Surface chemistry and corrosion behavior of Inconel 625 and 718 in subcritical, supercritical, and ultrasupercritical water

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Abstract

Corrosion behavior of Inconel 625 and 718 in subcritical, supercritical and ultrasupercritical water was studied as a function of temperature and time. The change in the chemistry of the as-received surface film on Inconel 625 and 718 after exposure to subcritical water at 325°C and supercritical water at 425°C and 527.5°C for 2 hours was studied. After exposure to 325°C subcritical water, the CrO_4^{2-} based film formed; however minor quantities of $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$ spinel compounds were observed. The oxide film formed on both alloys when exposed to supercritical water at 425°C consisted of $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$ spinel. The surface films on both alloys were identified as NiFe_2O_4 when exposed to supercritical water at 527.5°C. To characterize the fully developed oxide layer, studies were conducted at test solution temperatures of 527.5 and 600°C. Samples were exposed to these temperatures for 24, 96, and 200 hours. Surface chemistry was analyzed using X-ray diffraction, as well as Raman and X-ray photoelectron spectroscopies. Inconel 718 exhibited greater mass gain than Inconel 625 for all temperatures and exposure times. The differences in corrosion behavior of the two alloys are attributed to the lower content of chromium and increased iron content of Inconel 718 as compared to Inconel 625.

Keywords: supercritical; spinel; XRD; Raman; XPS

1. Introduction

Supercritical water (SCW) is capable of being used in a variety of applications, one of which is as a heat transfer medium for use in coal and nuclear power plants due to the increased theoretical Carnot efficiency associated with increased operating temperatures [1, 2]. For example, a 1000MW advanced coal plant that incorporates supercritical water is expected to have a reduction of ~15% in the amount of coal fed to the reactor when compared to a design that utilizes subcritical water conditions [2]. Coal fired power plants can use both SCW and ultrasupercritical water (USCW). These conditions are defined by operating temperatures and pressures above 375°C and 22.1MPa for SCW, while USCW is classified as operating conditions that are above 590°C and 25MPa [3]. The nuclear industry has a proposed Generation IV design that will incorporate supercritical water as the heat transfer fluid [1]. Utilizing supercritical water as the reactor coolant, the plant efficiency can be increased to 45%, compared to the ~33% efficiency of traditional light water reactors [4].

While there are similarities in plant design between the supercritical water reactor (SCWR) and current commercial reactors, candidate materials for the SCWR must be evaluated under the conditions of elevated temperature and alternate coolant phase required for operation. Nickel based superalloys have been extensively used for high temperature water applications in nuclear, coal, and natural gas power plants [5, 6]. The high corrosion resistance of these materials is attributed to the formation of stable and protective oxide films that suppress further oxidation even during long periods of exposure in this extreme environment [7, 8]. While the formation and stability of oxide films on these superalloys has been extensively studied under high

temperature liquid water conditions, a knowledge gap remains in understanding their oxidation process in SCW [7, 9-11]. Electrochemical oxidation theory provides the concepts essential to understanding the behavior of these materials in liquid water, but it cannot be applied beyond the critical point due to changes in the physical properties of the fluid [9, 12, 13]. The high temperatures and associated rapid kinetics encountered in supercritical water environments necessitate investigation of corrosion mechanisms to avoid failure of critical components [14].

This investigation aims to further the understanding of the behavior of nickel based alloys in SCW. Experimentation was conducted using the supercritical water loop (SCWL) facility at the University of Nevada, Reno. This work characterizes both the change in the chemistry of the as-received surface as it develops into the oxide films that are stable in SCW, as well as the more developed surface oxides that form over relatively longer exposure times. The first part of this investigation studies the alteration to the alloy surface that occurs as a result of 2 hour exposures to evaluate the initial effect of heating the system to reach 325°C, and SCW at 425 and 527.5°C. This information is crucial as all samples undergo exposure to the heating cycle of the reactor. The second portion of this investigation characterizes fully developed oxide layers that were formed upon exposure to SCW and USCW, for exposure times of 24, 96 and 200 hours.

2. Materials and Methods

2.1. Materials

Inconel 625 (I625) and Inconel 718 (I718) used in this study were purchased from HP alloys. The compositions of both alloys are given in Table I. All samples were laser cut into coupons measuring 2.2 by 2.5cm. To study the initial change in chemistry, it is essential to maintain the surface film on the coupons in their as-received and thus coupons for those studies were not

polished. Coupons were polished to a 1 μ m finish in the fully developed oxide layer characterization study.

2.2. Operation of Supercritical Water Loop

The pressure in the supercritical water loop was maintained at 27MPa during all experiments. The temperature was monitored using type K thermocouples, with an accuracy of $\pm 2.5^{\circ}\text{C}$. The SCWL test solution was 18M Ω deionized water that was continuously deaerated with nitrogen to maintain the dissolved oxygen content at less than 50ppb throughout operation. Experiments to determine the evolution of the as-received surfaces were conducted at solution temperatures of 325, 425 and 527.5 $^{\circ}\text{C}$. The exposure time utilized in this study was 2 hours for each temperature point. The fully developed oxide layer characterization studies were conducted at test solution temperatures of 527.5 and 600 $^{\circ}\text{C}$. Samples were exposed to these temperatures for 24, 96, and 200 hours.

2.3. Post Exposure Analysis

After removal from the autoclave, each sample was dried under low vacuum for 24 hours. An Ohaus Adventurer balance with a resolution of 100 μg was used to measure the mass of the samples before and after exposure testing. Grazing incidence X-ray diffraction (XRD) patterns were obtained using a Rigaku Smartlab with a Cu K α X-ray source, from $2\theta = 15$ to 95 degrees with a step size of 0.07 degrees and dwell time of 0.1 degrees/min with an angle of incidence of 0.5 degrees. PDXL2 software was used to analyze the crystallography of the oxide film. Samples were also studied using a Thermo Scientific DXR Raman using a 10mW 532nm laser. X-ray photoelectron spectroscopy (XPS) spectra were obtained using a PHI model 5600 spectrometer

using monochromatic Al K_{α} radiation with an 800 μ m diameter area of analysis, which was calibrated to the Ag 3d5/2 line at 368.3 $\pm$ 0.05eV. Spectra were charge corrected using the adventitious C 1s line at 284.6eV. Samples were analyzed with and without being subjected to 1 minute of argon ion sputtering. The sputtering rate was calculated to remove 7nm of tantalum oxide per minute. The spectra were subjected to 5 point smoothing and peak fit using SDP v4.6 software purchased from XPS International.

3. Results

3.1.1 Evolution of the As-Received Surface

Raman spectra obtained from the surfaces of I625 and I718 exposed to temperatures of 325, 425 and 527.5°C for 2 hours are displayed in Figures 1 and 2, respectively. It is well established that the passive nature of these alloys in ambient and high temperature liquid water is due to the formation of a stable Ni(OH)₂ and CrO₄²⁻ based oxide film [15-18]. The characteristic Raman feature of CrO₄²⁻ at 850cm⁻¹ is clearly observable on both I625 and I718 after exposure to liquid water at 325°C [19].

In addition to the feature attributed to the presence of CrO₄²⁻, the spectra shown in Figures 1 and 2 contain broad Raman features centered at 702cm⁻¹. Raman vibrational modes in the region between 702-685cm⁻¹ are attributed to the A_{1g} Raman mode of NiFe_xCr_{2-x}O₄ spinel structures, with lower wavenumber features characteristic of higher Cr content compounds [20]. Quantifying the value of x for a given NiFe_xCr_{2-x}O₄ spinel through Raman spectroscopy is difficult due to minor shifts in the A_{1g} mode that result from significant changes in composition; with reports observing less than a 20cm⁻¹ difference between NiFe₂O₄ and NiCr₂O₄ [21-28]. Furthermore, identification of oxide films formed on Ni-Fe-Cr-Mo alloys, notably I625 and I718,

in high temperature water has demonstrated the presence of a complex mixture of various spinel structures coexisting within a single surface film [26-32]. It has been reported that secondary features become apparent when NiCr_2O_4 and NiFe_2O_4 are present in quantities closer to purity, thus these features will be utilized for identification. Secondary features indicative of oxide films closer to pure NiFe_2O_4 are observed to occur between ~ 595 and 580cm^{-1} , as well as the F_{2g} mode at 490cm^{-1} , and E_g mode at 330cm^{-1} . Alternatively, NiCr_2O_4 exhibits secondary features at the following wavenumbers with their corresponding mode; $580\text{cm}^{-1}(\text{F}_{2g})$, $511\text{cm}^{-1}(\text{F}_{2g})$, and $425\text{cm}^{-1}(\text{E}_g)$.

Raman spectra taken from the as-received coupons of I625 and I718 contain no observable features. The Raman spectra of samples exposed to 325°C liquid water exhibit a broad A_{1g} feature, and none of the secondary modes that indicate the presence of pure NiFe_2O_4 or NiCr_2O_4 . This indicates that the spinel compounds formed on both I625 and I718 as a result of exposure to high temperature liquid water are $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$ spinel, where $x > 0$. This result is in agreement with previous reports on the corrosion of I625 and I718 following extended periods of exposure to high temperature subcritical water [29, 32].

After exposure to SCW at 425°C , the surface of neither alloy exhibited the Raman active mode characteristic of CrO_4^{2-} , but instead these spectra are dominated by a Raman feature characteristic of the previously discussed A_{1g} vibrational modes of $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$. The spectra obtained from the surface of I625 after exposure to SCW at 425°C is characterized by a broad peak in this region, and the lack of detectable E_g and F_{2g} modes suggests a mixed $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$ formation. On the other hand, the surface of I718 after being exposed to 425°C SCW exhibits intense secondary Raman modes, in addition to a well-defined A_{1g} feature. All of the four Raman features in this spectrum are in agreement with previously reported spectroscopic features of

NiFe₂O₄ [21-28]. The presence of a Fe based spinel on the surface of I718 is expected due to the 19wt% Fe in the alloy. The ratio of Cr to Fe in I625 is ~4.5:1, which is significantly greater than that of I718 which is ~1:1. The observation of a less defined NiFe_xCr_{2-x}O₄ surface film on I625 after being subjected to equivalent exposure is therefore attributed to the higher ratio of Cr to Fe in I625, resulting in the formation of Cr containing spinel.

After exposure to 527.5°C SCW both alloys exhibit well defined signals from all of the Raman modes indicative of NiFe₂O₄. The observation of the secondary Raman modes, in agreement with literature values, indicates the presence of a NiFe_xCr_{2-x}O₄ spinel with a value of x approaching 2 [21, 25-28]. The formation of Fe and Ni rich phases accompanying the increase in the temperature of exposure is in agreement with previous reports [9, 33, 34].

The presence of the shoulder peak at 850cm⁻¹ on the I625 sample exposed to SCW at 527.5°C is again attributed to the presence of CrO₄²⁻. It is hypothesized that the formation of CrO₄²⁻ occurred during the cooling period of the test solution before removal of the sample from the autoclave. If the surface film formed on I625 at 527.5°C was unstable and underwent partial disintegration, the exposed bulk I625 could form CrO₄²⁻ while interacting with subcritical water throughout the cool down period. The re-emergence of CrO₄²⁻ on the surface of I625 and not on the surface of I718 is likely due to the higher concentration of Cr and lower concentration of Fe in I625 compared to I718. Considering the ~5wt% of Fe in I625, it is suggested that the formation of the observed Fe rich spinel would rapidly lead to a depletion of Fe from the bulk material. It is postulated that the films formed on I625 are therefore less stable than those formed on I718, where Fe constitutes 19wt% of the alloy and CrO₄²⁻ was not observed after exposure to 527.5°C SCW.

The evolution of the hydroxide based film into the spinel oxide structures was confirmed using the O1s XPS spectra. The O1s spectra was fit with three peaks corresponding to oxide bonding, OH bonding, and adsorbed H₂O [35, 36]. The curve fit O1s spectra obtained from the surface of each of the I718 samples are shown in Figure 3a, similar results were obtained from XPS analysis of I625. The ratio of the O1s spectra attributed to oxide bonding compared to hydroxide bonding for each sample is shown in Figure 3b. The trend of an increase in oxide concentration and decrease in hydroxide concentration was observed with increasing temperature. This is evidence of the transformation of the Ni(OH)₂ film from the alloy surface, and the formation of an oxide based surface film after exposure to SCW.

3.2. Fully Developed Oxide Layer Characterization

3.2.1. Gravimetric Studies

The mass of all I625 and I718 coupons measured before and after exposure to SCW and USCW are presented in Table II. In exposure tests conducted for 24 hours in both SCW and USCW, I625 was observed to experience mass loss and had a greater percent change in mass when compared to I718. In exposure tests for 96 and 200 hours, the percent change in mass was greater for I718 when compared to I625. The mass change for coupons of I625 exposed to 600°C USCW for 96 hours compared to I718, expressed as a percent was 45% and when exposed for 200 hours was calculated to be 66%. For coupons exposed to 527.5°C SCW at exposure times of 96 and 200 hours, the percent mass change of I625 was found to be 30% and 35% of the percent mass change for I718.

3.2.2. X-ray Diffraction

XRD analysis was conducted on the longest duration exposure samples to observe the phases present in the most developed films of this study. The XRD patterns for I718 and I625 exposed to 527.5°C SCW and 600°C USCW for 200 hours are displayed in Figure 4. XRD patterns obtained from all surfaces of I625 and I718 contain features that could be attributed to the spinels NiFe_2O_4 , NiCr_2O_4 , and $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$, which were identified by JCPDS files 01-074-2081, 01-088-0108, and 01-078-3743, respectively. Each of the above spinels has an identical crystal structure that follows a pattern of $\text{A}^{2+}\text{B}^{3+}_2\text{O}^{2-}_4$, in which A and B are transition metal elements with a different valence. Each spinel has a nearly identical diffraction pattern, due to identical crystal structures but only differ in the spacing of specific crystal planes. Therefore it is difficult to conclude which specific spinel composition is present or absent on the surface as only minor shifts are observed between the separate phases, as indicated by the separate JCPDS files. In addition to the various spinels, Cr_2O_3 was observed on all surfaces analyzed, and was identified by JCPDS file 01-078-5443. These findings are in agreement with previous research, which has shown that NiFe_2O_4 , NiCr_2O_4 , and Cr_2O_3 are all present within the oxide layer structure that typically forms on Ni-based alloys when exposed to SCW [9, 31, 32].

3.2.3. Raman Spectroscopy

The Raman spectra obtained from the surfaces of all samples in this study are displayed in Figures 5 and 6. The most prominent feature that was observed on all samples was between $\sim 710\text{cm}^{-1}$ and 670cm^{-1} . As previously discussed, features in this range of Raman shift are attributed to the A_{1g} vibrational modes of the various Fe, Ni and Cr oxide spinels. These features

will be identified using the previous discussion of the Raman modes of spinel structures found in section 3.1.1.

The Raman spectra obtained from the surfaces of I625 subjected to the various conditions are displayed in Figure 5. These spectra exhibit a prominent feature at $\sim 702\text{cm}^{-1}$, which indicates NiFe_2O_4 and is observed on all I625 samples [26-32]. The A_{1g} features observed at $\sim 702\text{cm}^{-1}$ along with the absence of the previously identified secondary features in the spectra obtained from the surfaces of I625 samples exposed to 600°C USCW indicates some quantity of NiCr_2O_4 present in addition to NiFe_2O_4 . Raman spectra obtained from the surfaces of I625 exposed to 527.5°C SCW contain features at $\sim 702\text{cm}^{-1}$, 490cm^{-1} and 330cm^{-1} ; however features at 595 and 580cm^{-1} are absent from the spectra. This indicates that the oxide formed on the surface of I625 exposed to 527.5°C SCW is not pure NiFe_2O_4 , but is a mixed spinel with the formula $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$, where x is less than 2. The other prominent feature in the spectra obtained from the surface of I625 is observed at $\sim 553\text{cm}^{-1}$, which can be attributed to the presence of Cr_2O_3 [37, 38]. This feature appears to increase in intensity with the increasing exposure time when exposed to 527.5°C SCW. However, when it is exposed to USCW the feature is observed to be at its maximum when exposed for 96 hours, while a decreased intensity is observed on the sample exposed for 200 hours. For the spectrum obtained from the surface of I625 exposed to 600°C USCW for 200 hours, there was a shoulder peak detected at 850cm^{-1} . The feature at $\sim 850\text{cm}^{-1}$ is attributed to the presence of CrO_4^{2-} and is speculated to have formed in a similar manner discussed in section 3.1.1 [15-18].

The Raman spectra obtained from the surfaces of I718 subjected to the various experimental conditions are displayed in Figure 6. The most prominent feature in each spectrum is the characteristic Raman mode of NiFe_2O_4 which occurs at $\sim 702\text{cm}^{-1}$ on all samples with the

exception of the spectrum obtained from the surface of I718 exposed to 600°C USCW for 96 hours, on which this feature occurs at $\sim 710\text{cm}^{-1}$. This feature is still attributed to NiFe_2O_4 due to changes in the crystalline order that occurs on corrosion samples, as other authors have noted this feature can shift up to $\sim 13\text{cm}^{-1}$ above the reported 702cm^{-1} [26, 27]. The other features in all spectra obtained from the surfaces of I718 are observed at $\sim 553\text{cm}^{-1}$ for Cr_2O_3 , as well as 490cm^{-1} and 330cm^{-1} indicative of relatively pure NiFe_2O_4 [21, 25-28]. The spectra obtained from the surface of I718 exposed for 200 hours contained features between $\sim 600\text{cm}^{-1}$ and 550cm^{-1} indicating the presence of high purity NiFe_2O_4 . The observed features indicate no presence of Cr_2O_3 within the interaction depth associated with Raman spectroscopy. The presence of these Raman modes leads to the conclusion that NiFe_2O_4 is the prevalent species formed on the surface of I718 when exposed to SCW and USCW for 200 hours.

Based on the spectra shown in Figures 5 and 6, it can be ascertained that during the longest duration tests a surface film composed of NiFe_2O_4 formed on I718, while I625 formed a mixture of Cr_2O_3 and $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$. This is hypothesized to be a result of the increased Fe content in I718 (19wt%) when compared to I625 (5wt%), which favors the formation of an oxide layer that is primarily composed of Ni and Fe. Additionally, Raman spectroscopy of I625 demonstrated the presence of Cr oxides, namely Cr_2O_3 and the mixed spinel $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$.

3.2.4. X-ray Photoelectron Spectroscopy

XPS full range scans were used to identify the elements present on the surfaces of samples that were subjected to all the conditions tested. The spectra obtained from the surface of all I625 samples before and after 1 minute of sputtering are presented in Figures 7 and 8. The elements observed in detectable quantities on all surfaces studied before and after sputtering were nickel,

chromium, niobium, oxygen and carbon. However, it can be observed from Figures 9 and 10 that chromium was not observed on I718 exposed to SCW and USCW for 200 hours. This result indicates that no chromium was detected on the surface of I718 within the interaction depth of XPS, which is ~10nm. Based on this result and results from Figure 6, the surface film formed on I718 when exposed to SCW and USCW for 200 hours is deduced to be pure NiFe_2O_4 .

The composition of the surface films formed on I625 and I718 as determined from the wide scan spectra are provided in Tables III and IV, respectively. Compositions of I625 and I718 samples just after polishing to a 1 μm finish are also included for comparison. The compositions determined from on XPS spectra corroborate the Raman spectroscopy analysis. Based on Raman spectroscopy and XPS results, it can be inferred that the Cr content in the surface film generally decreases with increasing exposure time and increasing temperature. The exception to this trend occurred when I625 was exposed to 600°C USCW for 96 hours, which resulted in the largest concentration of Cr within the surface film. It is well known that composition calculated from XPS is not an accurate indicator of the composition of the surface film, as XPS only analyzes the top ~10nm, and that surface could vary significantly from the bulk. But the excellent correlation found between the composition obtained from XPS and the Raman intensity in this study indicates that the surface films may be more uniform than generally expected.

Figure 11 displays XPS narrow scans that are indicative of all elements of interest that were present on every sample, including; nickel, chromium, niobium and oxygen. The only exception was I718 samples exposed to SCW and USCW for 200 hours, in which chromium was not observed on the surface. These narrow scans are representative of the bonding state of the respective elements observed, however only one set is shown for the sake of brevity. The $\text{Ni}2\text{p}$ narrow scans before and after sputtering are displayed in Figure 11a(i) and 11a(ii), respectively.

The prominent feature at ~854.8 eV within the spectrum displayed in Figure 11a(i) can be attributed to the spinel complex $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$ [39]. Other Ni compounds are known to occur at this binding energy, such as NiOOH , however this compound was not identified using XRD or Raman spectroscopy [39]. As $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$ and NiFe_2O_4 were the only nickel compounds identified using the corroborative spectroscopic technique, it is hypothesized the $\text{Ni}2p$ spectral features shown in Figure 11a(i) are that of $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$. The $\text{Ni}2p$ spectrum obtained after sputtering is displayed in Figure 11a(ii) and contains features attributed to the presence of $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$ at ~854.8eV and Ni metal at ~852.6 eV. The occurrence of metallic Ni should not be mistakenly interpreted as being due to a thin oxide film, but is rather due to ion-induced reduction of NiO_x to metallic Ni, which has been well documented [40, 41]. Additional evidence for the presence of $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$ can be observed in Figure 11b, which provides the $\text{Fe}2p_{3/2}$ spectrum. Based on the results from the Raman spectroscopy which indicated NiFe_2O_4 as the only Fe containing compound on the surface, it is hypothesized that XPS results also indicate that NiFe_2O_4 is the only Fe containing compound formed. This is supported by previously published results that used similar fitting parameters [42]. The $\text{Nb}3d$ spectrum presented in Figure 11c is indicative of Nb_2O_5 [43-45]. Niobium oxide was detected on the surfaces of all samples by XPS. The $\text{Cr}2p$ spectrum is shown in Figure 11d indicates the presence of Cr_2O_3 , and was fit using previously published fitting parameters [37, 42, 46-50]. These parameters include fitting the $\text{Cr}2p_{3/2}$ and $\text{Cr}2p_{1/2}$ spectra with three peaks each to identify Cr_2O_3 [37, 42, 46-50]. Lastly, the spectrum for the $\text{O}1s$ line is displayed in Figure 11e and has been fit using the previously discussed fitting methodology for determining the presence of oxide, hydroxide, and adsorbed water [35, 36].

In Figure 12, it can be observed that the ratio of oxide to hydroxide O1s bonding obtained from the surface of all I625 and I718 samples is greater than 2. Based on previous statements made in section 3.1.1, this indicates that the hydroxide film has been removed from the surface.

4. Discussion

Previous research has reported that Ni-based alloys, including I625 and I718, exhibit minimal mass change upon exposure to SCW, and even noted weight loss for tests conducted for shorter durations [9, 31, 32, 51]. Additionally, previous gravimetric studies conducted on Ni-based alloys and austenitic steels have reported that Fe based materials are less resistant to oxidation when exposed to supercritical water [9, 31, 32, 35, 36, 51]. Therefore, in line with the observation in this study, the mass gain for I718 would be expected to be higher than I625 as a result of the elevated Fe content found in I718 when compared to I625 (19% for I718 and 5% for I625) [9, 31, 32, 35, 36, 51].

In this study, the characterization of the oxide layer indicated an amalgamation of Cr_2O_3 , Nb_2O_5 , and $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$. The compound $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$ was found to have an x equal to 2 on the surfaces of I718. Spectroscopic analysis obtained from the surfaces of I625 indicates that x is less than 2 in the compound $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$, indicating a mixed spinel that contains both Fe and Cr. This correlates well with other studies that have been conducted on the corrosion of Ni-based alloys in SCW, which have demonstrated that a layered oxide structure is formed consisting of an inner Cr rich layer, composed of Cr_2O_3 and $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$, and an outer layer composed of NiFe_2O_4 and NiO [28, 31, 32, 51-53]. NiO had been identified on the surface of I625 in studies with exposure times longer than 500 hours in SCW with a dissolved oxygen content of 2ppm [31, 32]. The lack of observable quantities of NiO in the current work is the most significant discrepancy between

this study and previous reports. This is suspected to be due to either the significant short exposure time of 200 hours and less in this study, or the decrease in dissolved oxygen content which was maintained below 50ppb [9, 31, 32, 51]. In this study, the XPS analysis of the oxide layer indicated that Nb_2O_5 formed on the surface of all the samples tested. In research performed by Allen *et al.*, in shorter term exposure testing in deaerated SCW (<200 hours and <25ppb O_2) Nb_2O_5 precipitates were detected on the surface of I625, and noted that this resulted in mass loss due to galvanic coupling [31, 32]. In this study it was observed that I625 exhibited mass loss when exposed to SCW and USCW for 24 hours. Based on what other studies have observed, it is hypothesized that this is a result of Nb_2O_5 formations on the surface [31, 32]. Furthermore, while the greater amount of Fe in I718 leads to consistent mass gain, it is speculated that the formation of a fully formed oxide layer could be preventing galvanic coupling between Nb_2O_5 and the base material. It is speculated the thicker oxide layer formed due to the elevated Fe content in I718 reduces the probability of spallation. Cr_2O_3 was observed to form on all surfaces of I718 and I625 exposed to SCW and USCW for longer than 24hours, however it was not observed on any samples exposed for 2 hours. It is observed that time is the main factor in the development and alteration to the surface chemistry observed in the current work. This is based on the fully developed oxide layer characterization, which indicated Cr_2O_3 formed on all surfaces of I625 and I718 exposed for at least 24 hours.

5. Conclusions

In the study of evolution of the as-received surface it was found that a protective $\text{Ni}(\text{OH})_2$ and CrO_4^{2-} film, also containing $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$, is present on the surface of both Inconel 625 and 718 after exposure to subcritical water at 325°C. The surface film identified at 325°C, degraded when exposed to 425°C SCW for 2 hours and formed a complex $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$ spinel on I625 and I718.

After exposure to 527.5°C SCW for 2 hours, the surfaces on I718 and I625 were characterized as NiFe_2O_4 . In addition to NiFe_2O_4 , CrO_4^{2-} was observed on the surface of I625 exposed to 527.5°C SCW for 2 hours.

During the fully developed oxide layer characterization, it was observed that I718 exhibited mass gain for all conditions tested, with the exception of sample 2 exposed to 527.5°C for 24 hours. However, it was observed that I625 averaged weight loss for all samples exposed for 24 hours, which could indicate destruction of the oxide film. Oxides identified on the surface of I718 included Nb_2O_5 , Cr_2O_3 , and NiFe_2O_4 , while the oxide layer on the surface of I625 was found to be composed of $\text{NiFe}_x\text{Cr}_{2-x}\text{O}_4$, Nb_2O_5 and Cr_2O_3 . A schematic for the oxide structures at each temperature point is displayed in Figure 13. The changes in the oxide structure are attributed to the differences in the percentage of Fe present within the given alloy (I718 contains 19% Fe while I625 contains 5%). It is postulated that the increase in Fe content of I718 leads to a more uniform layer based on composition analysis and gravimetric studies. Based on the results presented it appears the thicker oxide layer prevents the galvanic couple between Nb_2O_5 and the base material.

Acknowledgements

This study was supported by Nuclear Regulatory Commission (NRC) under awards NRC-38-10-949 and NRC-HQ-11-G-38-0039 and the Department of Energy (DOE) under contracts DE-NE0000454 and DE-NE0008236. D.R. and A.M. are supported under a Fellowship program funded by NRC. Ms. Nancy Hebron-Isreal and Mr. Kenny Osborne serve as the program managers for the NRC and DOE awards, respectively.

References

- [1] A Technology Roadmap for Generation IV Nuclear Energy Systems, Report No. GIF002-00, December 1, 2002., in: nuclear.gov.
- [2] J. Phillips, J. Wheeldon, Economic Analysis of Advanced Ultra-Supercritical Pulverized Coal Power Plants: A Cost-Effective CO₂ Emission Reduction Option, in: Advances in Materials Technology for Fossil Power Plants, ASM International, Santa Fe, New Mexico, USA, 2011.
- [3] Improving Efficiencies in Coal Power Plants, in: <http://www.worldcoal.org/coal-the-environment/coal-use-the-environment/improving-efficiencies/>.
- [4] K. Dobashi, A. Kimura, Y. Oka, S. Koshizuka, Conceptual design of a high temperature power reactor cooled and moderated by supercritical light water, Annals of Nuclear Energy, 25 (1998) 487-505.
- [5] S. Zhao, X. Xie, G.D. Smith, S.J. Patel, The corrosion of INCONEL alloy 740 in simulated environments for pulverized coal-fired boiler, Materials Chemistry and Physics, 90 (2005) 275-281.
- [6] A.F. Rowcliffe, L.K. Mansur, D.T. Hoelzer, R.K. Nanstad, Perspectives on radiation effects in nickel-base alloys for applications in advanced reactors, Journal of Nuclear Materials, 392 (2009) 341-352.
- [7] J. Hou, Q.J. Peng, K. Sakaguchi, Y. Takeda, J. Kuniya, T. Shoji, Effect of hydrogen in Inconel Alloy 600 on corrosion in high temperature oxygenated water, Corrosion Science, 52 (2010) 1098-1101.
- [8] W. Kuang, X. Wu, E.-H. Han, Influence of dissolved oxygen concentration on the oxide film formed on Alloy 690 in high temperature water, Corrosion Science, 69 (2013) 197-204.
- [9] T.R. Allen, Y. Chen, X. Ren, K. Sridharan, L. Tan, G.S. Was, E. West, D. Guzonas, 5.12 - Material Performance in Supercritical Water, in: R.J.M. Konings (Ed.) Comprehensive Nuclear Materials, Elsevier, Oxford, 2012, pp. 279-326.
- [10] H. Hirano, H. Takaku, T. Kurosawa, The relationship between the characteristics of oxide film and stress corrosion susceptibility of Ni-Cr-Fe alloy in high temperature water, Corrosion Science, 31 (1990) 557-562.
- [11] M. Marciuš, M. Ristić, M. Ivanda, S. Musić, Formation and microstructure of nickel oxide films, Journal of Alloys and Compounds, 541 (2012) 238-243.
- [12] S. Yesodharan, Supercritical water oxidation: An environmentally safe method for the disposal of organic wastes, Corrosion Science, 82 (2002) 1112-1122.
- [13] D.A. Guzonas, W.G. Cook, Cycle chemistry and its effect on materials in a supercritical water-cooled reactor: A synthesis of current understanding, Corrosion Science, 65 (2012) 48-66.
- [14] G. Stein-Brzozowska, D.M. Flórez, J. Maier, G. Scheffknecht, Nickel-base superalloys for ultra-supercritical coal-fired power plants: Fireside corrosion. Laboratory studies and power plant exposures, Fuel, 108 (2013) 521-533.

- [15] T. Chen, H. John, J. Xu, Q. Lu, J. Hawk, X. Liu, Influence of surface modifications on pitting corrosion behavior of nickel-base alloy 718. Part 1: Effect of machine hammer peening, *Corrosion Science*, 77 (2013) 230-245.
- [16] T. Jabs, P. Borthen, H.H. Strehblow, X-Ray Photoelectron Spectroscopic Examinations of Electrochemically Formed Passive Layers on Ni-Cr Alloys, *Journal of The Electrochemical Society*, 144 (1997) 1231-1243.
- [17] P. Kritzer, N. Boukis, E. Dinjus, Review of the Corrosion of Nickel-Based Alloys and Stainless Steels in Strongly Oxidizing Pressurized High-Temperature Solutions at Subcritical and Supercritical Temperatures, *Corrosion*, 56 (2000) 1093-1104.
- [18] X. Zhang, D.W. Shoesmith, Influence of temperature on passive film properties on Ni–Cr–Mo Alloy C-2000, *Corrosion Science*, 76 (2013) 424-431.
- [19] J.D. Ramsey, R.L. McCreery, In Situ Raman Microscopy of Chromate Effects on Corrosion Pits in Aluminum Alloy, *Journal of The Electrochemical Society*, 146 (1999) 4076-4081.
- [20] G.C. Allen, M. Paul, Chemical Characterization of Transition Metal Spinel-Type Oxides by Infrared Spectroscopy, *Applied Spectroscopy*, 49 (1995) 451-458.
- [21] B. Hosterman, Raman Spectroscopic Study of Solid Solution Spinel Oxides, in, University of Nevada, Las Vegas, 2011.
- [22] J. Kim, K.J. Choi, C.B. Bahn, J.H. Kim, In situ Raman spectroscopic analysis of surface oxide films on Ni-base alloy/low alloy steel dissimilar metal weld interfaces in high-temperature water, *Journal of Nuclear Materials*, 449 (2014) 181-187.
- [23] J.H. Kim, I.S. Hwang, Development of an in situ Raman spectroscopic system for surface oxide films on metals and alloys in high temperature water, *Nuclear Engineering and Design*, 235 (2005) 1029-1040.
- [24] J.E. Maslar, W.S. Hurst, W.J. Bowers, J.H. Hendricks, In Situ Raman Spectroscopic Investigation of Stainless Steel Hydrothermal Corrosion, *Corrosion*, 58 (2002) 739-747.
- [25] M. da Cunha Belo, M. Walls, N.E. Hakiki, J. Corset, E. Picquenard, G. Sagon, D. Noël, Composition, structure and properties of the oxide films formed on the stainless steel 316L in a primary type PWR environment, *Corrosion Science*, 40 (1998) 447-463.
- [26] M.N. Iliev, D. Mazumdar, J.X. Ma, A. Gupta, F. Rigato, J. Fontcuberta, Monitoring B-site ordering and strain relaxation in NiFe₂O₄ epitaxial films by polarized Raman spectroscopy, *Physical Review B*, 83 (2011) 014108.
- [27] J.E. Maslar, W.S. Hurst, W.J.B. Jr., J.H. Hendricks, In Situ Raman Spectroscopic Investigation of Stainless Steel Hydrothermal Corrosion, *Corrosion*, 58 (2002) 739-747.
- [28] J. Landon, E. Demeter, N. İnoğlu, C. Keturakis, I.E. Wachs, R. Vasić, A.I. Frenkel, J.R. Kitchin, Spectroscopic Characterization of Mixed Fe–Ni Oxide Electrocatalysts for the Oxygen Evolution Reaction in Alkaline Electrolytes, *ACS Catalysis*, 2 (2012) 1793-1801.
- [29] S.E. Ziemniak, M. Hanson, Corrosion behavior of NiCrMo Alloy 625 in high temperature, hydrogenated water, *Corrosion Science*, 45 (2003) 1595-1618.
- [30] M. Sun, X. Wu, Z. Zhang, E.-H. Han, Analyses of oxide films grown on Alloy 625 in oxidizing supercritical water, *The Journal of Supercritical Fluids*, 47 (2008) 309-317.

- [31] X. Ren, K. Sridharan, T.R. Allen, Corrosion Behavior of Alloys 625 and 718 in Supercritical Water, *Corrosion*, 63 (2007) 603-612.
- [32] L. Tan, X. Ren, K. Sridharan, T.R. Allen, Corrosion behavior of Ni-base alloys for advanced high temperature water-cooled nuclear plants, *Corrosion Science*, 50 (2008) 3056-3062.
- [33] M. Sun, X. Wu, Z. Zhang, E. Han, Analyses of oxide films grown on Alloy 625 in oxidizing supercritical water, *The Journal of Supercritical Fluids*, 47 (2008) 309-317.
- [34] J. Bischoff, A.T. Motta, Oxidation behavior of ferritic–martensitic and ODS steels in supercritical water, *Journal of Nuclear Materials*, 424 (2012) 261-276.
- [35] D. Rodriguez, D. Chidambaram, Oxidation of stainless steel 316 and Nitronic 50 in supercritical and ultrasupercritical water, *Applied Surface Science*, 347 (2015) 10-16.
- [36] D. Rodriguez, A. Merwin, D. Chidambaram, On the oxidation of stainless steel alloy 304 in subcritical and supercritical water, *Journal of Nuclear Materials*, 452 (2014) 440-445.
- [37] H. Asteman, J.E. Svensson, L.G. Johansson, M. Norell, Indication of Chromium Oxide Hydroxide Evaporation During Oxidation of 304L at 873 K in the Presence of 10% Water Vapor, *Oxidation of Metals*, 52 (1999) 95-111.
- [38] I.E. Wachs, Raman and IR studies of surface metal oxide species on oxide supports: Supported metal oxide catalysts, *Catalysis Today*, 27 (1996) 437-455.
- [39] M.C. Biesinger, B.P. Payne, L.W.M. Lau, A. Gerson, R.S.C. Smart, X-ray photoelectron spectroscopic chemical state quantification of mixed nickel metal, oxide and hydroxide systems, *Surface and Interface Analysis*, 41 (2009) 324-332.
- [40] N.S. McIntyre, D.G. Zetaruk, Quantitative analysis of thin oxide films using x-ray photoelectron spectroscopy and rastered ion bombardment, *Journal of Vacuum Science and Technology*, 14 (1977) 181-185.
- [41] A.R. González-Elipé, R. Alvarez, J.P. Holgado, J.P. Espinos, G. Munuera, J.M. Sanz, An XPS study of the Ar⁺-induced reduction of Ni²⁺ in NiO and Ni-Si oxide systems, *Applied Surface Science*, 51 (1991) 19-26.
- [42] M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A.R. Gerson, R.S.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni, *Applied Surface Science*, 257 (2011) 2717-2730.
- [43] G.C. Allen, S.J. Harris, J.A. Jutson, J.M. Dyke, A study of a number of mixed transition metal oxide spinels using X-ray photoelectron spectroscopy, *Applied Surface Science*, 37 (1989) 111-134.
- [44] F. Garbassi, J.C.J. Bart, G. Petrini, XPS study of tellurium—niobium and tellurium—tantalum oxide systems, *Journal of Electron Spectroscopy and Related Phenomena*, 22 (1981) 95-107.
- [45] E. Heracleous, A.A. Lemonidou, Ni–Nb–O mixed oxides as highly active and selective catalysts for ethene production via ethane oxidative dehydrogenation. Part I: Characterization and catalytic performance, *Journal of Catalysis*, 237 (2006) 162-174.

- [46] M.C. Biesinger, C. Brown, J.R. Mycroft, R.D. Davidson, N.S. McIntyre, X-ray photoelectron spectroscopy studies of chromium compounds, *Surface and Interface Analysis*, 36 (2004) 1550-1563.
- [47] P. Stefanov, D. Stoychev, M. Stoycheva, T. Marinova, XPS and SEM studies of chromium oxide films chemically formed on stainless steel 316 L, *Materials Chemistry and Physics*, 65 (2000) 212-215.
- [48] M.C. Bernard, A. Hugot-Le Goff, B.V. Thi, S. Cordoba de Torresi, Electrochromic Reactions in Manganese Oxides: I . Raman Analysis, *Journal of The Electrochemical Society*, 140 (1993) 3065-3070.
- [49] J. Jiang, A. Kucernak, Electrochemical supercapacitor material based on manganese oxide: preparation and characterization, *Electrochimica Acta*, 47 (2002) 2381-2386.
- [50] C.M. Julien, M. Massot, C. Poinsignon, Lattice vibrations of manganese oxides: Part I. Periodic structures, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 60 (2004) 689-700.
- [51] T. Fujii, K. Sue, S.-i. Kawasaki, Effect of pressure on corrosion of Inconel 625 in supercritical water up to 100 MPa with acids or oxygen, *The Journal of Supercritical Fluids*, 95 (2014) 285-291.
- [52] S.I. Cordoba-Torresi, A. Hugot-Le Goff, S. Joiret, Electrochromic Behavior of Nickel Oxide Electrodes: II . Identification of the Bleached State by Raman Spectroscopy and Nuclear Reactions, *Journal of The Electrochemical Society*, 138 (1991) 1554-1559.
- [53] D.A. Guzonas, J. Wills, T. Do, J. Michel, Corrosion of candidate materials for use in a supercritical water CANDU reactor, in: C.N. Society (Ed.) 13th International conference on environmental degradation of materials in nuclear, 2007.

Figure 1 Raman spectra of Inconel 625 obtained from samples that were analyzed after exposure to subcritical water at 325°C, and supercritical water at 425°C and 527.5°C. Instrument artifacts denoted by *.

Figure 2 Raman spectra of Inconel 718 obtained from samples after exposure to subcritical water at 325°C, and supercritical water at 425°C and 527.5°C. Instrument artifacts denoted by *.

Figure 3: a) Curve fit O1s spectra of the I718 surfaces after exposure to subcritical water at 325°C (left), and supercritical water at 425°C (middle), and 527.5°C (right). The increasing ratio of oxide to hydroxide with increasing solution temperature is evident. b) The ratio of the portion of the O1s XPS spectrum attributed to oxide bonding to hydroxide bonding on I625 and I718 surfaces subjected to exposure subcritical water at 325°C, and supercritical water at 425°C and 527.5°C.

Figure 4: XRD spectra for I625 and I718 samples that were exposed to 527.5 °C supercritical water and 600 °C ultrasupercritical water for 200 hours.

Figure 5: Raman spectra for all I625 samples exposed to supercritical and ultrasupercritical water. With each spectrum normalized to the highest intensity feature.

Figure 6: Raman spectra for all I718 samples exposed to supercritical and ultrasupercritical water. With each spectrum normalized to the highest intensity feature.

Figure 7: XPS spectra for I625 before sputtering exposed to supercritical and ultrasupercritical water. The features observed with their approximate binding energies are as follows: Nb3d at 207eV, C1s at 284eV, O1s at 530eV, Ni2p at 860eV, Cr2p at 570 eV and Ni KLL auger series from 650-800eV. With each spectrum normalized to the highest intensity feature.

Figure 8: XPS spectra for I625 after sputtering exposed to supercritical and ultrasupercritical water. The features observed with their approximate binding energies are as follows: Nb3d at 207eV, C1s at 284eV, O1s at 530eV, Ni2p at 860eV, Cr2p at 570 eV and Ni KLL auger series from 650-800eV. With each spectrum normalized to the highest intensity feature.

Figure 9: XPS spectra for I718 before sputtering exposed to supercritical and ultrasupercritical water. The features observed with their approximate binding energies are as follows: Nb3d at 207eV, C1s at 284eV, O1s at 530eV, Ni2p at 860eV, Cr2p at 570 eV and Ni KLL auger series from 650-800eV. With each spectrum normalized to the highest intensity feature.

Figure 10: XPS spectra for I718 after sputtering exposed to supercritical and ultrasupercritical water. The features observed with their approximate binding energies are as follows: Nb3d at 207eV, C1s at 284eV, O1s at 530eV, Ni2p at 860eV, Cr2p at 570 eV and Ni KLL auger series from 650-800eV. With each spectrum normalized to the highest intensity feature.

Figure 11: XPS scans for a) Ni2p spectra before (i) and after (ii) sputtering b) Fe2p_{3/2} c) Nb3d d) Cr2p e) O1s. These scans are representative of all samples.

Figure 12: The ratio of the portion of the O1s XPS spectrum attributed to oxide bonding to hydroxide bonding on I625 and I718 surfaces exposed to 527.5°C supercritical water and 600°C ultrasupercritical water for 24, 96 and 200 hours.

Figure 13: Schematic description of the surface films formed on Inconel 625 and 718 when exposed to subcritical water at 325°C and supercritical water at 425, 527.5 and 600°C.

Figure 1 Raman spectra of Inconel 625 obtained from samples that were analyzed after exposure to subcritical water at 325°C, and supercritical water at 425°C and 527.5°C. Instrument artifacts denoted by *.

Figure 2 Raman spectra of Inconel 718 obtained from samples after exposure to subcritical water at 325°C, and supercritical water at 425°C and 527.5°C. Instrument artifacts denoted by *.

Figure 3: a) Curve fit O 1s spectra of the I718 surfaces after exposure to subcritical water at 325°C (left), and supercritical water at 425°C (middle), and 527.5°C (right). The increasing ratio of oxide to hydroxide with increasing solution temperature is evident. b) The ratio of the portion of the O 1s XPS spectrum attributed to oxide bonding to hydroxide bonding on I625 and I718 surfaces subjected to exposure subcritical water at 325°C, and supercritical water at 425°C and 527.5°C.

Figure 4: XRD spectra for I625 and I718 samples that were exposed to 527.5 °C supercritical water and 600 °C ultrasupercritical water for 200 hours.

Figure 5: Raman spectra for all I625 samples exposed to supercritical and ultrasupercritical water. With each spectrum normalized to the highest intensity feature.

Figure 6: Raman spectra for all I718 samples exposed to supercritical and ultrasupercritical water. With each spectra normalized to the highest intensity feature.

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Figure 11: XPS scans for a) Ni_{2p} spectra before (i) and after (ii) sputtering b) Fe_{2p_{3/2}} c) Nb_{3d} d) Cr_{2p} e) O_{1s}. These scans are representative of all samples.

Figure 12: The ratio of the portion of the O 1s XPS spectrum attributed to oxide bonding to hydroxide bonding on I625 and I718 surfaces exposed to 527.5°C supercritical water and 600°C ultrasupercritical water for 24,96 and 200 hours.

Figure 13: Schematic description of the surface films formed on Inconel 625 and 718 when exposed to subcritical water at 325°C and supercritical water at 425, 527.5 and 600°C.

Table I. Composition of I625 and I718 in weight %

Table II: Recorded mass, mass change, percent change in mass and mass change per unit area of samples before and after exposure.

Table III: Composition of surface film formed on I625 as determined from XPS after 1 minute of sputtering.

Table IV: Composition of surface film formed on I718 as determined from XPS after 1 minute of sputtering.

Table I. Composition of I625 and I718 in weight %

Alloy	Ni	Cr	Fe	Mo	Nb	Mn	Cu	Al	Ti	Si
I625	58	20-23	5	8.0-10	3.15-4.15	0.5		0.4	0.4	0.5
I718	50-55	17-21	19	2.8-3.3	4.75-5.5	0.35	0.2-0.8	0.65-1.15	0.3	0.35

Table II: Recorded mass, mass change, percent change in mass and mass change per unit area of samples before and after exposure.

		527.5°C						600°C					
Time(hours)		24		96		200		24		96		200	
Mass (g)		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
I625	Before	14.3223	14.4709	14.5348	14.5852	14.5577	14.5432	14.5486	14.5352	14.5083	14.3492	14.5838	14.6852
	After	14.3221	14.467	14.5349	14.5857	14.5584	14.5437	14.5471	14.5353	14.5095	14.35	14.5848	14.687
	Change	-0.0002	-0.0039	0.0001	0.0005	0.0007	0.0005	-0.0015	0.0001	0.0012	0.0008	0.001	0.0018
	Average % Change	-0.0142		0.0021		0.0041		-0.0055		0.0069		0.0096	
	Average Mass Change Per Area (mg/cm ²)	-0.15		0.02		0.04		-0.05		0.07		0.10	
I718	Before	13.8017	13.8175	13.6067	13.5851	13.8116	13.4634	13.6791	13.4335	13.8352	13.772	13.5516	13.4927
	After	13.8172	13.802	13.6074	13.5863	13.8134	13.4648	13.6797	13.4341	13.8377	13.7737	13.5538	13.4944
	Change	0.0155	-0.0155	0.0007	0.0012	0.0018	0.0014	0.0006	0.0006	0.0025	0.0017	0.0022	0.0017
	Average % Change	0		0.007		0.0117		0.0044		0.0152		0.0144	
	Average Mass Change Per Area (mg/cm ²)	0.00		0.07		0.12		0.04		0.16		0.15	

Table III: Composition of surface film formed on I625 as determined from XPS after 1 minute of sputtering.

Conditions	Element (atomic %)					
	Ni	Fe	Cr	Nb	Mo	O
Polished no exposure	37.4	0	16.3	0.6	3.6	42.1
527.5 °C 24 hours	23.5	6.1	10.1	0.4	0	59.9
527.5 °C 96 hours	19.6	6.8	11.1	0.9	0	61.7
527.5 °C 200 hours	26.3	6.6	6.4	1.4	0	59.3
600 °C 24 hours	15.6	7.1	5.7	1	0	70.6
600 °C 96 hours	7.5	3.9	22.7	2.1	0	63.8
600 °C 200 hours	22.5	6	8	1.7	0	61.8

Table IV: Composition of surface film formed on I718 as determined from XPS after 1 minute of sputtering

Conditions	Element (atomic %)					
	Ni	Fe	Cr	Nb	Mo	O
Polished no exposure	24.7	0	15.5	2.1	1.2	56.5
527.5 °C 24 hours	10.6	11.3	9.3	0.2	0	68.5
527.5 °C 96 hours	10.5	8.9	10.3	0.9	0	69.3
527.5 °C 200 hours	17.7	12.4	0	0.4	0	69.6
600 °C 24 hours	13.6	10.5	5.2	0.5	0	70.1
600 °C 96 hours	19.9	12.2	2.4	0.7	0	64.9
600 °C 200 hours	23.8	10.2	0	1	0	65.1