Oxidation of Stainless Steel 316 and Nitronic 50 in Supercritical and Ultrasupercritical Water

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Abstract

Corrosion of stainless steel 316 and Nitronic 50 exposed to supercritical and ultrasupercritical water was studied as a function of temperature and exposure time. Post-exposure surface analysis was performed using Raman and X-ray photoelectron spectroscopies to determine the chemistry of the oxides formed as a result of the exposure. When exposed to supercritical water, Nitronic 50 and stainless steel 316 were observed to have similar weight gains; however, stainless steel 316 was found to gain less weight than Nitronic 50 in exposure tests performed in ultrasupercritical water. Stainless steel 316 developed surface films primarily composed of iron oxides, while the surface of Nitronic 50 contained a mixture of iron, chromium and manganese oxides. Based on these analyses, the differences in weight gain and oxidation characteristics of the two materials are attributed to the higher concentration of Cr and Mn in Nitronic 50 compared to stainless steel 316.

Keywords: Austenitic, Corrosion, Raman, XPS, and Oxide

Introduction

Traditional nuclear and coal power plants harvest roughly one third of the potential energy from their respective fuel sources [1]. Increasing the outlet temperature of these power plants will result in an increase in energy conversion efficiency [2]. To increase their efficiency, coal fired power plants currently use both supercritical water (SCW), classified as water above 375°C and 22.1MPa, and ultrasupercritical water (USCW), defined by an operating temperature and pressure above 590°C and 25MPa [1]. While the nuclear industry has yet to make use of supercritical water on a commercial scale, the supercritical water reactor (SCWR) is an advanced, generation IV, reactor design which is proposed to use SCW as a coolant. The SCWR would have similarities to traditional nuclear plant coolant loops, except for the fact that the temperature and pressure would be above that of the critical point of water. By employing a supercritical fluid as the reactor coolant, the plant efficiency can be increased to ~45%; in comparison, traditional reactors currently operate at ~33% efficiency [3, 4].

While there are similarities in plant design between the SCWR and current commercial reactors, the elevated temperature and alternate coolant phase requires that candidate materials be evaluated under these more extreme conditions. Extensive studies have been performed that describe the formation of oxide layers on austenitic steels in supercritical water [4-13]. It has been observed that oxide films form on austenitic steels in the following manner; first a porous chromium rich spinel (FeCr_2O_4) and Cr_2O_3 form on the surface of the alloy, allowing the diffusion of iron from the surface of the alloy through the film. The diffusing iron then forms magnetite (Fe_3O_4), which is subsequently oxidized to form hematite (Fe_2O_3) on the outermost surface. The rate of growth for hematite and magnetite can become problematic in high temperature water due to the increased likelihood of spallation at elevated temperatures and longer service life [4-8, 14-16]. However, literature review suggests that alloys containing greater than 2.5% Mn had not been previously investigated [4-13]. This study investigates the oxidation products formed on the austenitic steel, Nitronic 50 (N50), and compares it to stainless steel alloy 316 (SS316) in SCW and USCW. N50 was investigated in comparison to SS316 due to its higher concentration of Cr and Mn, that results in higher yield strength and better corrosion resistance compared to SS316 [17-19]. SS316 was chosen for comparison due to its frequent use in the nuclear and coal industries and is generally considered the benchmark

standard [20]. Experimentation was conducted using the supercritical water loop (SCWL) facility at the University of Nevada, Reno.

Experimental

Materials

N50 and SS316 used in this study were purchased from HP alloys and McMaster-Carr, respectively. The composition of both alloys is given in Table I. All Samples were laser cut into coupons measuring 2.2 by 2.5cm. Samples were polished to a 1 micron finish prior to exposure testing in the SCWL.

Operation of Supercritical Water Loop

The pressure in the supercritical water loop was maintained at 27MPa during all experiments. Material oxidation was studied at test solution temperatures of 530 and 600°C. Samples were exposed to these temperatures for 24 and 96 hours. Experiments were conducted using duplicate samples at two temperature points within the autoclave with four samples immersed at once. The temperature was monitored using a thermocouple with multiple sampling points that was supplied by Omega Engineering Incorporated. The areas where the samples were placed fluctuated by ± 0.5 °C once the system was operating at steady state. The SCWL test solution was 18M Ω deionized water that was continuously deaerated with nitrogen to maintain the dissolved oxygen at less than 50ppb.

Post Exposure Analysis

After removal from the autoclave, each sample was dried in a low vacuum chamber for 24 hours. An Ohaus Adventurer SL model AS214 scale with a resolution of 100 μ g was used to measure the mass of samples before and after exposure to the conditions of each experiment. A Thermo Scientific DXR Raman microscope was used to characterize the Raman vibrational modes of the surface films using a 532nm laser with 10mW power. A 2-d mapping technique was used to characterize the surface over an 0.25mm² area with an individual spot diameter of 0.7 μ m, and a 100 μ m step size in both x and y. Raman spectra were recorded for 25 unique spots, each spot utilizing 32 exposures at an exposure time of 5 seconds. The spectra from these

25 spots were then averaged to obtain a spectrum that was representative of 0.25mm² area of analysis. X-ray photoelectron spectroscopy (XPS) was performed using a PHI model 5600 spectrometer fitted with a monochromatic Al X-ray source with an 800µm diameter spot size. Samples were analyzed prior to sputtering and after 1 minute of argon ion sputtering. The spectrometer was calibrated to the Ag 3d_{5/2} line at 368.3±0.05eV. Spectra were charge corrected using the adventitious C 1s line at 284.6eV. The spectra were subjected to 5 point smoothing and peak fit using SDP v4.6 software purchased from XPS International.

Results

Weight Gain

The mass of all SS316 and N50 samples measured before and after exposure to SCW and USCW are given in Table II. It can be observed that all samples gained mass under every condition studied. After exposure to 530°C SCW, the mass changes in the two alloys were similar. However, N50 averaged slightly higher mass increase than SS316 after exposure to USCW at 600°C. After 24 hours, the ratio of the mass change observed in USCW conditions to that observed in SCW conditions was determined to be 2.35 for SS316 and 2.92 for N50. For the samples exposed for 96 hours, the ratio of the mass change observed in USCW conditions to that observed in SCW conditions was determined to be 2.0 for SS316 and 2.48 for N50. So, the mass increase was always found to be at least two fold or larger in USCW conditions when compared to SCW conditions for both alloys. Furthermore, mass increase for N50 was found to be more than that for SS316 under USCW conditions. These results suggest that either the kinetics of oxidation and/or the stability of the oxides formed as a result of exposure, is dependent on alloy composition.

Raman Spectroscopy

The Raman spectra of the surfaces of SS316 subjected to the various conditions are displayed in Figure 1. These spectra are characterized by a feature between ~667 and 685cm⁻¹. Features in this range of Raman shift are attributed to the A_{1g} vibrational mode of Fe₃O₄ at ~667cm⁻¹ and FeCr₂O₄ at ~685cm⁻¹ [15, 21-26]. The feature at ~677cm⁻¹ is between the known wavenumbers

for FeCr_2O_4 and Fe_3O_4 indicating a mix of the two oxides [21-26]. The prominent feature of the spectra for all USCW SS316 samples is observed at $\sim 667\text{cm}^{-1}$, indicating that the dominant species present on SS316 as a result of exposure to USCW is Fe_3O_4 . The other prominent feature in the spectrum for SS316 exposed to USCW for 24 hours, observed at $\sim 553\text{cm}^{-1}$, is attributed to Cr_2O_3 [27-30]. The spectrum obtained from the samples exposed to 530°C SCW for 96 hours did exhibit features that were different from the other three samples within the set, with features observed at ~ 677 , 553 and 460cm^{-1} . While the feature at $\sim 553\text{cm}^{-1}$ appears to demonstrate characteristics of both Cr_2O_3 and FeCr_2O_4 modes of vibration [27-31]. The Raman feature at $\sim 460\text{cm}^{-1}$ is associated with magnon excitation in magnetite [26, 32]. As stated previously, the formation of Fe_3O_4 , FeCr_2O_4 and Cr_2O_3 on SS316 after exposure to SCW agrees with previous reports [4-13].

The Raman spectra of the surfaces of N50 subjected to the various experimental conditions contain three primary features, and are displayed in Figure 2. The shoulders on the higher wavenumber side of the spectra are characteristic of Fe_3O_4 $\sim 670\text{cm}^{-1}$ and FeCr_2O_4 spinel structures $\sim 685\text{cm}^{-1}$. The features observed at $\sim 625\text{cm}^{-1}$ and 610cm^{-1} in Figure 2 are attributed to the Mn compounds, Mn_2O_3 and MnCr_2O_4 [27-30, 33-35]. N50 samples exposed to SCW for 24 hours and USCW for 96 hours were found to have the constituent Mn_2O_3 form on the surface, while MnCr_2O_4 formed on the surface of N50 exposed to SCW for 96 hours and USCW for 24 hours. The final feature was observed at $\sim 550\text{cm}^{-1}$ and is identified as Cr_2O_3 [27-30]. As seen in Table I, N50 has a significantly increased Mn content compared to SS316. The formation of Mn_2O_3 and MnCr_2O_4 on the surface of N50 as a result of exposure to SCW and USCW, and not on SS316, is therefore attributed to the elevated concentration of Mn in the N50 alloy. The surface of SS316 after exposure to the various test conditions was observed to be predominantly comprised of iron oxides. It is therefore suggested that the greater weight gain of N50 after exposure to USCW is attributed to the formation of a more diverse oxide layer deriving from its increased concentration of alloying elements compared to SS316.

X-ray Photoelectron Spectroscopy

Figures 3-6 show the XPS survey scans used to identify the elements present on the surfaces of SS316 and N50 samples that underwent exposure tests. The spectra obtained from the surface

of SS316 samples, given in Figures 3 and 4, showed the presence of only iron, oxygen and carbon before and after sputtering. Small features corresponding to Cr and Mn were observed in the SS316 sample exposed to SCW for 96 hours, however the signal observed in the narrow scans indicated that the elements were not present in any significant quantity and the signal/noise ratio was too low to allow any meaningful analysis. The sputtering rate was calculated and was found to remove 7nm of tantalum oxide per minute. The removal of the top few atomic layers from the sample decreased the signal intensity of carbon and increased the intensity of iron and oxygen. Furthermore, the iron auger emission is clearly visible after sputtering, as observed in Figure 3e-h, indicating that the surface contains fewer contaminants. The presence of chromium oxide was detected on the surface of the SS316 samples by Raman spectroscopy; however, Cr was not detected by XPS before or after sputtering. This is evidence that SS316 exposed to SCW and USCW forms a layer of iron oxide on its external surfaces that shields the Cr from being detected due to the limited interaction depth ($\sim 10\text{nm}$) of XPS. On the other hand, Raman spectroscopy has a larger depth of analysis ($\sim 1\mu\text{m}$) that enables the detection of constituents within the inner oxide layer.

XPS survey spectra obtained from the surface of N50 exposed to the various testing conditions before and after sputtering are shown in Figures 5 and 6. Manganese, chromium, oxygen, iron, and carbon were observable on these samples. In contrast with SS316, Cr and Mn were observed in detectable quantities on the surface of all N50 samples. The observation of these elements via XPS analysis indicates that the outer iron oxide layer formed on N50 is incomplete. The lack of an encasing iron oxide film allowed for the detection of the constituents identified by Raman analysis to comprise the inner oxide layer.

Figure 7 provides select narrow scans of the elements of interest to serve as examples indicative of the peak fitting methodology that was employed in this study. This methodology takes into account the multivalence nature of Fe_3O_4 by fitting peaks for the Fe^{2+} and Fe^{3+} separately, and fixing the ratio of Fe^{3+} to Fe^{2+} at 2:1 [15, 36]. Figure 7b displays the region for the O 1s scans and was fit using previously established fitting procedures created specifically for this system and the O1s spectra show the presence of oxide, hydroxide and adsorbed water in the film [15]. Figures 7c and d correspond to Cr 2p and Mn 2p respectively, and were fit using previously published XPS fitting parameters [27-30, 33-35]. A summary of the data obtained

through XPS analysis for all samples is given in Tables III. Iron oxide compounds were observed on all samples, and were therefore omitted from this table for clarity.

Discussion

It is well established that in the oxidizing SCW environment, austenitic steels form a dual layer structure [4-13]. This oxide structure is formed by the diffusion of alloying elements; with an inner layer consisting of FeCr_2O_4 and Cr_2O_3 , and Fe_3O_4 and Fe_2O_3 composing the outermost oxide layer [4-13]. While the well-established dual layer structure was observed on SS316 in the current study, N50 was observed to develop an alternative inner oxide layer. The inner layer of SS316 was found to be composed of FeCr_2O_4 and Cr_2O_3 , while the inner layer of N50 contained MnCr_2O_4 , Mn_2O_3 and Cr_2O_3 . The different composition of the inner layer observed on N50 is attributed to its higher Mn content. It has been observed that N50, and other steels with high Mn content, form Mn incorporated spinel compounds [37, 38]. It has also been shown that the inclusion of larger amounts of Mn improves the oxidation resistance of chromium and iron by stabilizing the surface film formed on the alloy [39-42]. In the current study, it was observed that magnetite and hematite were formed on the exterior surface of both N50 and SS316 and that the layer of iron oxide on SS316 did not allow for the identification of the inner oxide layer through XPS analysis. The identification of non-Fe oxide compounds through Raman spectroscopy as well as XPS signifies that the outer Fe oxide layer on N50 was heterogeneous in nature and did not cover the entire surface. This observation indicates that the increase in Mn and Cr content in N50 mitigated the diffusion of iron through the inner oxide layer and resulted in the formation of a fundamentally different oxide structure than that observed on austenitic steels exposed to SCW before. Longer term studies need to be conducted to understand the beneficial nature of this layer.

Conclusions

N50 exhibits greater weight gain when compared to SS316 as a result of exposure to 600°C USCW; however, weight gain results of samples exposed to 530°C SCW were comparable. This

effect is suggested to be, at least in part, due to the increase in manganese content in N50 compared to SS316, resulting in the formation of more stable oxides. The difference in alloy composition allows for the formation of a Mn_2O_3 and MnCr_2O_4 base oxide layer. XPS and Raman spectroscopies demonstrated the outermost surface of SS316 contained solely iron oxides, while underlying layer was chromium oxide. In contrast, iron oxides were formed on the outermost surface of N50 in addition to manganese and chromium oxides. While SS316 demonstrated lower weight gain results on average, surface analysis indicated an outer layer on SS316 comprised of more completely covered iron oxide which was different from the incomplete coverage observed on N50. The formation of a Mn based oxide layer may be beneficial as it limited the diffusion of iron to the surface.

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Table I. Composition of SS316 and N50.

Element (wt%)	C	Mn	P	S	Si	Cr	Ni	N	Mo	V	Nb	Fe
SS316	0.03	2	0.05	0.03	0.75	18	14	0.1	3	0.3 max	0.3 max	Bal
N50	0.03	4.89	0.02	0.001	0.49	21.26	12.18	0.28	2.1	0.14	0.18	Bal

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

		530C				600C			
Time(hours)		24		96		24		96	
Mass (g)		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
SS316	Before	12.5658	12.4445	12.4443	12.4203	12.5376	12.4809	12.6425	12.5972
	After	12.5673	12.4466	12.4476	12.424	12.5418	12.485	12.6503	12.6038
	Gain	0.0015	0.0021	0.0033	0.0037	0.0042	0.0041	0.0078	0.0066
	Average % change	0.014		0.028		0.033		0.057	
N50	Before	13.4532	13.3823	13.3897	13.4059	13.1521	13.0959	13.2794	13.1761
	After	13.455	13.3842	13.3953	13.408	13.1573	13.1014	13.2887	13.1858
	Gain	0.0018	0.0019	0.0056	0.0021	0.0052	0.0055	0.0093	0.0097
	Average % change	0.014		0.029		0.041		0.072	

Table III: Species present (before and after sputtering) in the oxide film formed on N50 sample surface

	Compound	Cr_2O_3	$\text{Cr}(\text{OH})_3$	Mn_2O_3	MnCr_2O_4
Before Sputtering	530C_24hrs	x	x	x	x
	600C_24hrs			x	x
	530C_96hrs			x	x
	600C_96hrs			x	x
After Sputtering	530C_24hrs	x	x	x	x
	600C_24hrs	x	x	x	x
	530C_96hrs			x	x
	600C_96hrs	x	x	x	x

Figure 1: Raman spectra for all SS316 samples exposed to supercritical and ultrasupercritical water with labels denoting which compounds were identified.

Figure 2: Raman spectra for all N50 samples exposed to supercritical and ultrasupercritical water with labels denoting which compounds were identified.

Figure 3: XPS spectra for SS316 before sputtering exposed to a) 530°C SCW for 24 hours b) 600°C USCW for 24 hours c) 530°C SCW for 96 hours d) 600°C USCW for 96 hours. The features observed with their approximate binding energies are as follows: C1s at 284eV, O1s at 530eV, Fe2p at 700eV and Fe KLL auger series from 780-900eV

Figure 4: XPS spectra for SS316 after 1 minute of argon sputtering exposed to a) 530°C SCW for 24 hours b) 600°C USCW for 24 hours c) 530°C SCW for 96 hours d) 600°C USCW for 96 hours. The features observed with their approximate binding energies are as follows: C1s at 284eV, O1s at 530eV, Fe2p at 700eV and Fe KLL auger series from 780-900eV

Figure 5: XPS spectra for N50 before sputtering exposed to a) 530°C SCW for 24 hours b) 600°C USCW for 24 hours c) 530°C SCW for 96 hours d) 600°C USCW for 96 hours. The features observed with their approximate binding energies are as follows: C1s at 284eV, O1s at 530eV, Cr2p at 570 eV, Mn2p at 640 eV Fe2p at 700eV and Fe KLL auger series from 780-900eV

Figure 6: XPS spectra for N50 after 1 minute of argon sputtering exposed to a) 530°C SCW for 24 hours b) 600°C USCW for 24 hours c) 530°C SCW for 96 hours d) 600°C USCW for 96 hours. The features observed with their approximate binding energies are as follows: C1s at 284eV, O1s at 530eV, Cr2p at 570 eV, Mn2p at 640 eV Fe2p at 700eV and Fe KLL auger series from 780-900eV

Figure 7: XPS narrow scans indicative of the peak-fitting for all samples: a) Fe 2p_{3/2} spectra with peaks corresponding to (i) Fe₃O₄ (Fe²⁺), (ii) Fe₃O₄ (Fe³⁺) and (iii) Fe₂O₃, b) O 1s spectra with peaks corresponding to (i) O²⁻, (ii) OH⁻ and (iii) H₂O (adsorbed), c) Cr 2p_{3/2} and Cr 2p_{1/2} spectra with peaks (i) and (iii) corresponding to Cr₂O₃ and (ii) and (iv) representing Cr(OH)₃ and d) Mn 2p_{3/2} spectra with peaks corresponding to (i) MnCr₂O₄, (ii) Mn₂O₃ and (iii) a shake-up satellite peak [27-30, 33-35].