that the concentrated crevice environments suppress lead-induced cracking relative to that seen in AVT water.[14,16,17] For the (static) C-ring tests, lead-induced SCC was only produced in the near neutral crevice environment and was more severe at 500 ppm than 100 ppm PbO. Comparable C-ring tests in AVT, show cracking with less than 1 ppm PbO.[14] An apparent increase in the lead threshold for cracking was also observed in the CERT tests but in this case the effect is less noticable because in CERT tests the threshold in AVT is ~100 ppm.[17] As stated above, in the C-ring tests cracking was only observed in the near-neutral crevice environment and not in the acidic environment, where increased susceptibility might be expected. This was also observed in the CERT tests where cracking was most severe in the neutral environment although some cracking/grain boundary attack was observed in acidic (pH 3.3) and in alkaline (pH 8.9) environments. Thus, the lead-induced SCC susceptibility of Alloy 600 in concentrated crevice environments appears greatest under near-neutral conditions and is lessened under mildly acidic and alkaline conditions. The relative roles of the concentrated salts and the lead under these conditions is presumably a complex one and may be different for static and dynamic tests, as suggested by this work. It has been noted before that cracking of Alloys 600[17] can be retarded/suppressed by chloride and sulphate in static tests. This is a possible explanation for the discrepancy between experimental crack growth rate data generated in simple AVT environments and service experience.

The C-ring tests indicated that a certain amount of resistance to cracking was imparted by heat treatment of tubing that resulted in sensitization. The beneficial effect of thermal treatment (TT) that results in grain boundary precipitation of Cr carbides has been reported previously.[14,18,19] It was also observed that after heat treatment cracking was transgranular in contrast to the intergranular cracking observed in as-received tubing. However, the fact that CERT tests on as-received non-sensitized tubing also promoted transgranular cracking, suggests that the cracking mode is dependent on deformation behaviour, inflenced by carbide precipitation rather than grain boundary Cr depletion. This is consistent with the reported change in cracking mode from intergranular to transgranular after higher temperature thermal treatments (TT) [14,18,19] that result in grain boundary carbides but not in Cr depletion.

CONCLUSIONS

Laboratory SCC test environments developed to simulate representative BNGS-A SG crevice chemistries have been used to determine the susceptibility of Alloy 600 to lead-induced SCC under plausible conditions. The results of this test program allow the following conclusions to be drawn:

(1) Cracking does not occur in the concentrated, 3.3 to 8.9 pH range, crevice environments investigated in the absence of lead contamination.

(2) The concentrated crevice environments suppress lead-induced cracking relative to that observed in AVT water.

(3) For the (static) C-ring tests, lead-induced SCC was only produced in the near-neutral crevice environment and was more severe at 500 ppm than at 100 ppm PbO.

(4) In the CERT tests cracking was most severe in the near-neutral crevice environment at all lead levels tested but some cracking/grain boundary attack was observed in acidic (pH 3.3) and alkaline (pH 8.9) environments.

(5) The C-ring tests indicated that a certain amount of resistance to cracking was imparted by simulated stress relief of tubing.

(6) Temperature has a dramatic effect on the cracking susceptibility of Alloy 600 in C-ring tests; at 280°C the susceptibility of SG tubing was remarkably lower that at 304/315°C but there was no change in SCC susceptibility between 304 and 315°C.

ACKNOWLEDGEMENTS

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DISCUSSION

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Paper: Lead-Induced SCC of Alloy 600 in Plausible Steam Generator Crevice Environments

Questioner: R.W. Staehle

Question/Comment:

This program represents an enormous effort. I have several comments:

(1) The effect of potential needs to be clarified since the potential is affected by hydrogen, hydrazine and the Pb/PbO equilibria. This variable is especially important with respect to:

(a) Accumulation of hydrogen in autoclaves with respect to reduced hydrogen in steam generators.
(b) Effects of hydrogen additives
(c) Shut-down oxygen
(d) The pH cell where higher pH produces lower potentials than more neutral cells.

(2) The effect of hydrazine and ammonia may be important from the point of complexing lead. The fact that lead is observed in crack tips suggests that lead is a negatively charged complex.

(3) You might review the EPRI work of Miglin et al. with respect to the occurrence of Pb-SCC in steam.

(4) With respect to your electrochemical work,

(a) You might also review the work of Kilian at Siemens.
(b) You need to be careful with electrochemical studies since lead is deposited from solutions at low potentials and would provide additional current as well as a higher E_{oc}. This deposited lead will oxidize as the potential is increased and will, therefore, give misleading currents.

(5) The EPRI curves of da/dt are absolutely misleading with respect to expectations as you will note. The real implication of the EPRI curve is that little work has been done in the mid-range of pH.

(6) The fact that 690 sustains SCC in Pb solutions, sometimes at much higher rates, also provides an important clue to the role of lead. This pattern is somewhat different from the effects of other species such as Cl^-, S^{2-}, etc.

(7) You should consider looking at Pb effects at lower temperature in view of possibly important contributions of shutdown effects.

Response:

Thank you for your comments. We do intend to investigate the effect of potential in a systematic way. The possible effects of complexing are about to be looked at. In this respect, we hope to be able to use an imaging XPS system to illuminate this.

Questioner: J. Gorman

Question/Comment:

(1) What examination techniques should be used for pulled tubes to check for lead?
(2) How can one estimate the concentration of lead in crevice solutions?
(3) How have controlled potential tests been done to explore ECP effects?

Response:

(1) No one technique is adequate but we think SIMS offers the most reliable results in terms of detection limits and we would caution against relying on SEM/EDX.
(2) We had information on lead concentrations in sludge, in tube deposits and on the distribution of lead within cracks from the failure investigations. We compared this with equivalent data from lab test in AVT and PbO and concluded an appropriate PbO concentration to be 100 to 1000 ppm.
(3) No, not yet but this is the next stage.

Questioner: Y.C. Lu, AECL

Question/Comment:

Roger Staehle mentioned that the accumulation of hydrogen in the static autoclave tests will change the ECP of the alloy and influence the lab SCC tests. But from ECP measurements done in static autoclave, we did not observe any continuous ECP decrease during the autoclave tests. If hydrogen was accumulating substantially, influencing the ECP of tube alloys, it should have been observed.