INTERNAL OXIDATION AS A MECHANISM FOR STEAM GENERATOR TUBE DEGRADATION

T.S. Gendron[1], P.M. Scott[2], S.M. Bruemmer[3], and L.E. Thomas[4]

ABSTRACT

Internal oxidation has been proposed as a plausible mechanism for intergranular stress corrosion cracking (IGSCC) of alloy 600 steam generator tubing. This theory can reconcile the main thermodynamic and kinetic characteristics of the observed cracking in hydrogenated primary water. Although secondary side IG attack or IGSCC is commonly attributed to the presence of strong caustic or acidic solutions, more recent evidence suggests that this degradation takes place in a near-neutral environment, possibly dry polluted steam. As a result, internal oxidation is also a feasible mechanism for secondary side degradation.

The present paper reviews experimental work carried out in an attempt to determine the validity of this mechanism. The consequences for the expected behaviour of alloys 690 and 800 replacement materials are also described.

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T.S. Gendron, P.M. Scott, S.M. Bruemmer, and L.E. Thomas

1. INTRODUCTION

Stress corrosion cracking (SCC) of mill-annealed alloy 600 (Ni~15%Cr~9%Fe) steam generator tubing has proven to be a serious operating problem resulting in extensive tube plugging, additional inspection costs, outage time and in several recent cases, premature steam generator replacement. This cracking has initiated on both the primary side (ID) and the secondary side (OD) of the tubes. Figure 1 shows that intergranular attack (IGA) and IGSCC of steam generator tubes, initiated from the secondary side is becoming increasingly prevalent world wide[1]. At the present time, this is almost exclusively found in mill-annealed alloy 600, although some recent evidence from North America suggests that thermally treated tubing is starting to show IGA/IGSCC.

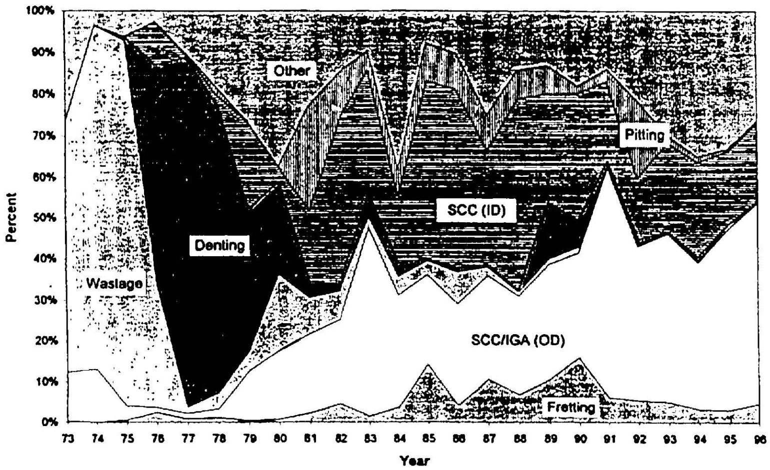


Figure 1: World Wide Causes of Steam Generator Tube Plugging[1]

Despite extensive research, there is no consensus on the mechanisms of primary water (PW)SCC or IGA/IGSCC. The advantages of a mechanistic understanding of these degradation processes are increased confidence in lifetime prediction models and remedial measures such as chemistry control and replacement alloys. Purely empirical strategies, particularly for time-dependent phenomena incorporating long incubation periods, can be unreliable.

The conventional mechanisms used to explain SCC based on anodic slip dissolution and hydrogen embrittlement have not been able to explain adequately the phenomenology of PWSCC. An alternate mechanism for PWSCC is based upon the phenomenon of internal oxidation[2]. It appears to offer a satisfactory explanation of the high activation energy and stress exponent, the influence of hydrogen overpressure, grain boundary carbide morphology and cold work, and the improved resistance of alloys 800 and 690 to PWSCC.

A more recent proposal[3] suggested that internal oxidation may also explain IGA/IGSCC on the secondary side. This idea originated from the growing belief that IGA/IGSCC occurs in near-neutral environments and evidence that the affected superheated crevices could be steam-blanketed.

This paper reviews the experimental data and evidence from pulled tubes in support of the internal oxidation mechanisms of steam generator tube degradation, the nature of additional work necessary to validate the hypotheses, and the inferred likely behaviour of alloys 800 and 690 if this mechanism applies.

2. THE INTERNAL OXIDATION MECHANISM

Internal oxidation is a phenomenon in which the minor element in an alloy is selectively oxidized and the main solvent metal remains largely unattacked. A necessary condition for internal oxidation is that the redox potential of the environment be close to the equilibrium oxidation potential of the main solvent metal to prevent it from contributing significantly to the formation of a protective (passive) surface film. This cannot occur if the minor element exceeds a critical concentration where it is capable of forming a passive film independently. In nickel-chromium alloys, the critical concentration of Cr for passivation at the Ni/NiO equilibrium increases with decreasing temperature.

Internal oxidation is well-known for Ni-Cr alloys in gaseous environments at temperatures above ~500°C[4]. For example, alloy 600 has been severely degraded by internal oxidation in methane-steam mixtures within a few months at 500°C in methane reforming plants. A critical question is whether the phenomenon can occur at temperatures as low as 300°C in water-hydrogen or steam-hydrogen mixtures. A study of the kinetics of IG oxidation cracking in nickel alloys as a function of temperature suggests that it is feasible[5]. Figure 2 shows the similarity in activation energies for crack growth of Ni_3Al in air and of alloys 600 and X-750 in PWR primary water or hydrogenated steam near the Ni/NiO equilibrium potential.

3. APPLICATION TO PWSCC

3.1 Proposed Mechanism

As explained above, a necessary condition for internal oxidation is that the redox potential of the environment be close to the equilibrium potential of the main solvent metal of the alloy. The hydrogenated primary coolant of water-cooled nuclear reactors satisfies this requirement for nickel-base alloys (assuming that hydrogen is the only specie affecting the corrosion potential of the alloy). Figure 3 shows the redox potential-pH zones corresponding to the CANDU heat transport system (HTS) and PWR primary water chemistry specifications, on the Pourbaix diagram for alloy 600 at ~300°C. The figure also illustrates that the region of susceptibility to

PWSCC from laboratory and field data is bounded by potentials +/-80mV relative to the Ni/NiO equilibrium potential. The zones indicating susceptibility to cracking and IGA are based on published laboratory and field data and may not be comprehensive.

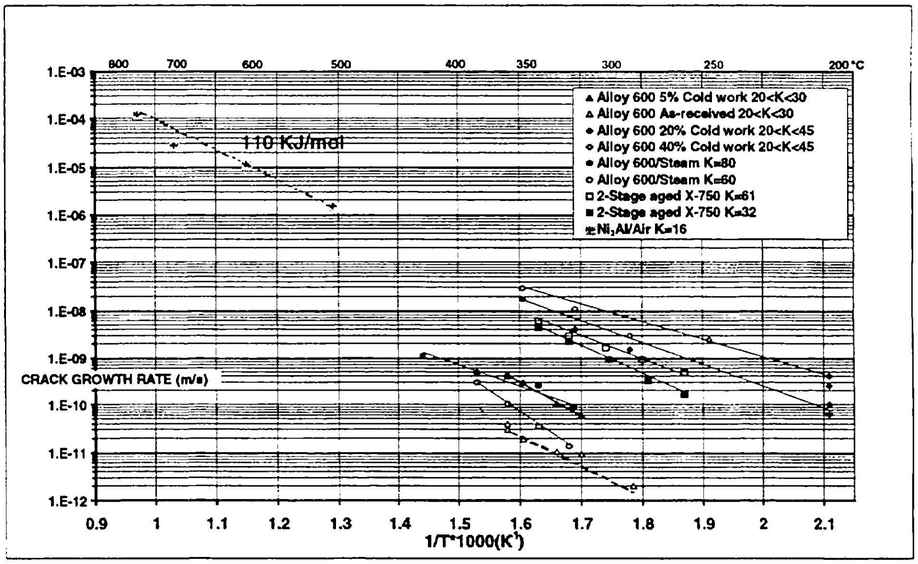


Figure 2: Arrhenius Plot of 'Plateau' Crack Growth Rates ($K_I \geq 16$ MPa√m) for Oxygen Induced Cracking of Ni_3Al and IGSCC of Alloys 600 and X-750 (5).

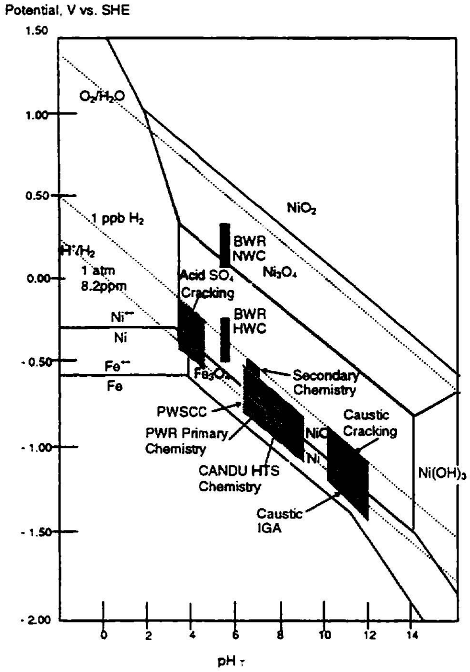


Figure 3: Pourbaix diagram showing the known modes of cracking in alloy 600 at ~300°C.

Two previous publications[2,5] have demonstrated that the kinetics of PWSCC and its activation energy were consistent with the IG diffusion rates for oxygen in nickel. Qualitatively, carbide morphology, plastic strain, and cold work would be expected to influence IG oxygen diffusion in alloy 600 and hence the PWSCC rate, as is observed.

By analogy with previous work on oxygen embrittlement of nickel alloys at high temperature[6], four different embrittling mechanisms were proposed: oxygen reaction with carbon and carbides to form CO/CO_2 bubbles, oxygen reaction with Cr or other strong oxide formers to form IG oxides, oxygen reaction with impurity precipitates to release damaging sulfur, and intrinsic oxygen atom embrittlement of the grain boundaries. Whatever the embrittling species, the kinetics of oxygen diffusion would be expected to follow a parabolic law and therefore crack propagation is envisioned to occur in this mechanism in a series of discrete steps as a critical depth of embrittlement was reached, dependent on the applied stress intensity.

3.2 Experimental Evidence

At least seven laboratories have independently examined this mechanistic hypothesis. At two laboratories,[7-13] thin foils of alloy 600 were exposed to PWR primary water at 360°C or to hydrogenated steam at 380° or 400°C and subsequently fractured at room temperature. Precautions were taken to remove absorbed hydrogen to avoid any contribution from hydrogen embrittlement. Grain boundary embrittlement was observed to shallow depths of up to a few microns. Figures 4a and b show grain boundary embrittlement to a depth of ~1µm in stress-relieved alloy 600 steam generator tubing after an 8-hour exposure to 400°C steam/hydrogen[13].

Figure 4a: SEM micrograph plan view of an alloy 600 foil showing grain boundary separation near the fracture surface.

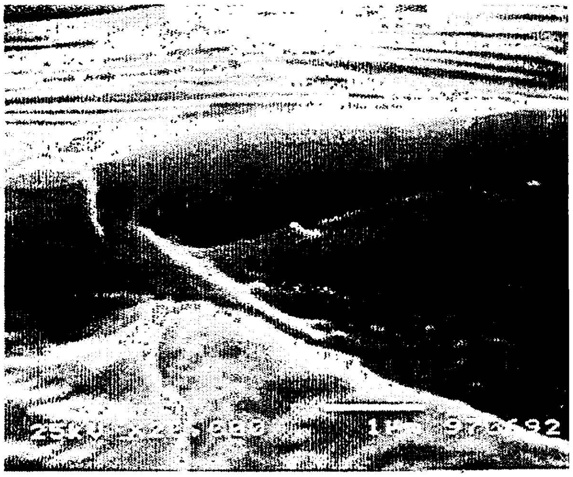


Figure 4b: SEM micrograph edge view of the fracture in Figure 4a showing one face of a separated grain boundary.

Two other investigators have reported similar embrittlement in conventional SCC specimens.[7,14] In the first case, small tensile specimens and half sections of steam generator tubes were exposed to primary water at 360°C, without any stress applied. The tensile specimens were pulled apart slowly in an electron microscope and the tube specimens were bent into the reverse U-bend geometry. Intergranular separation was observed, usually of a few μm but up to 10 μm in depth. In the second case[14], tensile specimens were exposed under stress to hydrogenated steam at 380°C. It was reported that the depth of the grain boundary embrittlement in these specimens went beyond any observable stress corrosion cracks and increased with tensile stress. The embrittled zone along grain boundaries was associated with dark shadow images observed by back-scattered electrons in the scanning electron microscope. Some evidence has been obtained to indicate that such embrittled zones are not simply closed-up cracks although doubts persist in the absence of positive proof. Similar dark shadow images of grain boundaries have been obtained in classical internal oxidation studies of stress-free specimens of nickel-chromium alloys with controlled minor element additions at higher temperatures in air[15].

Secondary ion mass spectrometry (SIMS) and Auger analyses,[9,16] together with some recent work using oxygen-18,[12] have confirmed the shallow penetration of oxygen into intact grain boundaries in unstressed alloy 600 foils and SCC specimens exposed to hydrogenated water or steam. One SIMS study[12] identified Cr_2O_3 at grain boundaries and also showed evidence for NiO and adsorbed oxygen in foils to depths corresponding to the observed crack depths after fracture. Kinetic information from the depths of oxygen penetration after different exposure times was, however, unable to explain the observed PWSCC crack growth rates. These observations were thought to be due to the rapid saturation of the depth of embrittlement following parabolic kinetics and the absence of stress to assist the diffusion rates. Alternatively, an additional contribution from hydrogen embrittlement of the oxygen-damaged grain boundaries was also proposed. The other SIMS study of alloy 600 reverse U-bend specimens exposed to hydrogenated water at 365°C showed IG oxidation to a depth of ~30μm beyond the visible crack tip.[16] This depth is rather large compared to depths observed in other studies, including the work described below. Therefore it seems possible that it is not all associated with intact grain boundaries.

Further evidence supporting the susceptibility of nickel-base alloys to internal oxidation at intermediate temperatures comes from corrosion fatigue studies in air at 400° and 550°C.[10,11] This work shows a step increase in growth rates occurring at a specific partial pressure of oxygen which is associated with the transition to IG cracking and the formation of a nickel oxide film on the fracture surface instead of a chromia film. Although the partial pressure of oxygen in these tests in a vacuum chamber did not correspond to the thermodynamic equilibrium pO_2 for NiO at the test temperature, further work on Alloy 718 in buffered H_2/H_2O mixtures at 593°C shows conclusively that the transition in growth rates and crack path does correspond to the thermodynamic pO_2 above NiO.[21] In addition, TEM specimens incorporating the crack tip revealed the presence of pure Ni nodules embedded in the NiO films on the fracture surfaces which is one of the indicators for the occurrence of internal oxidation.

In order to examine IGA and IGSCC characteristics at higher resolution, analytical transmission electron microscopy (ATEM) has been used to reveal grain boundary and crack-tip microstructures and microchemistries. A critical aspect of this work is preparation of electron-transparent cross-section samples by ion milling.[17,18] One laboratory reported only NiO at the IGSCC crack tip in both alloys 600 and X750 tested in hydrogen-deaerated primary water.[19] They did not detect oxides beyond the observable SCC crack. More recent high-resolution examinations of mill-annealed alloy 600 samples tested in 330°C primary water (1200 ppm boron as H_3BO_3, 2 ppm lithium as LiOH and 25-35 ml hydrogen per kg H_2O at STP)[20] have indicated that internal grain boundary oxidation does occur under these environmental conditions. Preliminary observations are summarized schematically in Figure 5 and described in the following paragraphs.

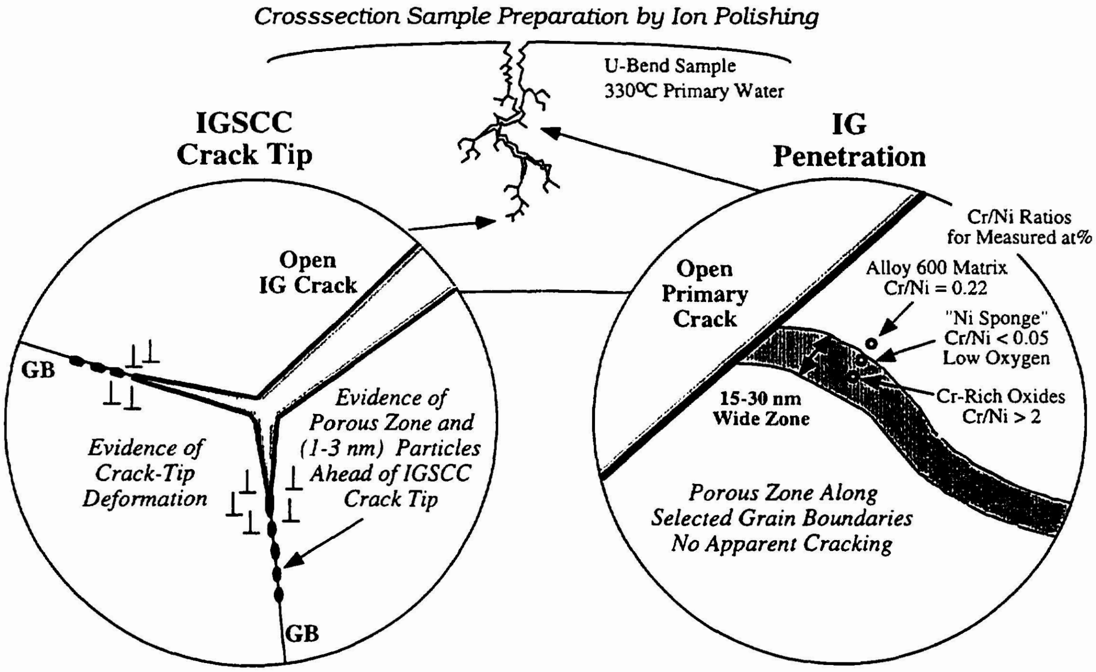


Figure 5: Schematic Illustrating Cross-sectional ATEM Observations of IG Penetration and IGSCC Crack Tip Regions in an Alloy 600 Sample After U-Bend Testing in 330°C Primary Water.

An example of the typical crack-tip microstructure is illustrated in Figure 6a showing the open crack ending in a sharp tip with an uncracked grain boundary extending ahead of the tip. Local strain concentrations appeared around the SCC crack tips, but it is possible that these strains arose during preparation of the thin-foil specimen. Careful imaging has revealed a narrow (~2 nm in width) porous region immediately ahead of the tip. A thin-film of polycrystalline, chromium- and iron-rich oxide with the NiO structure was identified on the SCC crack walls in the tip region as illustrated by the insert diffraction pattern in Figure 6b. This figure also presents a dark-field image of the grain boundary ahead of the crack tip revealing polycrystalline nm-sized particles. These fine particles were localized along the grain boundary within ~0.3 μm of the crack tip and could not be easily imaged using brightfield contrast.

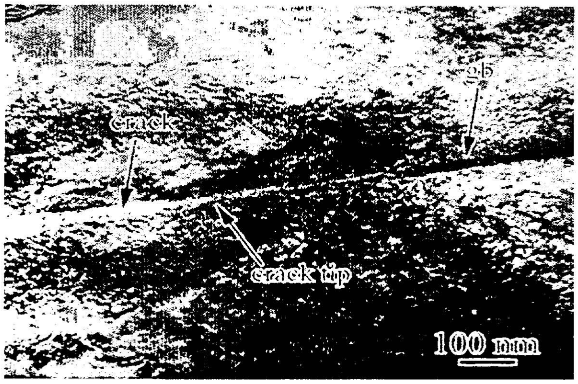


Figure 6(a): Brightfield TEM Image of a Sharp IGSCC Crack Tip in Alloy 600.

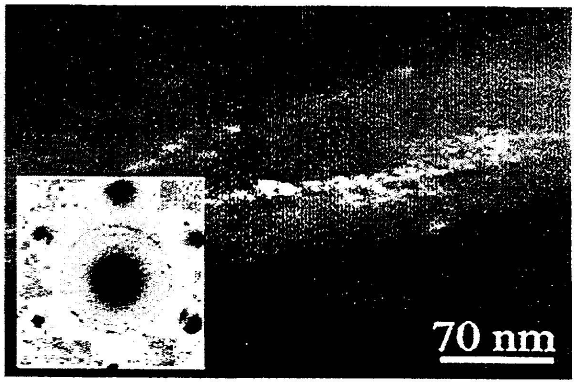


Figure 6(b): Darkfield TEM Image of the Grain Boundary Region Just Ahead of the Crack Tip Shown in Figure 6(a).

In addition to evidence of local oxidation ahead of an IGSCC crack tip, many grain boundaries showed obvious IG oxide penetration as documented in Figure 7. These degraded boundaries were not associated with an active SCC crack, but originated from the primary SCC crack wall (see schematic in Figure 5). The width (10-30 nm) and depth (up to several μm) of the oxidized regions were significantly greater for the IG penetrations than for IGSCC crack tips. Energy dispersive X-ray spectroscopy and electron energy loss spectroscopy (EELS) measurements showed that this IG penetration zone contained localized regions of Cr-rich oxides and porous Ni metal. EELS analysis of the penetrations showed no detectable boron or enrichment of carbon, indicating that these regions were isolated from the aqueous crack environment.

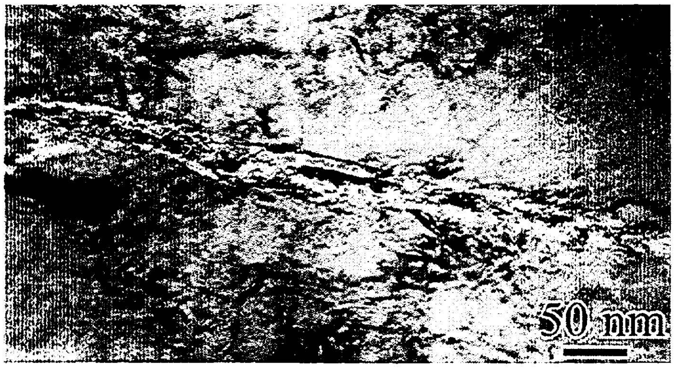


Figure 7: Brightfield Image of IG Penetration Region off the Primary SCC Crack as Illustrated in Figure 5.

High-resolution cross-section ATEM observations clearly suggest that grain boundary oxidation can occur in alloy 600 after exposure to high-temperature primary water. Further measurements are required to confirm these results and establish the role of oxygen penetration in IG degradation. Internally formed oxides of elements such as Cr, Mn, Ti, Si and Al, which could form at the equilibrium potential of Ni/NiO, are all credible possibilities for a grain boundary oxidation mechanism. However, in high temperature oxidation studies[15], only Cr and Al contribute to internal oxidation. This is consistent with the nanoscale measurements above where chromium-rich oxides and nearly pure nickel sponge has been detected within IG penetrations. It is important to note that TEM observations of crack-tip regions have not shown IG gas bubbles and it seems unlikely that this is a dominant contribution to the PWSCC mechanism.

If internal oxidation is confirmed to play a significant role in PWSCC, then the extensive knowledge of the phenomenon for nickel-chromium alloys at higher temperatures should provide some helpful guidance. For example, it is known that above a critical chromium content, which increases with decreasing temperature, a protective chromia film can form which protects the alloy from internal oxidation. This would explain the observed resistance of alloy 690 to PWSCC. In addition, iron-base or iron-rich chromium-containing alloys, for example, alloy 800, are intrinsically less susceptible (but not necessarily immune) to internal oxidation than nickel-base alloys at redox potentials close to that of Ni/NiO, which is effectively the corrosion potential for most structural materials in hydrogenated primary water (Figure 3).

4. POSSIBLE APPLICATION TO IGA/IGSCC

Most secondary side steam generator tube IGA/IGSCC has been attributed to either strongly caustic or strongly acidic solutions accumulated by hide-out in superheated crevices or under sludge piles of recirculating steam generators. More recent evidence suggests, however, that tube degradation occurs in a neutral to slightly alkaline environment.[3] This is deduced from frequent observations of a chromium-rich (but poorly protective) oxide film associated with IGA/IGSCC on pulled tubes at tube-support plate intersections, and the presence of alumino-silicate deposits in the crevices and adjacent to the heat transfer surfaces of the tubes.[22,23] Alumino-silicates are good buffering agents for caustic solutions implying a pH_T of less than 10. In addition, near-neutral or slightly alkaline solutions are now frequently deduced from MULTEQ calculations and hide-out return studies.[24,25] Examinations of complete tube-support plate intersections from retired steam generators have revealed widespread plugging of the crevice extremities by low porosity magnetite deposits rich in silica.[23,26] These silica-rich deposits are also observed on the tube surfaces (which is inconsistent with a strongly alkaline solution in contact with the tube). In the center of the tube-support plate crevices, magnetite porosities are much higher and the silica levels much lower away from the heat transfer surface. Such physical plugging of tube-support plate crevices in recirculating steam generators significantly restricts water flow. This combined with the generally low levels of adventitious soluble impurities in present-day steam generator feedwaters suggest that such superheated crevices are most likely steam-blanketed, albeit polluted with impurities.[3] Others[23] have drawn attention to the same characteristics, emphasizing that there are insufficient soluble impurities to fill the available crevices with a concentrated solution at a temperature close to that of the primary coolant and at the secondary side pressure. Thus, steam-blanketing appears to be inevitable although a thin film or droplets of concentrated solution may be present. In addition, heat transfer measurements on tubes removed from PWRs and CANDUs indicate that even free span deposits on the secondary side must be filled with a steam/water mixture.[27]

Recently, IGA/IGSCC has been observed in tubes in the superheated steam zone of once-through steam generators (OTSGs).[28] It has been suggested that this degradation may be the result of a thin quasi-stable alkaline film on the tube surfaces. The heat transfer mode in this OTSG region is transition boiling, a transient process where liquid droplets entrained in steam can momentarily wet the tube surface before evaporating. This alternate wetting and drying could, in principle, concentrate NaOH in a quasi-stable film until its boiling point is elevated to the temperature of the tube surface. However, this concentration process would be limited by the equilibrium established by revolatilization of NaOH into the steam phase. This liquid is proposed to penetrate flaws in the oxide to the underlying metal where caustic attack can then occur. The observation of chromium compounds on the external and crack surfaces have been proposed to be either reprecipitated corrosion products after the liquid becomes diluted by contact with the bulk coolant or the film formed during in-situ annealing of the steam generator. This degradation process would have to be intermittent to explain the slow kinetics of the field cracking in comparison with the rapid kinetics of cracking observed in caustic solutions in the laboratory (where little or no chromium is observed to remain in the oxide films).

The above hypothesis of OTSG steam zone IGA/IGSCC can be compared with observations made in laboratory once-through loop tests using radioactive tracers.[29,30] At realistic feedwater sodium concentrations (several 10's of ppb of sodium), either an adsorbed monolayer of sodium forms on top of tube deposits from droplets carried over by the superheated steam splashing onto the tube surfaces or the sodium is incorporated chemically and irreversibly into the deposits. The adsorption process is reversible when pure steam flows over the adsorbed layer, with a half life of about 200 seconds. Only when sodium concentrations exceed the solubility limit in steam (~100 ppb) do caustic liquid phases form. In this case, the OTSG IGA/IGSCC would be difficult to explain by the caustic hypothesis because of the implied low concentrations of NaOH.

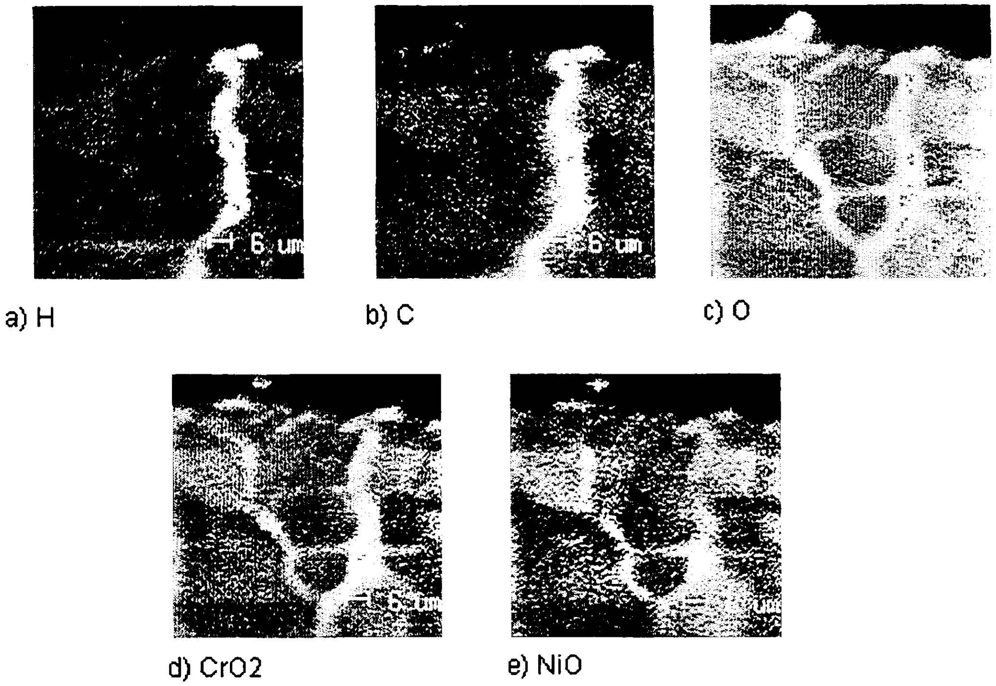
We suggest that IGA/IGSCC in the steam zone of OTSGs could also be the result of internal oxidation in polluted or "doped steam", a mechanism which could be equally applicable to steam-blanketed areas of recirculating steam generators.[3] If dry steam pockets are formed in recirculating steam generators, volatile reducing agents (hydrogen and possibly oxidizable organic species) could accumulate locally where they would depress the corrosion potential towards the region associated with PWSCC. This is not possible in the secondary coolant liquid phase where boiling maintains hydrogen at a few ppb at most, and therefore the corrosion potential is about 150 mV more positive than for the primary side (see Figure 3)[3]. Moreover, the presence of impurities such as chloride, acid sulfate, reduced sulfur, and lead, capable of damaging the passive film on the tubes, very probably enlarges the potential range over which the passive film can be sufficiently degraded to allow IGA/IGSCC to occur and at considerably lower stresses than those associated with PWSCC. This is supported by the fact that the well-known "doped steam" test for PWSCC is much more aggressive towards alloy 600 than the pure hydrogenated steam test at 400°C.

Recent examinations of tubes pulled from OTSGs showing areas of nearly pure nickel beneath a chromia-rich external oxide film[28] is a strong indication of selective internal oxidation as well as caustic attack. It should also be noted that the tube deposits had an unusually high carbon content, presumably coming from decomposition of organic materials. As indicated earlier, catalytic oxidation of hydrocarbons could lead to a depression of the redox potential toward the Ni/NiO equilibrium.

Further examinations of OTSG tubes using high resolution SIMS at AECL (for EPRI/Duke Power) have revealed evidence for oxides at grain boundaries beyond the tip of physically open cracks and at other apparently intact grain boundaries.[31] Na^+, SiO^-, and other species indicative of access by the secondary coolant (or possibly contamination from handling) were only detected at physically open grain boundaries. Figure 8 shows a metallographic cross section of an IG crack at the OD surface of a tube section removed from just above the 10th support plate in an OTSG at Oconee-3. Note that adjacent grain boundaries are apparently intact but show some definition even in the unetched condition. Such grain boundaries on other areas of the tubing broke open upon application of tensile stress.

Figure 8: Metallographic Cross Section of Alloy 600 Steam Generator Tubing with an OD Crack and Adjacent Grain Boundary Definition, 500X magnification

Figure 9 is a series of SIMS microprobe images of the area in Figure 8 showing C^-, H^-, O^-, CrO_2^-, and NiO^- at the open crack but only the oxygen species at adjacent grain boundaries. The presence of hydrogen and carbon ions at grain boundaries are believed to be evidence for access by hydrocarbons and/or water. The presence of carbides is revealed by C_2^- secondary ions. In addition, some evidence for oxidation beyond the visibly open crack was observed. These results imply that grain boundary degradation, consistent with internal oxidation, has taken place without access by the secondary coolant. It has been recommended that this be confirmed by ATEM examinations.



a) H b) C c) O

d) CrO2 e) NiO

Figure 9: SIMS Microprobe Images for a) H$^-$, b) C$^-$, c) O$^-$, d) CrO_2^-, and e) NiO$^-$

If internal oxidation is confirmed as a viable mechanism for IGA/IGSCC, this would have important consequences for steam generator secondary water chemistry and life management. For example, in the chemical industry where such degradation of alloy 600 is seen in methane reforming plants, the remedy is to make the environment more oxidizing and not more reducing as is the present trend in the nuclear steam generators. Moreover, replacement alloys such as alloys 690 and 800 would be expected to be inherently less susceptible to internal oxidation, although the influence of coolant impurities on their respective passive film stabilities and on the redox potential would have to be carefully considered in this context.

CONCLUDING REMARKS

Experimental evidence has been obtained to support the mechanism of internal oxidation to explain PWSCC of alloy 600 steam generator tubes. This suggests that grain boundary oxides containing Cr and Ni are a probable cause of crack advance. No convincing evidence for gas bubble formation has been obtained. Further work is required, particularly using high resolution surface analytical and electron optical techniques, to confirm positively whether the presence of oxygen-containing embrittling species beyond the tips of open cracks is generally true for PWSCC. In this respect, greater emphasis should be placed on examining pulled tubes where embrittled zones are expected to be better developed than in laboratory specimens from relatively short-term tests, and on avoiding plastic deformation prior to examination.

Internal oxidation could also be a mechanism of IGA/IGSCC, in circumstances where affected areas could be steam-blanketed. This is based upon an argument that reducing agents can accumulate in a steam phase and reduce the redox potential closer to the regime associated with PWSCC. Aggressive impurities such as lead, acid sulfate, reduced sulfur compounds, and chloride, capable of degrading the passive film on alloy 600 are expected to increase its susceptibility to this mechanism. As above, the examination of pulled tubes is likely to be the most effective way in the short term, to demonstrate whether this mechanism is viable or not.

Intrinsically, if internal oxidation plays a role in the degradation of steam generator tubes, alloy 690 with its higher Cr content and alloy 800 with its higher Cr and Fe contents are expected to be more resistant. However, the relative roles of concentrated secondary coolant impurities on passive film breakdown for this mechanism would need to be demonstrated. The water chemistry management implications of this mechanism would have to be carefully considered. For example, the installation of reverse osmosis purification systems for the secondary side feedwater could be advantageous by reducing the silica and organic impurity concentrations in the steam generators.

A collaborative international program is underway, led by the authors of this paper, to investigate this mechanistic hypothesis through the careful examination of pulled steam generator tubes as well as some laboratory cracked specimens.

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DISCUSSION

Authors: T.S. Gendron, P.M. Scott, S.M. Bruemmer, AECL, Framatome, Pacific Northwest National Laboratory

Paper: Internal Oxidation as a Mechanism for Steam Generator Tube Degradation

Questioner: R.W. Staehle

Question/Comment:

(a) In order for the internal oxidation idea to be viable, it is necessary to explain low potential SCC of the Fe-Ni binary. It is also necessary to explain that the "U" shaped hydrogen dependence does not apply at lower temperatures. It is necessary also to demonstrate that the grain boundary diffusivity of oxygen is consistent. Finally, it is necessary to explain why the very low oxygen activity at these potentials provides the necessary oxygen, especially as the potential is further reduced.

(b) With respect to applying this model to the secondary side, it is necessary to explain the fact that all the secondary side SCC can proceed by a transgranular mode, although this is not always observed in practice. Further, it is necessary to explain the SCC of binary Fe-Ni alloys. Finally, it is necessary to explain why the secondary side SCC occurs at temperatures as low as 100°C.

Response:

It is not our intention to explain SCC of all systems by the internal oxidation mechanism. However, some of the examples you raised could be consistent with internal oxidation.

The formation of Cr_2O_3 at grain boundaries is not necessary to explain SCC by internal oxidation. In the presentation, I also mentioned that intrinsic oxygen atom embrittlement, the formation of gas bubbles (CO, CO_2), reaction of oxygen with precipitates to release S, and the formation of the solvent metal sponge have been causes of embrittlement associated with grain boundary oxygen diffusion in high temperature studies (including, of Ni 200). It is possible that one or more of these embrittlement mechanisms could be responsible for SCC in Fe-Ni binary alloys.

The general consistency of grain boundary oxygen diffusivity with PWSCC was demonstrated in the original paper by Scott and LeCalvar[2] (see also reply to Garg). However, it is acknowledged that better data would be useful to confirm their proposal.

In a Ni-Cr alloy where Cr oxidation is a suspected mechanism of embrittlement, in principle, oxidation could take place at potentials as low as the Cr/Cr_2O_3 equilibrium provided that the external film allows transport of oxygen through it. Within the lower potential limits of LPSCC (i.e. at low oxygen activity and where the 'U'-shaped hydrogen dependence does not apply), Cr oxidation is still possible. In addition, the other embrittlement mechanisms cited above, except gas bubble formation may be possible.

The possible contribution of lead to internal oxidation was briefly mentioned in the paper. In the follow-up work described, an example of in-service lead-induced cracking of a steam generator tube is planned in which we will be looking for similarities with previously described examples of internal oxidation..

Questioner: J. Gorman

Question/Comment:

Most pulled Alloy 600 tubes show widespread IGA on the primary side. Have you had an opportunity to investigate the crack top region of primary side IGA to help determine the mechanism involved?

Response:

In the pulled-tube specimens we have examined to-date, primary side IGA was believed to be associated with pickling procedures during fabrication. Examination of these areas was not within our scope of work.

Questioner: B. Michaut, Framatome, Lyon, France

Question/Comment:

From many experiments on PWSCC, it was shown that the crack growth stops when hydrogen is eliminated and increases again when hydrogen is established again. How is this experimental observation explained with an internal oxidation based mechanism?

Response:

The proposed role of hydrogen in the internal oxidation mechanism is to fix the potential within a range close to the equilibrium oxidation potential of the alloy solvent metal (Ni in alloy 600) where the risk of internal oxidation is greatest. Within this range, it is believed that Ni cannot contribute significantly to the formation of a sufficiently protective external film, allowing transport of oxygen to the alloy surface and subsequent diffusion down grain boundaries. However, we do not rule out hydrogen embrittlement at low temperatures of oxygen pre-damaged grain boundaries (as has been demonstrated in nickel) or some other symbiotic effect of hydrogen as a contributor to PWSCC.

Questioner: A. McIlree

Comment:

Based on experience with the eddy current response (i.e. voltage increase) to tubes plugged and then unplugged after some time in SG service, one can postulate that hydrogen diffusion from the primary side is influencing the redox reactions on the secondary side. So, tubing in service could be close to the hydrogen line even on the secondary side.

Response:

Thank you for your comment. Hydrogen diffusion from the primary side is one possible source of hydrogen on the secondary side, as is hydrogen from general corrosion and hydrogen from decomposition of organic materials.

Questioner: R. Garg

Question/Comment:

Does your work consider predicting the crack growth rate by looking at the O_2 ingress in the metallography structure from the pulled tubes of SG?

Response:

It is believed that examination of pulled tubes would not be an ideal method to establish crack growth kinetics. Scott and LeCalvar[2] explained PWSCC crack growth by an interrelationship between oxygen diffusivity and fracture of a "process zone". Gendron et. al.[12] found that grain boundary oxygen penetration of *unstressed* alloy 600 specimens underestimated PWSCC crack growth rates. A specific study of oxygen diffusivity (perhaps using ^{18}O) in alloy 600 grain boundaries as a function of alloy microstructure and stress and the determination of the size of the process zone that fractures under a given stress intensity would be required.