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Steve Bruemmer
Peter Ford
Gary Was
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—Water Reactors—

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FOREWORD

The Ninth International Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors was held in Newport Beach, California, August 1st-5th, 1999. As with the previous bi-annual meetings the conference provided a forum for the exchange of the results of research and plant operating experience associated with material degradation. The topics covered the degradation phenomena peculiar to the various reactor subsystems, i.e., BWRs, PWR primary, PWR secondary, as well as general materials aspects, e.g., degradation of low alloy steels and zircaloy, irradiation effects, etc. In view of the aging of the international light water reactor fleet, two new sessions were introduced; one dealing with regulation aspects associated with license renewal and life extension, and the other dealing with repair techniques.

The conference attracted 220 scientists and engineers from 18 countries representing the utilities, regulators, reactor vendors, regulators, national laboratories and universities, thereby attesting to the wide international support and interest in this conference topic. The number of papers presented (122), and the number that are published in the proceedings (128), was a marked increase over previous years.

The organizing committee dedicated a considerable amount of time establishing the conference structure and, with the session chairmen, coordinating and promoting the discussions during the presen-
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Abstract

The main purpose of the present paper is to compare the results of recent high resolution microscopy of intergranular stress corrosion cracking of alloy 600 in various environments encountered during the operation of PWRs with the hypothesis that cracking is caused by the phenomenon of internal oxidation. Some of the points of criticism, which have arisen as to the applicability of the internal oxidation mechanism at typical PWR operating temperatures and corrosion potentials, are also addressed. These are specifically the problem of reconciling the apparent rate of intergranular diffusion of oxygen in nickel base alloys with the observed rates of cracking and the thermodynamic requirement for internal oxidation that the corrosion potential be at or below the Ni/NiO redox potential. The latter point is of particular concern if this mechanism is invoked to explain secondary side steam generator tube IGA/IGSCC.

Introduction

Internal oxidation was first proposed as a plausible mechanism of intergranular stress corrosion cracking (IGSCC) of the nickel base alloy 600 in hydrogenated primary water of Pressurized Water Reactors (PWR) by Scott and Le Calvar in 1993 (1). Internal oxidation occurs when atomic oxygen dissolves into an alloy at the external oxide-metal interface and diffuses into the metal matrix to oxidize a more reactive alloying element than the solvent metal. By necessity therefore, the oxidation potential at the reaction site in the alloy is less than the equilibrium oxygen potential of the solvent metal oxide and the concentrations of oxygen and the alloying element are sufficient to exceed those corresponding to the solubility product of the oxide in the alloy. It is a well-known and much studied phenomenon at high temperatures, usually between 500 and 1200°C in the context of nickel base alloys. At the lower end of this temperature range (500 to 800°C), intergranular internal oxidation predominates.

Since 1993, several experimental studies have been undertaken to test this hypothesis for IGSCC in alloy 600 in water or steam at temperatures between about 300 and 400 °C. These were last reviewed by the present author in 1996 (2). More recently, some detailed examinations of both primary and secondary cracks in alloy 600 using Secondary Ion Mass Spectrometry (SIMS) and Analytical Transmission Electron Microscopy (ATEM) have been carried out and some of the early results have already been published (3). These investigations are described in detail elsewhere and in other papers in this conference (4,5). The purpose here is to examine the results of these various studies with reference to the originally proposed internal oxidation mechanism and to deduce to what extent the hypothesis is supported or contradicted. In so doing, various criticisms of the mechanistic hypothesis that have been made are addressed (6).

Interest in the mechanism(s) of intergranular cracking in alloy 600 in PWRs stems from the continuing occurrences of IGSCC in highly stressed primary circuit components such as (recirculating) steam generator (SG) tubes and upper head penetrations as well as secondary side intergranular attack (IGA) and IGSCC of SG tubes. In the case of IGA, the applied stress plays a much less important even negligible role. Although such problems were first encountered in mill annealed alloy 600 tubes of recirculating SGs, intergranular cracking has gradually extended to forged as well as thermally treated (16 hours at 700°C) products. Latterly, even the low strength, thermally sensitized tubes of Once Through Steam Generators (OTSG) have been affected (7,8). Despite the obvious difficulties that have been encountered in achieving a consensus, the pursuit of a mechanistic understanding of these cracking problems is still a worthwhile objective. It is not just an intellectually challenging academic pastime but is also of great importance to the formulation of effective remedial measures and to building confidence in the longevity of replacement materials such as alloys 690 and 800. It will be seen later that optimal management of secondary water chemistry, in particular, to combat these problems in alloy 600 depends critically on the perception of the damage mechanism.

The paper is divided into three main sections devoted respectively to a description of the thermodynamic aspects of the metal - environment interactions associated with IGSCC, to the morphology of intergranular cracking in alloy 600, and to the kinetics of IGSCC. In each case comparisons are made with expectations based on the internal oxidation mechanistic hypothesis as well as with other competing mechanistic interpretations. Attention is also drawn to the practical consequences of the perceived mechanisms of IGSCC.

Thermodynamics

The starting point for a discussion of IGSCC mechanisms in alloy 600 is to characterize as clearly as possible the chemical and electrochemical parameters associated with normal operating conditions. In the case of secondary side tube cracking in recirculating SGs, it is also necessary to assess how such conditions may be modified in superheated crevices with restricted fluid circulation. These are compared with the normally observed thermodynamic requirements for internal oxidation and other mechanisms of IGSCC.

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Normal PWR Primary Chemistry

The important redox characteristics of PWR primary and secondary water are given in Figure 1 in the form of a Pourbaix diagram together with nickel and its oxidation products at 300 °C. Primary circuit temperatures can range typically from 286 °C in the reactor cold leg to 322 °C in the hot leg and 342 °C in the pressurizer. The use of lithium hydroxide and boric acid in the PWR primary coolant fixes the pH at operating temperature to very close to the Ni/NiO equilibrium, even apparently, when difficulties with solution resistance effects on the reliable control and measurement of potential have been resolved with modern potentiostats (10,11). There is no immediately obvious explanation known to the author of this apparent disconnect between observations with dissolved hydrogen concentration and potentiostatically controlled potentials. However, since the former corresponds to the realistic operating situation and is free of possible experimental artifacts, conditional only on the hydrogen partial pressure or dissolved hydrogen being reliably measured, it seems prudent to this author to place more credence on results obtained without externally imposed polarizing currents.

Nothing said thus far points specifically to internal oxidation as the mechanism of IGSCC in alloy 600 exposed to PWR primary water but can be rather susceptible to hydrogen induced internal oxidation since a well known pre-condition is that the solvent metal of the alloy must not participate significantly in the formation of a protective external oxide film. Thus high temperature internal oxidation studies are typically carried out in environments whose equivalent partial oxygen partial pressure is close to that of NiO at the particular temperature concerned.

Normal PWR Secondary Chemistry

On the secondary side of SG tubes an All Volatile Treatment (AVT) is most commonly used in both recirculating SGs and OTSGs. A relatively alkaline pH is maintained to minimize magnetite solubility and reduce sludge transport to a minimum. This is achieved by using a combination of ammonia, hydrazine (to scavenge oxygen in the feed water) and frequently organic amines such as morpholine or ethanolamine to reduce further general corrosion of carbon steel parts of the secondary circuit. Any hydrogen generated by general corrosion or diffusing from gases at the condenser. An estimate of the average hydrogen

![Diagram](https://example.com/diagram.png)

Figure 1: Main domains of IGA and IGSCC of alloy 600 in aqueous solutions at ~300°C.

Laboratory studies of IGSCC in PWR primary water or in superheated steam as a function of dissolved hydrogen content have generally shown consistent behavior both in time to failure tests of initially smooth specimens or in crack growth rate tests (9). Thus, maximum susceptibility to IGSCC is observed when the corrosion potential is close to the Ni/NiO equilibriuim and decreases at both higher and lower potentials within a band of about ±80 mV. This is the classical sign of an oxidation or dissolution controlled mechanism of stress corrosion cracking although not necessarily of internal oxidation. The improved resistance to IGSCC at potentials lower than the Ni/NiO equilibrium is especially difficult to reconcile with a hydrogen embrittlement mechanism. Moreover, the well known trend in austenitic materials for hydrogen induced cracking susceptibility to peak at temperatures around 100 to 150 °C, then to decrease with increasing temperature and finally become negligible at ~300 °C is inconsistent with a hydrogen embrittlement mechanism for IGSCC in high temperature aqueous environments. This is true even for relatively hard and brittle alloys. The equally well known trend of grain boundary carbides to improve IGSCC resistance in PWR primary water is also opposite to the trend observed in hydrogen embrittlement testing of alloy 600 at low temperatures. In the second case, grain boundary carbides enhance cracking susceptibility. Indeed alloy 690 with its higher chromium content (29% as against 16% in alloy 600) and heavy grain boundary carbide precipitation in the thermally treated condition shows excellent resistance to IGSCC in PWR primary water but can be rather susceptible to hydrogen induced intergranular failure at low temperatures.
concentration thereby established is 1 to 10 ppb which is three orders of magnitude less than on the primary side. As a consequence, the corrosion potential in the absence of any significant amount of oxygen is nearly 200 mV more positive than on the primary side as shown in Figure 1. From this viewpoint, no distinction is necessary between recirculating SGs and OTSGs. It should be noted, however, that even a few ppb of dissolved oxygen at the high mass transfer rates that can exist in the secondary circuit wherever flow is not impeded can give rise to significantly more positive corrosion potentials.

One controversial point of particular relevance to the IGSCC mechanism debate concerns the role of hydrazine and its influence on electrochemical corrosion potential on the secondary side. The main aim of hydrazine addition is to lower the oxygen concentration in the secondary water to less than a few ppb, the reaction products being nitrogen and water. Typically the hydrazine concentration is 5 to 10 times the feed water residual oxygen of 10 to 15 ppb achieved by mechanical de-aeration. If the objective is to reduce hematite formation to a minimum in the SG blow-down, then hydrazine has to be 30 to 40 times the oxygen concentration in the feed water. Excess hydrazine decomposes at high temperatures to ammonia, nitrogen and hydrogen. Several measurements have been made of the corrosion potential in secondary circuits that are consistent with the potential being controlled by the residual hydrogen concentration when the oxygen falls below a few ppb. There is no evidence of any strong electrochemical influence of hydrazine itself on corrosion potential as shown by the examples in Figure 2 (12).

![Figure 2: Corrosion potentials measured in PWR steam generator feed water systems (12).](image)

**Superheated Crevices in Recirculating Steam Generators**

Most secondary side IGA/IGSCC has so far mainly affected mill annealed alloy 600 tubing although it is generally expected that thermally treated alloy 600 tubing will be affected in due course. In the past, this tube damage has been usually attributed either to strongly caustic or strongly acidic solutions accumulated by hide-out of impurities in superheated crevices or under sludge piles of recirculating SGs. The known pH – potential zones associated with these forms of attack are also illustrated in Figure 1. Existing secondary side chemistry guidelines concerning the acceptable limits on feed water impurities and maintenance of rather strongly reducing conditions with hydrazine additions are largely based on these perceptions of the origin of tube damage. More recent evidence coming from examinations of pulled tubes suggests, however, that tube degradation occurs in neutral to slightly alkaline environments (13). This is deduced from frequent observations of chromium-rich (but poorly protective) oxide films associated with IGA/IGSCC on pulled tubes, and the presence of alumino-silicate deposits in the crevices and adjacent to the heat transfer surfaces of the tubes (14,15). Alumino-silicates are good buffering agents for caustic solutions implying a pH of less than 10, which is very close to the lower threshold for caustic attack of alloy 600. In addition, near-neutral or slightly alkaline crevice conditions are now frequently deduced from MULTeq calculations and hideout return studies (16,17).

Examinations of complete tube-support plate intersections from retired SGs have revealed widespread plugging of the crevice extremities by low porosity magnetite deposits rich in silica (15,18). In the center of the tube-support plate crevices, magnetite porosity is much higher and the silica levels are much lower with the exception of a thin film directly in contact with the tube heat transfer surface. Such physical plugging of tube-support plate crevices in recirculating SGs significantly restricts water flow. This combined with the generally low levels of adventitious soluble impurities in present-day SG feed waters suggest that such superheated crevices are most likely steam-blanketed, albeit polluted with impurities. The alternative hypothesis advanced in the past is of a liquid, necessarily extremely concentrated in soluble impurities, with a boiling point close to the primary circuit temperature in order to be physically stable relative to steam at the secondary side pressure (13).

Other authors have drawn attention to the same characteristics, emphasizing that there are insufficient soluble impurities to fill the available crevices with such concentrated solutions (15). Thus, steam blanketing appears to be inevitable although some authors hypothesize that a thin film or droplets of concentrated solution could still be present. It is, however, difficult to reconcile the presence of such a liquid phase, necessarily very concentrated in soluble impurities, with the observations of silica rich deposits, especially those in contact with the tube surface where the cracking must initiate.

The continuing progression of IGA/IGSCC in alloy 600 tubes in crevices where the likelihood of forming concentrated solutions of extreme pH seems remote, focuses attention on the possibility of a superheated steam phase attack mechanism. Clearly, the hideout process concentrates impurities in superheated crevices but it is most unlikely under present day operating conditions to lead to a liquid phase but rather to a polluted, superheated steam blanket. In addition, volatile substances such as hydrogen and hydrazine could also concentrate in such an occluded steam pocket. Significantly, recent experiments using an instrumented, simulated, superheated crevice have drawn attention to a significant lowering of the crevice potential by about 200 mV when hydrazine was present in the bulk fluid relative to an analogous experiment without hydrazine (19). It is important to note that in order to make any electrochemical measurement at all in this experiment, it was necessary to interrupt the heat flux to the secondary side crevice so that the steam bubble that was...
present then collapsed. This allowed a conducting fluid generated by hideout at the liquid–vapor interface near the crevice extremities to be drawn into the crevice thereby establishing electrochemical contact between the electrode and the tube. Although the origin of the negative shift of potential was attributed to hydrazine concentration in the crevice without further comment from the original authors, the observation is consistent with concentration of volatile hydrazine in a steam bubble and its thermal decomposition leading to an increase in local hydrogen concentration. In any event, the measured potential in the simulated crevice falls right in the range of that expected on the primary side albeit, most probably in practice, in a steam pocket. The local conditions are then similar to the so-called and well known "doped steam" test in which intergranular attack of alloy 600 occurs more extensively and at much lower stresses than in pure, hydrogenated steam. This is of very great significance for the possible mechanisms of secondary side attack.

To summarize, there is a strong a priori case that secondary side IGA/IGSCC of alloy 600 can occur in polluted steam impurities concentrated by the classical hideout mechanism. Areas in recirculating SGs whose environmental characteristics are similar to the "doped steam" test. In this case, the mechanism of attack can be very similar to the primary side but aggravated by the secondary water impurities concentrated by the classical hideout mechanism.

It should also be pointed out that evidence for a steam phase degradation process affecting SG tubes has been provided by recent observations of IGA/IGSCC on the free spans of OTSG tubes in the superheated steam zone after almost twenty years of service (7,8). The tube degradation is mainly attributable to IGA/IGSCC of alloy 600 in polluted steam impurities concentrated by the classical hideout mechanism. The alloy 600 in question had very few intergranular carbides and was known to be very sensitive to primary water induced IGSCC. The oxidation extended up to 10 μm in length from the main crack and was 10 to 20 nm wide on average. Practically all high angle grain boundaries intercepted by the main crack were oxidized in this way before narrowing to the unattacked grain boundary. Similar features were observed at the tip of the main intergranular crack although they were much more difficult to characterize in detail due to their extremely small dimensions and the high density of dislocations in this zone. The separation of metallic nickel and Cr2O3 near the penetration tip and the formation of a NiO-structure oxide behind the leading edge are the striking features in Figure 3. Porosity and tunnels of nanometer dimensions were also seen in the oxidized grain boundary tips with some tunnels apparently extending into the unoxidized metal. The NiO-structure oxide was also found on the walls of the main crack.

Primary Side IGSCC

Figure 3 shows the morphology of the tips of oxidized intergranular penetrations branching off the main intergranular crack in alloy 600 exposed to PWR primary water at 330°C (5). The alloy 600 in question had very few intergranular carbides and was known to be very sensitive to primary water induced IGSCC. The oxidation extended up to 10 μm in length from the main crack and was 10 to 20 nm wide on average. Practically all high angle grain boundaries intercepted by the main crack were oxidized in this way before narrowing to the unattacked grain boundary. Similar features were observed at the tip of the main intergranular crack although they were much more difficult to characterize in detail due to their extremely small dimensions and the high density of dislocations in this zone. The separation of metallic nickel and Cr2O3 near the penetration tip and the formation of a NiO-structure oxide behind the leading edge are the striking features in Figure 3. Porosity and tunnels of nanometer dimensions were also seen in the oxidized grain boundary tips with some tunnels apparently extending into the unoxidized metal. The NiO-structure oxide was also found on the walls of the main crack.

Morphology

Several specimens of mill annealed alloy 600 containing primary side or secondary side cracks, including pulled SG tubes, have been selected and examined with a combination of two techniques, SIMS and ATEM, the latter focussing on crack tips. The specific aim has been to determine whether any morphological details revealed by those two techniques could give clues as to the mechanism of cracking. Detailed descriptions of the results obtained to date are given elsewhere, including other papers in this conference (3,4,5,8).

The choice of these two techniques, SIMS with its relatively poor spatial resolution but excellent compositional detection, especially on the light elements, and ATEM which has excellent spatial resolution with good compositional sensitivity, has produced some remarkable new results with very good agreement between them where results are comparable. Surprisingly, very similar intergranular crack morphologies at the nanometric scale have been observed for the primary water (330°C) and secondary (OTSG dry steam zone) side cracks, which was not at all expected. (At the time of writing no results are yet available for secondary side cracks from a crevice zone of a recirculating SG tube). The main features of both are summarized below highlighting the unusual common features and the few differences. The ATEM results for crack tips are shown schematically in Figures 3 and 4. These are then compared to crack morphologies from known examples of internal oxidation of nickel base alloys at higher temperatures and of other cracking mechanisms where these are available.

Figure 3 shows the morphology of the tips of oxidized intergranular penetrations branching off the main intergranular crack in alloy 600 exposed to PWR primary water at 330°C (5).

Figure 3: Summary of crack tip morphology of an intergranular penetration due to IGSCC of alloy 600 in PWR primary water (5).