Oxidation Products of INCONEL Alloys 600 and 690 in Pressurized Water Reactor Environments and Their Role in Intergranular Stress Corrosion Cracking

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In this work, thermodynamic arguments for the stability of Ni and Cr compounds developed under pressurized water reactor environments ($P_{\text{H}_2\text{O}}$ and $P_{\text{H}_2}$) were experimentally tested. A mechanism is proposed to explain crack initiation and propagation alloy 600 along the grain boundaries, where Cr$_2$O$_3$ has formed from the leaching of Cr from the matrix, leaving behind a porous Ni-rich region. The mechanism is based on the thermodynamic potential for the transformation of a protective NiO surface layer into an amorphous nonprotective Ni(OH)$_2$ gel. This gel would also form along the grain boundaries and when hydrogenated steam reaches the porous Ni-rich regions. Crack initiation is then favored by tensile stressing of the grain boundary regions, which can easily rupture the gelatinous film. The leaching of matrix Cr to form nonprotective CrOOH gel at the crack tip followed by the exposure of fresh porous Ni to the environment could explain crack propagation in INCONEL alloy 600. The proposed crack initiation mechanism is not expected to occur in alloy 690 where a protective Cr$_2$O$_3$ film covers the entire metal surface. However, crack propagation along the grain boundaries in alloy 600 and precracked alloy 690 is expected to be active as hydroxide-forming reactions weaken the boundaries.

I. INTRODUCTION

INCONEL* alloy 600 used in pressurized water reactor (PWR) environments is often found to undergo stress corrosion cracking (SCC). Under these conditions, hydrogenated steam at temperatures above 300 °C in combination with a stressed susceptible microstructure can lead to crack development. Several important results show the importance of grain boundaries in SCC of alloy 600 in PWR environments including the necessity of grain boundaries for the initiation of cracks,[1] the degree of carbide precipitation at grain boundaries affecting crack growth rates, penetration of oxides into the grain boundaries at the alloy surface,[2] and intergranular attack being found at grain boundaries that intersect the crack.[3] Airey states that “in-service degradation was exclusively intergranular in nature.”[4] Thus, consideration of the behavior of the material will be limited to only intergranular SCC (IGSCC) even though transgranular and pseudo-intergranular cracking of the alloy have been reported.

Research indicates that alloy 600 will not crack in pure steam or dry H$_2$ environments.[1,7–10] Hence, any proposed cracking mechanism must account for the role of H$_2$ in combination with steam. In particular, it has been reported that the highest SCC susceptibility occurs when the H$_2$ partial pressures are near the Ni/NiO stability boundary.[10] Magnin et al.[11] studied crack initiation in single- and poly-crystalline samples of alloy 600 in PWR environments. They found that cracks initiated and propagated in the poly-crystalline sample, but no cracks could be initiated or propagated in the single crystal unless it had been precracked by fatiguing. This suggests that without existing cracks, SCC cracks initiate at surface grain boundaries.

The susceptibility of alloy 600 to IGSCC has led to costly repairs and development of other alloy alternatives such as INCONEL alloy 690, which contains roughly twice as much Cr as alloy 600 (15 wt pct in alloy 600 vs 30 wt pct in alloy 690). Alloy 690 is considered to be insensitive to cracking. Mitieux et al.[5] tested Reverse U-Bend samples for over 10,000 hours and some for over 25,000 without finding cracking. However, another experiment in similar conditions showed that cracks could be propagated in precracked MWOL alloy 690 specimens in hydrogenated steam.[6] This suggests that the Cr content helps to inhibit crack initiation, yet it is not as effective in hindering crack propagation.

II. OXIDATION STUDIES

Since crack initiation is a surface phenomenon, alloy oxidation either in pure O$_2$, pure H$_2$O, or H$_2$O/H$_2$ mixtures provides key information on the active crack initiation mechanisms and has been investigated in these environments.[11–15] Surface oxidation studies in H$_2$O and H$_2$O/H$_2$ environments concentrated on the alloy surface without specifically targeting the grain boundary. Because of the importance of grain boundaries in cracking behavior, the extensive work done for this case in Ni-Cr alloys in pure O$_2$ by Calvarin and others[13,14,15] will be described so that the type of the oxide at the grain boundary in the H$_2$O environment might be estimated. Another important reason to describe the scales formed in pure O$_2$ is that in the process of forming the alloy 600 piping, a scale is developed from exposure to O$_2$, which will initially exist when the piping is placed in service. If the material is mill annealed and
placed directly in service without an attempt to remove the oxide, it would be expected that the description provided below for Ni-Cr alloys in pure O₂ at 600 °C is applicable. Then, it should be noted that scale formed under H₂O or H₂O/H₂ environments would only be applicable to metal freshly exposed by an advancing crack.

A. Alloy 600

It has been found that in Ni-Cr alloys exposed to pure O₂, the type and structure of the surface oxide layers depends on both the Cr concentration and the exposed temperature. In alloys containing 10 to 30 wt pct Cr (i.e., those analogous to alloy 600), NiO and Cr₂O₃ form simultaneously on the alloy surface. However, Cr diffusion kinetics is prevalent and NiO rapidly develops a continuous layer. Cr₂O₃ forms preferentially at grain boundaries where the Cr diffusion rate is relatively high. Hence, given enough time, a Cr₂O₃ sublayer will grow outward from underneath the NiO layer by internal oxidation. As long as Cr diffusion is limited due to the relatively low temperatures (i.e., below 700 °C), the isolated grain boundary Cr₂O₃ film will not be able to form a continuous film.

Oxidation studies in alloy 600 under pure H₂O at PWR operating temperatures show a structure similar to the scales reported for pure O₂ previously. When the alloy is exposed to water vapor, a needlelike scale is produced while pure O₂ forms columnar oxide scales. The condition and type of oxide at or near the grain boundaries was not determined in the H₂O only environment. However, based on the similarities between the oxide structures of pure O₂ and pure H₂O, it might be reasonable to assume that Cr₂O₃ is formed at the grain boundaries in pure H₂O also.

As stated previously, INCONEL alloy 600 is most susceptible to IGSCC in H₂O/H₂ with H₂ pressures near the Ni/NiO equilibrium boundary. In this case, the four-layered scale consists of (1) a thick, needlelike NiO as the outermost layer, (2) a thin "Cr-rich" oxide layer, (3) a thin Ni-rich metal layer, and (4) a matrix metal of the alloy composition.

Oxide morphology within cracks and along the grain boundaries is somewhat similar to the surface oxide structures. In transmission electron microscopy (TEM) investigations by Thomas and Bruemmer of alloy 600 exposed to PWR conditions where cracking occurred, it was found that there were two types of attacks, as shown in Figure 1. The first was intergranular attack (IGA) on almost every high-angle grain boundary, with IGA sometimes to depths of several microns. The attack is shown schematically in Figure 1(a). Inside the crack, every high-angle grain boundary exposed by the opening crack was similarly attacked and degraded. The IGA penetrated the grain boundaries forming distinct regions that were found to be (1) mostly porous NiO-structured film with some localized areas of Cr₂O₃, surrounded by porous, Ni-rich metal (indicating that Cr had leached out wherever the oxide had formed); (2) nano-crystalline Cr₂O₃ at the tip of the penetration; (3) nano-sized pores ahead of the attack tip (likely from the leaching of Cr); and (4) matrix metal of the alloy composition. The oxide film was apparently not ruptured nor were any dislocation structures evident. Thus, the four-layered IGA structure and the four-layered H₂O/H₂ surface structure are remarkably similar. Thomas and Bruemmer also investigated several IGSCC crack tips and observed that, in the region ahead of the crack tip, there was a porous oxide similar to the one found in the IGA region. However, the tip of the porous oxide region had undergone heavy plastic deformation. They did not detect Cr₂O₃ or nano-sized pores, possibly as a result of the severe plastic deformation.

The observation of IGA within the crack was unexpected as no proposed IGSCC mechanism predicted this type of grain boundary attack. Therefore, it may not be too much of a stretch to consider that the IGSCC cracking is the same as the IGA within the crack described previously, but altered in that it starts at the surface of the material originally exposed to the PWR environment and is assisted by the applied stresses that create plastically deformed regions at the tip of the attack (crack tip).

B. Alloy 690

In alloys containing more than 30 wt pct Cr (i.e., those analogous to alloy 690), exposure to pure O₂ also causes NiO and Cr₂O₃ to form simultaneously on the exposed surfaces. However, in this case, the high Cr levels apparently cause Cr₂O₃ growth kinetics to dominate resulting in a continuous Cr₂O₃ layer. Panter et al. studied oxidation scales of alloys 600 and 690 in H₂O/H₂ environments. Although the oxide scale on alloy 690 was not identified ("mixed oxide of nickel, chromium, and iron"), it was described as much less thick and more fine grained than that formed on alloy 600. Beneath the scale in both alloys, they found a Cr-depleted region of the same approximate thickness as the oxide scale. These findings at least hint at a continuous Cr₂O₃ layer similar to that for pure O₂.

![Fig. 1](image-url) —Schematic representation of IGA and crack morphology of alloy 600 from TEM investigations.