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# High resolution analysis of oxidation in Ni-Fe-Cr alloys after exposure to 315 °C deaerated water with added hydrogen

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## ABSTRACT

Alloy 600 (Ni-16Cr-9Fe) and Alloy 800 (Fe-35Ni-23Cr) were exposed to simulated primary water at 315 °C. Oxidation phenomena were studied using high resolution electron microscopy. Extensive intergranular oxidation was observed in Alloy 600. In Alloy 800, only shallow intergranular oxygen penetration was detected. The mechanism of intergranular embrittlement in Alloy 600 is likely analogous to internal oxidation. Internal oxidation may not apply to Alloy 800 due to the formation of external rather than internal oxides. Comparisons are made to previous experiments in high temperature hydrogenated steam to validate the latter's use as an accelerated primary water simulant environment.

## 1. Introduction

Ni-Fe-Cr alloys are used for several components on the primary side of nuclear power plants, such as steam generator tubing. Alloy 600 (Ni-16Cr-9Fe) was originally selected during construction of some plants due to its perceived high resistance to stress corrosion cracking (SCC). However, Coriou published results in 1960 which suggested that the 600 alloy would be susceptible to SCC in a deaerated high temperature pure water environment [1]; at the time no primary water stress corrosion cracking (PWSCC) was observed in-service and this finding was largely ignored. In the following decades Alloy 600 was found highly susceptible to PWSCC. In recent years the 600 alloy has been replaced by Alloy 800 (Fe-35Ni-23Cr) in most Canada deuterium uranium (CANDU) reactors and Alloy 690 (Ni-30Cr-10Fe) in most pressurized water reactors (PWR); some plants use thermally treated (TT) Alloy 600 which is more resistant to PWSCC due to intergranular Cr carbide precipitation. Alloys 690 and 800 are thought to be more resistant to PWSCC than Alloy 600 because of their high Fe and/or Cr content(s) which permits the formation of more passivating oxides.

The temperature of primary water ranges from 280 °C to 320 °C in CANDU reactors. Lithium hydroxide is added to maintain a room-temperature pH between 10.2 and 10.8. Also, the dissolved hydrogen concentration is maintained between 0.30 and 0.90 $mol/m^3$, quoted at standard temperature and pressure (STP), in CANDU reactors to avoid net decomposition of water by radiolysis in the reactor. The addition of hydrogen reduces the potential of primary water into the range of the Ni/NiO equilibrium potential; at 315 °C, the Ni/NiO equilibrium potential is attained at a hydrogen concentration in water of approximately 0.72 $mol/m^3$ [2,3], quoted at STP. The PWSCC susceptibility of Alloy 600 is well known to peak in the vicinity of the Ni/NiO equilibrium electrode potential [2–6], suggesting that the mechanism of cracking is somehow related.

In 1993, Scott and Le Calvar proposed that the reducing conditions of primary water may promote internal oxidation in Alloy 600 leading to intergranular embrittlement [7]. Internal oxidation is a phenomenon observed in alloys with a dilute and reactive solute metal and a noble solvent metal. In an environment or at an external oxide-metal interface with a nominal oxygen partial pressure within range of the equilibrium oxygen dissociation pressure of the noble metal oxide, the solute element, when below a critical concentration, can possibly oxidize internally. Internal oxidation results in large compressive stresses which, in some cases, are relieved through transport of the noble solvent metal to the surface [8–15]. The phenomenon is usually observed at higher

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temperatures, such as 800 °C, where the kinetics would support significant inward atomic oxygen diffusion and outward solvent metal expulsion. For internal oxidation to be operating at the lower temperatures of primary water, substantial short circuit diffusion paths must be available, particularly in the lattice where diffusion is essentially negligible below 480 °C over laboratory testing timescales. In contrast, grain boundary diffusion is dominant at lower temperatures and accelerated transport of oxygen intergranularly may be feasible.

Since being proposed, internal oxidation as the mechanism of PWSCC in Alloy 600 has gained significant support in 300–360 °C primary water [16–26] and 400–480 °C hydrogenated steam [9–12,27–36]. Several studies have reported selective intergranular Cr oxidation and embrittlement to a depth of up to 10 μm in Alloy 600 after exposure to primary water in the 300–360 °C temperature range [16–26]; the majority of these studies were carried out in conditions at or above the Ni/NiO equilibrium electrode potential. Solvent metal, Ni, expulsion to the surface has never been reported in primary water over laboratory timescales, but should not be ruled out over longer intervals, such as decades of exposure in nuclear power plants. Lozano-Perez and Titchmarsh have reported Ni enrichment ahead of intergranular internal oxides [20] in Alloy 600 after exposure to representative primary water, which might be Ni displaced as a result of intergranular oxide growth. Further work is needed on the Ni-metal side of the Ni/NiO equilibrium to better evaluate the roles of Cr and Fe in oxidation and embrittlement.

High temperature hydrogenated steam is often used to simulate an accelerated primary water environment. Economy et al. determined that PWSCC initiation times in Alloy 600 U-bend samples exhibited an Arrhenius relationship over temperatures ranging from 300 °C primary water to 400 °C hydrogenated steam [37]; therefore, observations related to the mechanism of PWSCC were likely to be similar in both environments. Gendron et al. reported intergranular internal oxidation and embrittlement in Alloy 600 after exposure to 400 °C hydrogenated steam, similar to the observed embrittlement in primary water [30–32]. Further work by Scenini et al. showed that internal oxidation and solvent metal, Ni, expulsion was possible in Alloy 600 after exposure to 480 °C hydrogenated steam [27]. Persaud et al. extended the studies and showed that intragranular internal oxidation was possible in other Ni-Fe-Cr alloys, such as Alloys 690 [11] and 800 [38]. Classical internal oxidation and solvent metal expulsion in Alloy 690 and Alloy 800 is likely possible due to negligible lattice diffusion over the applied time durations and is remarkable given the high Fe and/or Cr content(s) of these alloys.

Limited data for SCC testing on Alloy 800 in primary water conditions is available. However, the 800 alloy is known to be susceptible to SCC in secondary side environments, such as acid sulfate [39–41] and caustic [41,42]. Arioka et al. recently reported localized and shallow cracking in 20% cold-worked Alloy 800 after exposures to 320 °C primary water for 6903 h [26]. No instances of PWSCC have been reported for Alloy 800 in the absence of severe cold work. Given the limited studies in the primary literature, further SCC testing and oxidation studies are needed for Alloy 800 in primary water environments.

In the current work, Alloy 800 and Alloy 600 are exposed to 310–315 °C deaerated water with added hydrogen maintaining a potential on the Ni-metal side of the Ni/NiO equilibrium potential. High resolution analytical electron microscopy is used to study oxidation in Alloys 600 and 800 both inter- and intragranularly. The oxidation tendency, internal or external, of the alloys will be reported. Results will be compared to previous work performed in high temperature hydrogenated steam to further verify whether its use as a simulated primary water environment is valid. Final remarks will be made on internal oxidation as a potential mechanism of PWSCC, and the influence of observed oxidation phenomena on the PWSCC susceptibility or resistance of Alloys 600 and 800.

## 2. Experimental methods

### 2.1. Materials and sample preparation

1.3 mm thick Alloy 600 and Alloy 800 sheets were purchased from Rolled Alloys Inc. and used for all exposures; the compositions of the materials are reported in Table 1. Flat samples were cut from the sheets measuring 0.5 cm by 2 cm. Samples were solution annealed at 1050 °C in Ar-5% $H_2$ gas for one hour and immediately water quenched.

Samples were ground using 400, 800, and 1200 grit paper. Following this, step-wise fine polishing was done using diamond paste (9 μm, 3 μm, and 1 μm) and alumina suspension to a 0.05 μm finish. Coupons were ultrasonically cleaned in ethanol and de-ionized water for 10 min each between polishing stages and dried with air. A desiccator was used to preserve samples for a short period during transport to Canadian Nuclear Laboratories (CNL) for exposure.

Prior to exposure samples were ultrasonically cleaned in ethanol and de-ionized water for 10 min each. Coupons were then placed in ceramic trays, which encased three sides of the samples leaving the polished flat sides open for exposure. The samples were secured to the ceramic trays using polytetrafluoroethylene tape. Ceramic spacers were used to separate samples in the tray to avoid a galvanic effect. The secured samples were placed in a ½ inch 304 stainless steel (SS) tube and attached to the H5 loop at CNL; further description of the H5 loop is provided in Section 2.2. The ceramic tray combined with polytetrafluoroethylene tape shielded the samples from contact with the 304SS pipe.

### 2.2. Experimental conditions and equipment

The environment consisted of 310–315 °C simulated primary water with the potential maintained well below the Ni/NiO equilibrium electrode potential. Dissolved $H_2$ content was used to control the corrosion potential of the metal in the simulated primary coolant. Andresen et al. [2,6] and Morton et al. [3–5] outlined methods to calculate the dissolved $H_2$ content or dissolved oxygen concentration at the Ni/NiO equilibrium electrode potential. Eq. (1) from Andresen et al. can be used to estimate the $H_2$ fugacity at the Ni/NiO equilibrium $\left(f_{H_2,\mathrm{Ni/NiO}}\right)$ [2], quoted at STP; a hydrogen concentration of 0.72 mol/m$^3$ will maintain conditions at the Ni/NiO standard electrode potential in 315 °C water.

$$f_{H_2,\mathrm{Ni/NiO}} = 10^{(0.0111\times T(^\circ C)-2.59)} \tag{1}$$

The calculated dissolved hydrogen content is within range of experimental data; at 315 °C no film formation and Ni oxide reduction was reported in Alloy 600 exposed to primary water with a dissolved $H_2$ content at STP maintained at 0.90 mol/m$^3$ or higher [2,6]. In the current work, dissolved $H_2$ content is maintained between 1.21 and 1.23 mol/m$^3$, quoted at STP, which sets the potential well below the Ni/NiO equilibrium electrode potential at 315 °C, on the Ni-metal side of the peak on the PWSCC growth rate versus potential curve.

Experiments were carried out in the H5 loop at CNL. The H5 loop is primarily constructed using 304SS and has been used to simulate primary coolant in a CANDU reactor successfully at temperatures up to 305 °C; for experiments in the current study, temperature is increased and maintained at 315 °C ± 5 °C by increasing the electric heater output. The time needed to reach the desired exposure temperature was approximately 2 h. During the heating period the high hydrogen concentration should maintain conditions well in the Ni-

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