Replicating PWR Primary Water Conditions in Low Pressure H₂-Steam Environment to Study Alloy 600 Oxidation Processes

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The effects of thermodynamic parameters associated with low pressure H₂-steam on the oxidation behavior of Nickel have been investigated to simulate PWR primary water conditions. An Y₂O₃-ZrO₂ solid state reference electrode operated between 372 and 480 °C, and exposed to variable hydrogen partial pressures, was used to obtain in-situ potential measurements to identify the Ni/NiO transition. Microstructural analyses on Alloy 600 coupons exposed to H₂-steam under different oxidizing conditions showed a marked dependence of the intergranular oxidation processes, as expected for a PWR environment. Overall, the H₂-steam simulated an environment that can be considered to be representative of PWR primary water.

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It is well known that the operating electrochemical corrosion potential of structural alloys in the primary circuit of a Pressurized Water Reactor (PWR) is located in the proximity of Ni/NiO transition where Alloy 600 (Ni-15Cr-10Fe) and its related welding alloys display the highest susceptibility to Primary Water Stress Corrosion Cracking (PWSCC) initiation and propagation. The main parameter controlling the potential is the dissolved H₂ (DH), which is generally added to the primary water to suppress the formation of radiolytic products and decrease the electrochemical corrosion potential of Ni-base alloys. Consequently, identifying the exact environmental condition associated to the Ni/NiO transition is a requirement to perform laboratory experiments that are relevant to nuclear power plant operation.

The environmental condition to reproduce the Ni/NiO transition has been identified in high temperature water and in supercritical water, since these environments have been already employed to replicate nuclear power plant operating conditions. Specifically, Attanasio et al. employed Constant Electric Resistance (CER) techniques on Alloy 600 samples to identify the amount of DH associated to the Ni/NiO transition at temperatures between 260 °C and 360 °C. However, whilst the thermodynamic transition was identified, it was shown that the values of enthalpy and entropy were not in complete agreement with those reported in the older literature. More recently, Moss and Was identified the environmental condition to reproduce the Ni/NiO transition using Ni coupons exposed from 320 °C to 450 °C at 25 MPa in both subcritical and supercritical water at different DH concentrations. The experimental values of the standard enthalpy of formation (ΔH_f,NiO) and standard entropy of formation (ΔS_f,NiO) for NiO were close to the values reported by Attanasio et al. in subcritical water.

In more recent years, a low pressure super-heated H₂-steam system has been employed to perform oxidation and SCC experiments relevant to the PWR primary water environment. In this paper ex situ characterization techniques were also employed to consolidate the electrochemical results; specifically, Grazing Angle X-Ray Diffraction (GA-XRD) and XRD analyses were performed on commercially pure Ni-200 coupons and highly sensitive Ni powder exposed to low pressure H₂-steam. Moreover, two examples of the highly sensitive dependence of Alloy on the oxidation in the proximity of the Ni/NiO transition are reported with the focus on the intergranular oxide penetration, which is believed to be the main responsible factor for the occurrence of the PWSCC. It is worth noting that the work reported in the literature mainly focused on the behavior of Alloy 600 in the Ni stable region and not across the Ni/NiO transition that is presented in this work.

Experimental

H₂-steam environment.—A low pressure super-heated H₂-steam system was used to create an environment that is relevant to the
mixture was then vented in a fume hood. The H₂ and Ar gas flow evaporator before being injected into the reaction tube. The outlet gas was varied accordingly to maintain the total gases flow rate (H₂ and steam, and consequently the oxidizing potential; inert Ar gas, 

\[
\text{Ar} \quad \text{g}
\]

was equal to 40 cc/min. The total flow of 40 cc/min was chosen to be consistent during the multiple measurements.

**Thermodynamic calculations.**—The desired oxygen partial pressure \( p_{O_2} \) was controlled by changing the ratio between steam and H₂ according Eq. 1, under the assumption that the ratio between the partial pressures was equal to the volume ratio at atmospheric pressure between steam and H₂. The \( p_{O_2} \) (Eq. 2) can be calculated using the standard Gibbs free energy of decomposition of H₂O(g), defined as \( \Delta G_{f,H_2O}^\circ \).

\[
\begin{align*}
H_2O(g) & \equiv H_2 + \frac{1}{2} O_2 \tag{1} \\
p_{O_2} &= p^\circ \cdot \left( \frac{1}{P_{PR}} \right)^2 \exp \left[-\frac{2\Delta G_{f,H_2O}^\circ}{RT} \right] \tag{2}
\end{align*}
\]

Where \( p^\circ \) is the standard pressure, equal to 1 atm, \( \Delta G_{f,H_2O}^\circ \) is the standard Gibbs free energy of formation for H₂O(g) as defined above, \( R \) is the universal gas constant, \( T \) is the absolute temperature in Kelvin and \( P_{PR} \) is equal to \( p_{H_2}/p_{H_2O} \). For a given temperature, the \( p_{O_2} \) is dependent by the square of the ratio between the partial pressure of hydrogen over the partial pressure of steam (PPR) and by the standard Gibbs free energy of formation of water \( \Delta G_{f,H_2O}^\circ \), as reported in Eq. 2.

It is worth noting that PPR was originally defined by Capell and Was \( p_{O_2,Ni/NO} \) and it is usually less than 1. Since the decomposition of steam in H₂ and H₂O was considered in this paper, the reciprocal of this parameter (i.e. \( PPR^{-1} \)) is more convenient to be considered. The expression of the dissociation pressure at Ni/NiO transition \( p_{O_2,Ni/NO} \) is reported in Eq. 4 and it was calculated similarly to Eq. 2 from the Gibbs free energy of formation of NiO \( (\Delta G_{f,NiO}^\circ) \) associated with the Reaction 3.

\[
Ni(g) + \frac{1}{2} O_2(g) \equiv NiO \tag{3}
\]

\[
p_{O_2,Ni/NO} = p^\circ \cdot \exp \left[-\frac{2\Delta G_{NiO}^\circ}{RT} \right] \tag{4}
\]

**Characterization of the H₂-steam environment.**—**In situ electrochemical characterization.**—The equilibrium potential associated with the decomposition of the water (Eq. 1), normalized with respect to the Ni/NiO formation can be expressed according the Nernst equation (Eq. 5), where the electrochemical potential is reported as function only of the PPR\(^{-1}\) corresponding to the Ni/NiO transition \( (PPR_{Ni/NO}) \) over the PPR.

\[
E_{eq \; \text{vs. } Ni/NiO} = \frac{RT}{4F} \ln \left[ \frac{\left( \frac{p_{H_2}}{p_{H_2O}} \right)^{2}}{PR_{Ni/NO}} \right] = \frac{RT}{2F} \ln \left[ \frac{PPR_{Ni/NO}}{PPR} \right] \tag{5}
\]

The redox potential expressed in Eq. 5 was experimentally measured using an Ivium potentiostat COMPACTSTAT.h connected to a Pt wire and an yttria stabilized zirconia SSRE, which were exposed to the hydrogenated steam and schematically represented in Fig. 1.

The experimental approach in identifying the electrochemical potential and the Ni/NiO transition was similar to that used by O’Neill \( ^{23} \) who, however, did not characterize the Ni/NiO transition in H₂-steam environment.
environment. The cell consists of two electrodes, separated by a Y2O3-ZrO2 membrane, acting as oxygen-conducting electrolyte. The method measures the difference between the two cells in terms of oxygen partial pressure; if one is known, the other can be calculated, as shown in Eq. 5 for the PPR. Usually, the only known cell consists of a metal/oxide stable phase mixture, such as Cu/Cu2O or Fe/FeO.

The Ni/ NiO yttria stabilized zirconia SSRE used in this study was a replica of a Cu/Cu2O SSRE used in Ref. 26 with a mixture of Ni and NiO powder used as reference placed in the Y2O3-ZrO2 tube, a schematic representation of which is shown in Fig. 2. A Ni wire was used to create the electrical contact between the mixture powder and the potentiostat. A working Pt electrode wire was coiled at the sensing tip of the reference electrode to minimize the electrical resistance (see inset in Fig. 2). Pt, a noble metal, was chosen, as it is inert in this environment and, therefore, the measured redox potential corresponds to potential associated with Eq. 1. The redox potential was monitored at 372 °C, 400 °C, 430 °C and 480 °C. For each temperature, the PPR was kept stable for 700 s, then the H2 flow rate (and hence PPR) was varied and the redox potential was recorded every second.

Since the oxygen sensor used different metals in contact with the corresponding electrodes, the thermoelectric voltage due to this couple of metals was considered and used to correct the sensor voltage. The thermoelectric voltage of the Pt-Ni couple was measured by spot welding a Ni wire to the Pt coil in a similar setup used for the SSRE; this value was 4.5 mV at 372 °C, 4.9 mV at 400 °C, 5.7 mV at 430 °C and 7.5 mV at 480 °C.

Ex situ characterization.—Complementary ex situ GA-XRD, XRD, and microstructural analyses were performed to consolidate the electrochemical measurements. Commercially pure 99.6% Ni-200 coupons were exposed to the environment and subsequently analyzed with a grazing angle XRD using an incident angle equal to 3°. The characterization was conducted before and after exposure to H2/steam environment at PPR−1 equal to 59.4 for 200 h at 480 °C. The grazing angle XRD analyses were performed at 2θ between 30° and 85° with a 0.05° step size with a Philips X’Pert MPD system equipped with a Cu Kα source with a scanned angle. These experiments were also repeated on pure (99.999%) Ni powder with a particle diameter between 3–5 μm with the advantage of having a very large effective surface and hence the ability to detect very small amount of a thin surface oxides using a conventional XRD. 5 grams of Ni powder were placed in a quartz boat and inserted in the stainless-steel reaction tube (Fig. 1) for exposure to H2/steam environment at PPR−1 equal to 54.9 and then to 632.5 for 200 h at 480 °C. The XRD analyses were performed before and after exposure of the powder in H2/steam environment. These analyses were performed using a Philips X’Pert MPD system equipped with a Cu Kα source with a 2θ between 5° and 85° with a 0.05° step size. The experimental peaks of both conventional and grazing angle XRD were compared with the Ni reference data (PDF card no. 00-004-0850) and the NiO reference data (PDF card no. 00-044-1159) for Cu Kα source.

Further microstructural characterizations were performed on coupon samples of Alloy 600 after exposure to the H2/steam mixture. The alloy was provided by B&W Tubular Products Division and supplied by Westinghouse with the chemical composition reported in Table I. The material was solution annealed at 1100 °C for 30 minutes and water-quenched within 10 seconds to suppress the formation of intergranular carbides. Further details can be found in Ref. 12. Squared samples of 20 × 20 × 2 mm3 were cut, ground and metallographically polished with a 3 μm and a 1 μm diamond polishing suspension. A 24–40 nm Silica Oxide Polishing Suspension (OPS) was used to remove any surface deformation due to the previous grinding polishing that can affect the oxidation behavior of the material and to have a surface more representative of the bulk material. The samples were exposed to H2/steam at 480 °C for 210 hours in the Ni stability (PPR−1 = 54.9) and NiO stability (PPR−1 = 1305) of the Ni/ NiO transition. After the exposure, the samples were characterized using a Field Emission Gun (FEG) – Scanning Electron Microscope (SEM) Zeiss Sigma FEG-SEM equipped with an Oxford Instruments X-max 150 silicon drift detector (SDD) and an Aztec analysis system for Energy dispersive X-ray spectroscopy imaging and analysis was used to characterize the surface of the coupon samples after the exposure to H2/steam environment. Secondary electron (SE) and annular selective backscattered (BSE) detectors were used at 5 kV accelerating voltage to analyse the morphology of the surface in the vicinity of grain boundaries. For each sample, twenty FIB cross-sections were prepared for specific sites containing at least one oxidized grain boundary using an FEI Helios 660 Dual Beam SEM/FIB. The SE and BSE detectors were used at 5 kV to image the cross-section microstructures.

Results

Measurement of the redox potential of the H2/steam mixture.— The redox potential associated with the H2/steam gaseous mixture for each value of PPR was monitored as function of time, and a representative set of measurements performed at 400 °C of the redox potential associated with the H2/steam mixture are shown in Fig. 3. During each test the temperature was kept constant and the hydrogen content was progressively decreased (i.e. PPR−1 increased) nine times whilst the tenth acquisition was at conditions identical to the first one. Although for very reducing conditions the potential required a few hundred seconds to stabilize, the potential of steam was very sensitive to the changes in environmental conditions. The value of redox potential associated with the decomposition of steam in hydrogen and oxygen changed from −67 mV (at PPR−1 = 40.3) to +30 mV (at PPR−1 = 1641), thus spanning the region from Ni stability to NiO stability. A 10° measurement was performed using the same PPR−1 used for the acquisition of the first transient region at the end of the acquisition in order to verify a possible excess of O2 in the yttria stabilized zirconia tube. The SSRE demonstrated a minimal hysteresis since the redox

| Table I. Chemical composition (wt%) of Alloy 600 used in this study. |
|-----------------|---|---|---|---|---|---|---|---|---|---|---|---|
| Heat no.        | C  | Mn | S  | P  | Si | Cr | Ni | Cu | Al | Ti | Fe |
| 93510           | 0.047 | 0.23 | 0.002 | 0.005 | 0.30 | 15.42 | 74.43 | 0.01 | 0.19 | 0.34 | 8.94 |

Figure 2. Schematic representation of the Ni/ NiO Yttria Stabilized Zirconia SSRE. The inset shows the virtual cross section of the tip filled with Ni/ NiO powder mixture with a Pt wire coiled around the tip which acted as working electrode.
Thus, it is reasonable to assume that oxygen saturation in the reference function of the was regenerated prior each set of measurements. The average of the evaluate the reproducibility of the results and the reference electrode $^\circ$

\[ \frac{\text{data were compared with the theoretical redox potential at 400}^\circ\text{C calculated from the free energy of dissolution for water (black solid line).}^9 \]

Experimental redox potential associated with the H$_2$O equilibrium with H$_2$ and O$_2$ at 400$^\circ$C behavior as function of PPR$^{-1}$. The experimental data were compared with the theoretical redox potential at 400$^\circ$C calculated from the free energy of dissolution for water (black solid line).$^9$

Further experiments were conducted at 372$^\circ$C, 430$^\circ$C and 480$^\circ$C in order to evaluate the response of the reference electrode as function of the temperature. A summary of the evolution of the redox potential for the temperature examined in this work is reported in Fig. 5. The experimental curves at 372$^\circ$C and 400$^\circ$C agreed well with the theoretical data, confirming the Nernstian behavior of the potential as function of the PPR$^{-1}$ in H$_2$-steam environment. However, at 480$^\circ$C (blue downward triangle in plot d), a considerable deviation of the experimental potential from the theoretical data was observed in the more oxidising conditions with respect to the Ni/NiO transition.

**XRD**—Grazing angle XRD analyses were performed on commercially pure Ni-200 coupons before and after exposure in the H$_2$-steam environment. A representative grazing angle diffractogram for Ni coupon before the exposure (a) is shown in Fig. 6, which confirmed the absence of any external oxide on the surface, since the only peaks present in the plot are characteristic of Ni. The coupon was then exposed in the H$_2$-steam environment at 480$^\circ$C for 200 h at the PPR$^{-1}$ equal to 54.9, which is a reducing condition with respect to the Ni/NiO value (i.e. the measured redox potential of Pt was $-59$ mV vs. the SSRE). The diffractogram (b) of Fig. 6 showed the main peaks of pure Ni,$^{41}$ confirming that the coupon was exposed in a reducing environment, however secondary peaks approximately at 38, 65$^\circ$ and 78$^\circ$ were identified after the exposure. These peaks did not correspond to the NiO peaks, but they are consistent with the formation of iron silicate (Fe$_2$SiO$_4$ at 20 = 38$^\circ$ and 78$^\circ$)) and manganese oxide (MnO$_2$ at 20 = 65$^\circ$), as expected from the minor impurities present in the commercially pure Ni-200.

Further experiments were also conducted using Ni powder to corroborate the previous results and exclude the possibility that a very thin oxide what might have been undetected by the grazing angle XRD. Two tests were conducted: one in a reducing condition (b) and the other in an oxidizing condition (c) with respect to the Ni/NiO. The XRD results are shown in Fig. 7 alongside the baseline powder characterization. The diffractogram of the Ni powder exposed at PPR$^{-1}$ equal to 54.9 exhibited only the peaks associated with metallic Ni and no evidence of NiO. This result confirmed that the environment was more reducing than the Ni/NiO transition, in fact, from Fig. 5 a steam redox potential of $-59$ mV was predicted. The second test was conducted at PPR$^{-1}$ equal to 632.5 ($E_{eq} = 20.8$ vs. Ni/NiO), and the characteristic XRD peaks of NiO can be clearly identified in the diffractogram in Fig. 7c. Specifically, the main NiO reflections were located at 20 values of 37.3$^\circ$, 43.3$^\circ$ and 63$^\circ$,$^{42,43}$ as well as those for the baseline Ni matrix; no Ni(OH)$_2$ was identified by XRD for the powder exposed to the more oxidising conditions (Fig. 7c). It was thus experimentally observed that the Ni/NiO transition at 480$^\circ$C occurred at PPR$^{-1}$ between 54.9 and 632.5. Whist this range of PPR$^{-1}$ is relatively wide, it is worth noting that Ni was predicted to be in the oxidized state even at PPR$^{-1}$ equal to 11, significantly lower than the PPR$^{-1}$ = 54.9 according to Capell and Was.$^{20}$

**Microstructural characterization of alloy 600.—**The work reported in the literature by those laboratories who used low pressure H$_2$-steam to simulate electrochemical conditions of a PWR primary water environment is limited to very reducing conditions with respect to the Ni/NiO transition$^{2,19,21,31,34,44}$ whilst the effect of oxidizing potential has not been investigated. In the present work, Alloy 600 SA coupon samples were exposed in H$_2$-steam environment at 480$^\circ$C for 210 h, either in reducing or oxidizing conditions with respect to the Ni/NiO transition. Recalling that PWSCC susceptibility is highest in the proximity of the Ni/NiO transition, a similar trend would also be expected for the evolution of preferential intergranular oxide (PIO) penetration. Consequently, if such a correlation was found, this would provide confidence on the validity of using low pressure hydrogenated steam system as a surrogate for PWR primary water.

Representative SE and BSE micrographs of the surface of the sample exposed to reducing conditions (PPR$^{-1}$ = 54.9 and $E_{eq} = -52$ mV

Figure 3. Evolution of the redox potential of steam in H$_2$ and O$_2$ at 400$^\circ$C as function of the time. Each transient region was obtained keeping constant a desired PPR for 700 seconds.

Figure 4. Experimental redox potential associated with the H$_2$O equilibrium with H$_2$ and O$_2$ at 400$^\circ$C behavior as function of PPR$^{-1}$. The experimental data were compared with the theoretical redox potential at 400$^\circ$C calculated from the free energy of dissolution for water (black solid line).$^9$
Figure 5. Experimental redox potential of steam trend as function of the $PPR^{-1}$ at (a) 372 °C, (b) 400 °C, (c) 430 °C and (d) 480 °C. The experimental data were also compared with the theoretical redox potential of steam (solid black line) for the temperatures examined calculated from Reference 9.

Figure 6. Grazing-angle XRD spectra of Ni coupons before (a) and after exposure in H$_2$-steam environment for 200 h at 480 °C at $PPR^{-1} = 54.9$ (b). The diffractograms are shifted in the Y-axis for clarity.

Figure 7. XRD spectra of high purity Ni powder before (a), after exposure in H$_2$-steam environment at 480 °C for 200 h at $PPR^{-1} = 54.9$ (b) and at $PPR^{-1} = 632.5$ (c). The diffractograms are shifted in the Y-axis for clarity.

Figure 8. The surface appeared to be uniformly covered with randomly dispersed brightly-imaging (in BSE images) particles that are consistent with metallic Ni nodules that are known to form as a consequence of the internal compressive stresses generated by the formation of internal oxides. The surface appeared to be protruded and to form “split-ridges”, highly decorated with brightly-imaging particles; furthermore, on both side of the grain boundaries, an approximately 2–3 μm nodule-free zone was observed as in previous studies. Conversely, the surface of the sample exposed to the more oxidising environment ($PPR^{-1} = 1305$ and $E_{eq} = +52$ mV vs. Ni/NiO) showed a completely different surface morphology. The SE-SEM
images showed a rough appearance of the surface, indicating a possible external oxide layer that uniformly covers the surface of the sample (Fig. 9a). The BSE-SEM image (Fig. 9b) showed a bright region of $\approx 2 \mu m$ along the grain boundary (GB), traversed by a continuous and undulated dark feature; this feature, being darker, is consistent with a lower atomic number and it may indicate the presence of a thin surface oxide.

Marked differences between the two samples can be also observed from the SE images of the FIB cross-sections shown in Fig. 10a and Fig. 10b that contained at least one oxidized grain boundary. The grain boundaries were decorated with fine intergranular M$_2$C$_6$ carbides, identified in previous studies of this alloy via electron diffraction, and are clearly visible as fine darkly-imaging features on the grain boundaries. For the sample exposed in the more reducing environment (Fig. 10a), a coarse, continuous and highly interconnected darkly-imaging feature was observed along the grain boundary indicating the occurrence of PIO, and consistent with previous detailed microstructural studies. However, it is also possible that local variations in oxidation tendency depending on grain boundary angle and grain orientations are present, but this has not been investigated in detail in this work and it is the subject of ongoing investigations. In contrast, no intergranular oxidation was observed along the grain boundary (Fig. 10b) of the sample exposed in the more oxidizing environment.

**Discussion**

The experimental redox potential associated with the H$_2$/steam gaseous mixture shown in Fig. 4 can be considered, with good approximation, to be the potential associated with the redox equilibrium of the Reaction 1. In fact, the decomposition of the steam on the Ni metal surface is much greater than the dissolution of the Pt working electrode, which did not interact with the environment and alter the measured redox potential. The oxygen partial pressure inside the yttria stabilized zirconia tube sensor was kept constant by the presence of two stable phases (Ni and NiO) and the redox potential measured was only associated with the decomposition of steam and hence influenced only by the $p_{O_2}$ in the system. The redox potential of H$_2$/steam mixture shown in the previous plot of Fig. 4 was compared with the $PPR^{-1}$ values imposed during the acquisition and reported in the plot of Fig. 11. As expected, $PPR^{-1}$ and the redox potential were proportional to each other. A good correspondence between the experimental redox potential and the thermodynamic predictions was noted. However, for the highest temperature and for more oxidizing environments, the experimental data deviated slightly and the potential of steam was underestimated by up to $\approx 10$ mV. The buffer capacity of H$_2$/H$_2$O mixtures became very poor for high $PPR^{-1}$, as shown in the plot d (blue downward triangle in plot d) of Fig. 5.

The values of $PPR^{-1}$ associated with the Ni/NiO transition extrapolated from the data in Fig. 4 and Fig. 5 were calculated, reported in the Arrhenius plot in Fig. 12, and compared with the data from other laboratories. From the results of the present work

![Figure 8](image1.jpg)

**Figure 8.** (a) SE and (b) BSE images of the surface in the proximity of grain boundary regions for the sample exposed in the more reducing environment ($PPR^{-1} = 54.9$ and $E_{eq} = -52$ mV vs. Ni/NiO).

![Figure 9](image2.jpg)

**Figure 9.** (a) SE and (b) BSE images of the surface in the proximity of the grain boundary regions for the sample exposed in the more oxidizing environment ($PPR^{-1} = 1305$ and $E_{eq} = +52$ mV vs. Ni/NiO).

![Figure 10](image3.jpg)

**Figure 10.** SE images of the FIB-prepared cross-section of a grain boundary region for the Alloy 600 sample exposed in (a) more reducing environment than the Ni/NiO transition ($PPR^{-1} = 54.9$ and $E_{eq} = -52$ mV vs. Ni/NiO) showing interconnected and deep PIO; and (b) in more oxidizing environment than the Ni/NiO transition ($PPR^{-1} = 1305$ and $E_{eq} = +52$ mV vs. Ni/NiO) where no relevant PIO was detected.

![Figure 11](image4.jpg)

**Figure 11.** Evolution of the experimental redox potential of steam (solid black line) acquired during the experiment and overlapped with the expected redox potential of steam for the desired $PPR^{-1}$ ratio (dashed red line).
presented in Fig. 12 it was determined that $\Delta H^{\circ}_{f,mix}$ was equal to 12430 J/mol and the $\Delta S^{\circ}_{f,mix}$ was equal to 30.51 J/mol·K, where $\Delta H^{\circ}_{f,mix} = H^{\circ}_f(H_2O) - H^{\circ}_f(NiO)$ and $\Delta S^{\circ}_{f,mix} = S^{\circ}_f(H_2O) - S^{\circ}_f(NiO)$. These experimentally-derived values are in good agreement with previous values calculated by Kubaschewski et al. ($\Delta H^{\circ}_{f,mix} = 12091.9$ J/mol and $\Delta S^{\circ}_{f,mix} = 30.51$ J/mol·K) shown as the black line in the evolution (Fig. 12). Moreover, the $PPR_{Ni/NiO}^{-1}$ corresponding to the Ni/NiO transition (i.e. green points shown in Fig. 12) were used to calculate the theoretical redox potential using Eq. 5; importantly, the results shown in Fig. 13 indicate that the discrepancy between experiments and theory is negligible.

In contrast, Capell and Was$^{20}$ predicted the Ni/NiO phase transition to be at a much lower value of $PPR_{Ni/NiO}^{-1}$ for 400°C (11 vs. 337 measured in this work) with a predictable discrepancy of $E_{eq} = -100$ mV calculated using Eq. 5. The discrepancy by Capell and Was might be due to the fact that their experimental results were based on the formation of Ni(OH)$_2$, which was detected via XPS and not NiO. Furthermore, although they claimed that their Gibbs activation energy was in good agreement with the high pressure water results of Attanasio et al., the thermodynamic conditions associated with the Ni/NiO transition depend on the state of the media, which was different. In fact, the different physical condition of water influences the $\Delta S^{\circ}_{f,mix}$ and, for this reason, thermodynamic data obtained at high pressure and low-pressure systems cannot be compared. It is also not surprising that the data extracted from Moss et al.$^8$ (also reported in Fig. 12, $\Delta H^{\circ}_{f,mix} = 19281$ J/mol and $\Delta S^{\circ}_{f,mix} = 37.32$ J/mol·K = 37.32), are different from the values identified in the present study.

One of the objectives of this work was to validate the superheated low pressure H$_2$-steam environment as a possible surrogate system to perform oxidation and SCC experiments relevant to the PWR primary water environment. For this reason, two Alloy 600 oxidation tests were conducted to understand the oxide morphology evolution (Fig. 8 to Fig. 10). Specifically, tests conducted at $PPR_{Ni/NiO}^{-1}$ equal to 54.9 ($E_{eq} = -52$ mV vs. Ni/NiO), showed that the surface appeared to be covered with randomly dispersed discrete, brightly-imaging particles, identified in previous studies as Ni-nodules.12,21,51 Metallic Ni nodules are formed to counteract the internal compresses stresses generated by the formation of discrete internal oxides of Cr (i.e., Cr$_2$O$_3$).12,14,15 Internal oxidation can occur in an alloy when the $PPR_{Ni/NiO}^{-1}$ are sufficient to oxidize one of the less noble alloying elements.47 A similar oxidation process can be attributed to the protracted grain boundary, and previous studies have already shown significant PIO along grain boundaries with “split-ridge” oxide morphologies in such environments.12,14,15,21,31,34 In contrast, Alloy 600 samples tested at $PPR_{Ni/NiO}^{-1}$ equal to 1305 ($E_{eq} = +52$ mV vs. Ni/NiO) were characterized by a surface covered with an external oxide layer, probably enriched in NiO, Fe-rich oxides and spinels, such as NiCr$_2$O$_4$.48 The morphology of the grain boundaries was different from that observed in the sample exposed to the more reducing environment. The undulated black linear features associated with the grain boundaries observed in the BSE image of Fig. 9 appear to be related to presence of the surface oxide. The SE images of the FIB cross-section (Fig. 10) showed a negligible PIO as well as a less internal oxidation in contrast to the sample exposed to the more reducing environment. The thin surface oxide layer above the GBs (Fig. 9) can act as a barrier layer inhibiting further inward oxygen diffusion. In contrast, the grain boundary exposed to the more reducing environment (Fig. 10a) showed an interconnected and deep PIO penetration of ≈500 nm.

Therefore, the oxide characterization conducted in this study highlighted a very high sensitivity of PIO to the electrochemical potential with respect to the Ni/NiO equilibrium electrode potential, whereby significant, deep PIO was identified in the Ni stability region.

Recalling that PIO is considered to be the main precursor event of PWSCC of Alloy 600,30,35 a good correlation was identified between the behavior of Alloy 600 in low pressure hydrogenated steam environment and in high pressure simulated PWR primary water. PWSCC initiation has been shown to predominantly occur in reducing simulated PWR primary water environments,4 and to exhibit a maximum of crack growth for conditions close to the Ni/NiO transition, but in the Ni stability region.1 A probable diffusion induced grain boundary migration$^{46,50}$ associated with the formation of the PIO and external oxide layer was identified in the SE images in Fig. 10a and Fig. 10b. This phenomenon was already observed for Alloy 600 exposed to high temperature H$_2$-steam environment$^{12,14-16,21,33,34}$ and it was reported to occur also at lower temperatures on Alloy 600 exposed to simulated PWR primary water.$^{16,35,51}$ This suggests that the

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**Figure 12.** Arrhenius plot showing the $PPR_{Ni/NiO}^{-1}$ vs. 1000/T for the experiments carried out in this work, the data of Attanasio et al.$^3$ Moss et al.$^5$ Capell et al.$^5$ and the theoretical standard Gibbs free energy of the mixture H$_2$O-NiO, calculated from Kubaschewski et al.$^9$

**Figure 13.** Comparison between the theoretical redox potential (red, dashed line) and experimental redox potential (black circles) associated with the dissolution of steam at the Ni/NiO transition.
mechanism is similar in both environments. This work has also shown low pressure hydrogenated steam is valid as an accelerating environment that can be considered to be representative of PWR primary water.

**Concluding Remarks**

The aim of this study was to validate the super-heated low pressure H2-equivalent environment as surrogate to a PWR primary water environment. The following conclusions can be drawn from this investigation:

- The environmental conditions producing the Ni/NiO transition in a low pressure super-heated H2-equivalent were identified at temperatures between 400 °C and 480 °C using an Y2O3-ZrO2 solid-state reference and ex situ XRD characterization of Ni-200 coupons and pure Ni powder.
- The Gibbs free energy associated with the formation of NiO and decomposition of H2O was dependent on the media considered, i.e. high-pressure water or steam vs. superheated low-pressure steam. The results of this work showed that the Kubaschewski et al.’s data can be used to predict the oxidizing potential in H2-equivalent. However, our findings are in disagreement with the activation energy calculated by Capell and Was, who conducted the experiments in a low-pressure superheated system.
- The oxidation of Alloy 600 coupons was used to highlight the high dependence of this alloy to preferential intergranular oxidation as a function of the oxidizing potential in the H2-equivalent. These results also provide confidence that superheated H2-equivalent can be used to reproduce the similar oxidizing conditions to those of PWR primary water, thereby providing accelerated test conditions for PWSCC-related research.

All the data discussed are directly presented in the paper and therefore they are immediately accessible.

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