Analysis of Inconel 600 Oxidized Under Loss-of-coolant Accident Conditions: A Multi-Modal Approach

Trishelle M. Copeland-Johnson[a,f], Charles K. A. Nyamekye[c,d], Lynne Ecker[b], Nicola Bowler[a], Emily A. Smith[c,d], Raul B. Rebak[e], Simerjeet K. Gill[d*]

[a]Department of Materials Science & Engineering, Iowa State University, Ames, IA, United States

[b]Nuclear Science & Technology Department, Brookhaven National Laboratory, Upton, NY, United States

[c]Department of Chemistry, Iowa State University, Ames, IA, United States

[d]Ames Laboratory, U.S. Department of Energy, Ames, IA, United States

[e]General Electric Research, Schenectady, NY, United States

[f]Idaho National Laboratory, U.S. Department of Energy, Idaho Falls, ID, United States

∗Corresponding author - gills@bnl.gov

Email addresses: trishelle.copelandjohnson@inl.gov (Trishelle M. Copeland-Johnson), gills@bnl.gov (Simerjeet Gill), lecker@bnl.gov (Lynne Ecker), nbowler@iastate.edu (Nicola Bowler), nyamekye@iastate.edu (Charles K. A. Nyamekye), esmith1@iastate.edu (Emily A. Smith), rebak@ge.com (Raul Rebak)

Abstract

Understanding the performance of cladding materials during a loss-of-coolant accident scenario is crucial for developing next-generation accident tolerant nuclear fuel rod claddings. We describe a multi-modal approach combining synchrotron-based diffraction, and Raman spectroscopy with nano-scale electron microscopy techniques for investigating oxidation of Inconel 600 (A600) in steam and air environments at 1200°C for 2 h. We report that A600 exposed to steam develops a Cr_2O_3-enriched surface layer while a mixed phase oxide layer containing $NiFe_2O_4$, Cr_2O_3, Fe_3O_4 and $Fe_{(3-x)}Cr_xO_4$ is formed in air. Mechanism of oxidation for A600 in air and steam environments is discussed.

Keywords:

Superalloys, Raman spectroscopy, SEM, XRD, atmospheric corrosion, oxidation

1. Introduction

Efforts are underway to enhance the safety margins of Generation III light water nuclear reactors in the aftermath of the Fukushima Daiichi accident in 2011. The degradation of nuclear fuel claddings constructed from the current industry standard, zirconium-based alloys (i.e., Zircaloy™), contributed to the hydrogen explosions observed during the loss-of-coolant accident (LOCA) in 2011 [1–3]. Zircaloys are commonly used for cladding due to their neutron transparency, good mechanical integrity, and

ability to passivate under reactor conditions [3,4]. Notably, fuel rod claddings contribute to reactor operation safety by producing a passivating oxide surface that encapsulates the remainder of the cladding and fuel, isolating them from the operating reactor environment [5]. Zircaloy, while exhibiting optimal oxidation performance at normal reactor operating temperatures (~290°C), is unable to withstand the reactor environment temperatures between 997 and 1,227°C, corresponding to the onset of a LOCA scenario [2,3].

Inconel 600 (A600) is part of a series of conventional structural materials used in nuclear applications, which are being assessed for their suitability for constructing nuclear fuel claddings with accident tolerant capabilities [6–10]. These accident tolerant claddings (ATCs) exhibit oxidation performance that can withstand conditions observed during a beyond-design-basis accident (such as LOCA) scenario, enhancing the safety margins of domestic light water reactors [11–13]. A600 is an austenitic Ni-Cr superalloy [14,15] used in a wide variety of applications, including nuclear reactors, as standard material for constructing critical components, such as steam generator tubing, heat exchangers, and components for pressure vessels [3,16]. The extensive versatility of A600 originates from its oxidation resistance and optimal mechanical properties over a wide temperature range [15,16]. Changes in the oxidation performance of A600 have been predominantly reported below the onset temperature of a LOCA scenario (i.e., 1,200°C) at long timescales (from approximately 10 to 100 h) [17–23]. Very limited data is available on how A600 responds at timescales under 10 h, which is crucial to understand early stage corrosion such as onset of oxide growth. As a candidate for constructing ATCs, it is important to assess the oxidation performance of A600 at the onset of LOCA conditions–namely, in the presence of steam at 1,200°C, by characterizing the oxidation products and extent of oxidation. Knowledge of the oxidation products at the onset of LOCA conditions is essential for a comprehensive understanding of the oxidation mechanism of A600 under a LOCA. Measuring the extent of oxidation on A600 provides a relevant metric for assessing oxidation performance with respect to Zircaloy fuel claddings. For instance, the U.S. Nuclear Regulatory Commission (NRC) dictates that the extent of oxidation of Zircaloy cladding must not exceed 0.17 times the original thickness of the cladding [24]. While this metric holds relevance in regulatory bodies of work, this investigation utilizes the extent of oxidation to provide insight on early stages of oxidation using multi-modal approach from fundamental/mechanistic point of view. In this work, we evaluate the oxidation products and extent of oxidation of A600 in both steam and air environments at 1,200°C, where exposure to air is used as the reference environment. Detailed investigation of oxidation products is performed, and their distribution in the surface oxide layer is determined using a multi-modal approach employing scanning electron microscopy (SEM), Raman spectroscopy, and synchrotron X-ray diffraction. We have utilized this approach in the past to elucidate oxidation mechanisms of FeCrAl alloys, providing insights into their ability to withstand LOCA temperatures and their potential to improve safety margins of nuclear reactors [8,10]. Studying the oxidation mechanisms of ATC candidate alloys under conditions of LOCA onset is novel, given that most studies focus on long-term exposure, usually ~10 to 100 h [19,20,22,23] as compared to early stage corrosion.

2. Material and Methods

2.1 Sample Preparation

A600 specimens were acquired by collaborator Rebak at General Electric. Nominal composition of the alloy is available in [DATA REPOSITORY]. Surface oxidation was induced by simulating the temperature and atmospheric composition observed during LOCA scenarios. Specimens exposed to 100% steam or laboratory air at 1,200°C for 2 h in the Superheated Steam System (SSS), a retort furnace managed by General Electric [7]. Exposing specimens to air served as an environment to compare the impact of water vapor on the oxidation mechanism of each alloy. Three sets of A600, alongside Zircaloy-2 specimens to evaluate the extent of oxidation, were studied for each condition (i.e., control, air, and steam). The A600 specimens with dimensions are shown in Figure 1. Control specimens were unoxidized segments, which were then compared to their exposed counterparts. Specimen coupons were hole-punched (~1.5 mm diameter) and ground on 320 SiC grit paper, then rinsed with acetone, isopropanol, and deionized water before being blown dry. Afterwards, specimens were loaded into the SSS and suspended using Pt wires (through their punched hole) from the horizontal platforms within the chamber. The SSS chamber was then sealed and purged with dry argon gas at a rate of 30 cm^3/min up to 2 h during heating and cooling steps. For steam exposure, once the SSS was at operating temperature, steam generated from 18 MΩ ultra-high purity water was injected at a rate of 2.5 g/min through alumina diffusers, to preheat and homogeneously distribute the steam within the chamber. To mitigate against recirculation, steam was condensed as it exited the chamber, and the removed volume monitored to ensure steady-state conditions. The system was operated near ambient pressure. Air oxidation was performed using the same procedure but without injecting steam. After exposure, specimens were stored in a desiccator at ambient temperature and $\leq$ 10% relative humidity in between characterization sessions. Cross-sectioned segments were prepared using standard metallographic techniques used for sample preparation for SEM analysis [25], mounted in resin, sectioned, and then ground and polished down to 1 μm finish with a series of SiC and diamond polishing slurry steps, respectively.

2.2 Characterization Methods

2.2.1 Scanning Electron Microscopy (SEM)

SEM, with energy-dispersive X-ray spectroscopy (EDS), was utilized to capture information on morphology, changes in elemental composition through the oxidized layers and bass metal that exhibited oxygen ingress, and to estimate the extent of oxidation of the exposed samples. SEM was conducted using a JEOL 7600F analytical high-resolution microscope at tube voltages ranging between 10 and 15 keV. The elemental composition analysis was performed on the same system using an Oxford Instruments EDS 80 mm^2 X-Max silicon drift detector with 129 eV resolution operated through the INCA™ software suite. For surface analysis, bulk specimens were secured to the specimen stage by a 25-mm-diameter pin stub using double-sided carbon and Cu tape. Cross-sectioned mounts were loaded into a 25-mm-diameter stage adapter with adjustable height and secured with side screws. The height of the mount was lowered until the polished surface of the specimen was level with the edge of the

adapter. The extent of oxidation was estimated from at least 50 measurements, acquired from multiple images over the 2-mm width of the cross-section, using the image analysis software ImageJ [26]. Images were rotated to a horizontal orientation and calibrated based on their scale bar. A grid was then overlaid on top of the reoriented image to provide guidelines for measuring the oxide thickness with the line tool. The extent of the oxidation was calculated and reported as a percent ratio of the thickness of the oxidation layer over the original thickness of the specimen. Reported uncertainties are based on a standard error of the mean multiplied by a coverage factor k = 2, corresponding to approximately the 95% confidence level.

2.2.2 Raman Spectroscopy

Raman spectroscopy was performed on the top surface and cross-sectioned surface of the specimens to identify the oxidation products of A600 treated in air and steam at 1,200°C for 2 h. Raman measurements were conducted at room temperature using an XploRA Plus Raman confocal microscope with signal collected in the epi-direction (HORIBA Scientific, Edison, New Jersey). A 100-µm slit width, a 300-µm confocal pinhole, and a 1,200-gr/mm grating with 5 cm^{-1} resolution were employed.

The confocal microscope was equipped with a thermoelectrically cooled Synapse EMCCD camera operating at -70°C (HORIBA Scientific, Edison, New Jersey). Raman spectra of the surface of steam- and air-oxidized A600 specimens were acquired with Olympus 20× (0.40 numerical aperture) and 50× (0.50 numerical aperture) objectives, respectively. A 3.4-µm step size was used to image the steam oxidized surface specimens, and a 1.6-µm step size was used for the air-oxidized surface specimens. Heating effects were avoided by utilizing a solid-state 532-nm diode laser operated at 3-mW. An acquisition time of 30 s with three accumulations was used for all the surface Raman measurements. Raman imaging of the cross-sectioned air- and steam-oxidized specimens were analyzed with a 50× objective (0.50 numerical aperture) with a 1.2-µm step size. A laser power of 1.4 mW and 20 s acquisition time with three accumulations were used for the cross-sectioned A600 specimens. Any reported uncertainties with Raman shifts are standard deviations, originating from averaging of Raman spectra.

All Raman spectra were normalized and background corrected. The Raman images were analyzed using MatLab R2016a (The MathWorks, Inc., Natick, MA). The chemical compositions of various oxidation products were identified using published spectra and the RRUFF database [27]. Lastly, the Raman measurements were compared with SEM/EDS elemental analysis and XRD spectra to reveal similarities in the chemical composition, the stoichiometry, and the phases of the oxidation of A600 on the surface and cross-sectioned specimens.

2.2.3 X-ray Synchrotron Diffraction

Synchrotron X-ray powder diffraction (XRD) provided high-throughput, high-resolution patterns for qualitative phase identification of major and minor oxidation products grown on A600 [28]. Analysis was conducted at the ID-28-2 beamline at the National Synchrotron Light Source II (NSLS-II) with incident X-rays at 0.24 Å wavelength (52 keV energy) targeting the specimen through a shallow angle beam reflection setup. Diffracted X-rays were then captured with a silicon-based, flat-panel detector, generating a two-dimensional (2D) projection. An LaB_6 standard was used to calibrate the specimen-to-

detector distance and detector tilt with respect to the beam. The raw 2D patterns were processed to remove contribution from the background.

The processed 2D detector images were radially integrated to obtain one-dimensional powder diffraction patterns. Qualitative analysis was conducted using the PDF-4+ software published by the International Center for Diffraction Data (ICDD). The precision of a match between a standard and experimental pattern was quantified by a goodness-of-match (GOM) score, higher precision associated with a higher score, the maximum being 8000.

3. Results

3.1 SEM Analysis

Analysis of oxidized A600 with SEM includes microstructural characterization using backscattered electron (BSE) imaging and elemental composition analysis via EDS. In addition, BSE imaging of surface and cross-sectioned segments conveys morphology, grain structure, porosity, and differences in composition based on absorption contrast at acquisition sites. EDS analysis illustrates elemental distribution over the surface and throughout the oxidized ingress and alloy elemental composition estimates, reported in [DATA REPOSITORY], along with reported composition from literature.

3.1.1 Air-Oxidized A600

Surface analysis of air-oxidized A600 using EDS, Figure 2, indicated that the alloy underwent significant changes in its morphology during exposure. After exposure to air, two different oxidized structures were observed: (1) large, highly faceted bulky grains and (2) a smoother structure comprising highly compacted, equiaxial grains, Figure 2a. The bulky granular oxidized regions exhibit Fe enrichment with some Ni-enriched sites, Figure 2b. The smoother oxidized regions exhibit Cr enrichment. Si enrichment is observed adjacent to the Cr-enriched region, Figure 2c. Regions of extensive but inhomogeneous spallation are observed all over the surface, revealing exposed alloy dotted with Cr-enriched oxidized precipitates.

Cross-sectional analysis complements the regions observed from surface analysis, Figure 3. There are four distinct compositions observed through the oxidized ingress: (1) the top Ni-Fe-enriched layer observed from surface analysis, (2) followed by the Cr-enriched layer, (3) the Si-enriched region, which is revealed to be a thin interfacial layer, along with (4) a region of Al-Cr-enriched precipitants embedded within the alloy, characteristic of an internal oxidation zone (IOZ). The extent of the oxidation experienced by A600 after exposure to air is estimated at 8.8 ± 0.8 μm or 0.37 ± 0.03% of the original thickness of the specimen. Compared with a 2.61-mm-thick Zircaloy-2 specimen exposed under the same conditions, Figure S1a)-S1b) in [DATA REPOSITORY], the extent of oxidation is 1.3 ± 0.2 mm or 50 ± 8% of the original specimen thickness, which further conveys from this investigation the superior oxidation performance of A600 under the same conditions."

3.1.2 Steam-Oxidized A600

Surface analysis of steam-oxidized A600 shows a clear change in morphology after exposure, Figure 4. The smooth surface of the unoxidized alloy, Figure 4a, when oxidized becomes rough, comprised of small, clearly defined equiaxial grains that amass into compact regions with notable Cr enrichment. The Cr-enriched regions are disrupted by extensive inhomogeneous spallation, as evidenced by regions belonging to the Ni-Cr superalloy A600. These spalled regions possess a significantly rougher morphology than the control alloy and are discontinuously spotted with Cr-enriched oxidized precipitates throughout. These spalled regions will be referred to as exposed alloy for the remainder of this text. Cr-enriched oxide regions display a few Fe-enriched areas, Figure 4b. Si enrichment is also observed adjacent to the Cr-enriched oxide regions, Figure 4c.

Cross-sectional analysis of the steam-oxidized A600 surface, Figure 5, reveals three distinct regions extending through the oxidized ingress, Figure 5a-c: (1) the Cr-enriched surface region that was observed at the surface, (2) the Si-enriched region, which is a thin interfacial region between the Cr-enriched oxidized region and exposed alloy, and (3) the region of Al-enriched precipitates that are akin to an IOZ. The extent of the oxidized region of A600 after exposure to steam is estimated at 6.1 ± 0.3 µm or 0.26 ± 0.01% of the original thickness of the specimen. Compared with a 2.62-mm-thick Zircaloy-2 specimen exposed under the same conditions, Figure S1c)-S1d) in [DATA REPOSITORY], the extent of oxidation is 0.28 ± 0.04 mm or 11 ± 0.01% of the original specimen thickness, which is less severe than that observed in air but still illustrates the superior oxidation performance of A600."Some Mn enrichment is also observed in the outer layer of both air- and steam-oxidized A600 specimens.

3.2 Raman Spectroscopy

Raman spectroscopy was utilized to chemically identify oxide phases formed on the surface of A600, specifically those containing the alloying elements Cr, Fe, and Ni, observed at enriched oxidized regions with SEM analysis. Both surface and cross-sectional analyses were performed to reveal the distribution of oxide species formed at the surface and throughout the oxidized ingress.

3.2.1 Air-Oxidized A600

Cr-enriched and Fe-Ni-enriched oxidized regions observed at the surface with EDS correspond to Raman shifts illustrated in surface spectra 1 and 2, **Error! Reference source not found.**, indicating the presence of Cr_2O_3 and $NiFe_2O_4$, respectively [27,29–31]. Raman shifts in surface spectrum 1 are observed at 330, 496, 565, 627, and 690 cm^{-1}, which can be attributed to the presence of $NiFe_2O_4$ based on reported literature [31]. In surface spectrum 2, Raman shifts located at 298, 350, 529, 555, 617, and 716 cm^{-1} indicate the presence of Cr_2O_3 and $NiFe_2O_4$. Broadening of the Raman shift located at 716 cm^{-1} can be attributed to alterations in the structure of Cr_2O_3 and $NiFe_2O_4$ due to crystalline defects and the heterogeneous composition of the oxidized region at the acquisition site [29].

Cr-enriched and Ni-Fe-enriched oxidized regions observed from EDS cross-sectional analysis, Figure 3, are observed to contain combinations of Cr_2O_3, $Fe_{(3-x)}Cr_xO_4$, and $NiFe_2O_4$ based on Raman spectra acquired from a cross-sectioned segment of an air-oxidized A600 specimen, **Error! Reference source not found.**. Cross-section spectrum 1 features Raman shifts at 295, 350, 527, 553, 615, and 713 cm^{-1}, indicating Cr_2O_3 [27,29,30]. Cross-section spectrum 2 features Raman shifts at 534 cm^{-1} that agree with

$Fe_{(3-x)}Cr_xO_4$, and shoulders at 639 and 681 cm^{-1} that indicate Cr_2O_3 and $Fe_{(3-x)}Cr_xO_4$ [27,32,33]. Cross-section spectrum 3 features a Raman shift at 549 cm^{-1}, which is characteristic of Cr_2O_3, and shoulders at 640 cm^{-1} and 691 cm^{-1}, which may originate from a mixed contribution of $NiFe_2O_4$ and Cr_2O_3 [31].

Raman imaging of the surface, **Error! Reference source not found.**, and a cross-sectioned segment, **Error! Reference source not found.**, indicate two Raman shifts around 553 and 692 cm^{-1}, due to Cr_2O_3 and a mixed contribution of $NiFe_2O_4$ and Cr_2O_3, respectively.

3.2.2 Steam-Oxidized A600

Fe- and Cr-enriched oxide surface regions observed with EDS connects to multiple oxide species (i.e., $Fe_{(3-x)}Cr_xO_4$, Fe_3O_4 and Cr_2O_3) illustrated with surface spectra 1 and 2, Figure 10. Raman shifts were detected at 448, 519, 550, 580, 624, and 683 cm^{-1}. The Raman shift at 550 cm^{-1} that appears in spectra 1 and 2, Figure 10, displays a geometry of a sharp peak housed within very broad shoulder peaks centered at 519 and 580 cm^{-1}. The sharp peak can be attributed to the characteristic Raman shift of Cr_2O_3. The overall shoulder geometry is characteristic of Fe_3O_4. In both spectra, a number of Raman shifts can be attributed to multiple species, notably at 550 and 680 cm^{-1}, to Cr_2O_3, Fe_3O_4, or $Fe_{(3-x)}Cr_xO_4$. With the exception of Cr_2O_3, these species are categorized as spinel compounds, exhibiting a crystalline structure involving Cr, Fe, and O. These similarities manifest in their characteristic Raman shifts, particularly for the Raman shift at 683 cm^{-1}. The presence of Cr_2O_3 as a major phase in Cr-enriched oxide regions is further confirmed by Raman shifts displayed in surface spectrum 3. Raman images of the steam-oxidized surface have been acquired to illustrate the distribution of the 555 ± 2 cm^{-1} and 684 ± 4 cm^{-1} Raman peaks, Figure 11 .

Cr- and Fe-enriched oxide regions were shown, by EDS, to traverse into the oxide ingress, agreeing with species identified in cross-sectioned segments by Raman spectroscopy analysis [DATA REPOSITORY], the identified chemical species also detected in surface spectra. Imaging of cross-sectioned segments, Figure 12, highlights the Raman shifts at 553 ± 2 cm^{-1} and 684 ± 2 cm^{-1}. The former Raman shift corresponds to Cr_2O_3, while as stated previously, the latter Raman shift can correspond to the presence of multiple species, including Cr_2O_3, Fe_3O_4, or $Fe_{(3-x)}Cr_xO_4$.

3.2.3 XRD Analysis

The oxide phases identified at the surface of A600 after exposure to air and steam by Raman spectroscopy are also identified by XRD qualitative analysis. Comparison of diffraction patterns of A600 before and after oxidation in steam and air are featured in Figure 13, while observed oxide phases are listed in Table 1.

For steam-oxidized A600, the Cr- and Fe-enriched oxidized surface regions first noted by EDS were identified as $Fe_{(3-x)}Cr_xO_4$, Fe_3O_4 and Cr_2O_3 by Raman surface analysis and XRD. The presence of Ni metal, corresponding to the alloy, was indicated by XRD. For air-oxidized A600, Cr- and Ni-Fe-enriched oxidized regions were confirmed as Cr_2O_3 and $NiFe_2O_4$, respectively, by Raman spectroscopy and XRD.

	Species	Powder Diffraction File (PDF)	Goodness-of-Match (GOM)
Air-Oxidized A600	Cr_2O_3	04-015-7583	7748
	$NiFe_2O_4$	01-007-9720	7671
	Ni	01-071-4653	4698
Steam-Oxidized A600	$Fe_{(3-x)}Cr_xO_4$	04-022-3116	7010
	Fe_3O_4	04-008-4511	6970
	Cr_2O_3	04-015-7583	6939
	Ni	04-011-8029	6786

Table 1: Species identified by XPD in air- and steam-oxidized A600

4. Discussion

The arrangement of the various oxide phases formed via selective diffusion of alloying elements following air oxidation of A600 is illustrated in Figure 14a. The surface of air-oxidized A600 contains $NiFe_2O_4$, which is the product of Fe and Ni diffusing from the base alloy to react with O [34]. Ni- and Fe-based oxidation products, such as $NiFe_2O_4$, Fe_3O_4, NiO, and Fe_2O_3, have been reported previously, after exposure to both air [20,35] and steam [19,36]. In addition, slower-diffusing Cr [37], which has been demonstrated to diffuse predominantly along grain boundaries in Ni-based alloys, such as A600 [38,39], forms a Cr_2O_3-enriched layer. The formation of Cr_2O_3 is commonly cited in Ni-Cr alloys (i.e., A600) [5,17,18,20,22,23,39–41] since these alloys preferentially generate Cr_2O_3 at their surfaces [42–44]. Cr_2O_3 possesses a low concentration of defect routes to sustain oxide growth through ion diffusion, resulting in a stable oxidation product, which imparts surface passivation, making Ni-based alloys good candidates for high temperature applications [5,41]. Within the Cr_2O_3-enriched region, Cr diffusion is accompanied by Fe diffusion, resulting in localized regions of mixed Fe- and Cr-based oxide comprised of $Fe_{(3-x)}Cr_xO_4$ spinel phase. $Fe_{(3-x)}Cr_xO_4$, while more stable than pure Fe-based oxides, such as Fe_3O_4, is not a passivating in nature [5]. Such formation of mixed phase regimes of Cr_2O_3 alongside $Fe_{(3-x)}Cr_xO_4$ spinel compounds has been reported [42,45]. The formation of the Cr_2O_3-enriched layer on surface results in Cr-depleted regions below the surface, which encourages the diffusion of Al and Si to form Si- and Al-based oxides that are most likely SiO_2 [42] and Al_2O_3 [42,44], respectively. The Si-based oxide forms a thin-discontinuous oxide layer while Al_2O_3 manifests as precipitates below the SiO_2 layer in a region akin to an IOZ. Al_2O_3 precipitates manifest because Al has a higher affinity to react with O than Cr; however, since Al exists at quantities below the critical value (i.e., < 3 wt.%) for generating a continuous layer, resulting in precipitation of Al_2O_3 [43]. Cr_2O_3 precipitates exist alongside the Al_2O_3 precipitates within the IOZ. The presence of Cr_2O_3 precipitates, in addition to a Cr_2O_3-enriched layer, suggest that the oxide growth has yet to reach equilibrium during the exposure period in our study.

The arrangement of the various oxide phases formed after oxidation of A600 in steam is illustrated in Figure 14b, where the surface Cr_2O_3-enriched region, including localized areas of Fe_3O_4 and $Fe_{(3-x)}Cr_xO_4$ [46,47], is followed by a Cr-depleted region that sustained the formation of SiO_2 [5]. Previous reports by Alstrup et al. [20] noted that the addition of H_2O to the environment results in selective oxidation of Cr_2O_3.

There is no uniform model explaining the oxidation products of A600 at or near LOCA temperatures, as literature reports varying composition as well as distribution of oxidation products. Such variations in the reported products can be attributed to several factors, including surface treatment, alloy composition, variations in oxidation environment, or the detection limitations of characterization techniques, such as EDS. Nonetheless, there are two common trends. The first is the observation of a bi-layer oxide region comprised of an outer layer enriched with a Ni-based oxide, such as NiO, $NiFe_2O_4$, or $NiCr_2O_4$, followed by a sub-surface Cr_2O_3-enriched layer [20,38,39,48]. The second observed trend is only a Cr_2O_3-enriched layer with localized regions of Mn- and Ni-based oxidation products, such as $(Mn,Ni)Cr_2O_4$, concentrated near the outer region of the oxide growth [5,19]. In this investigation, A600 after oxidation in air exhibited a bi-layer comprised of an outer $NiFe_2O_4$-enriched region followed by Cr_2O_3-enriched layer. However, for samples oxidized in steam, the $NiFe_2O_4/Cr_2O_3$ bi-layer was absent, and the surface layer was predominantly comprised of Cr_2O_3. Previous reports by Wright and Dooley [5] noted this observation as a general behavior for Ni-16Cr alloys (i.e., A600) exposed to steam at temperatures higher than 700°C and Abe et al. [19] observed such formation of a Cr_2O_3 layer at 800°C after exposure to steam for 360 h.

Our experimental results, illustrated in Figure 15a and Figure 15b, clearly demonstrate that the oxidation environment plays a role in controlling the diffusion of alloying elements in A600 and controlling the surface passivation of the alloy surface. Initial formation of Cr_2O_3 in Ni-Cr austenitic alloys, such as A600, can be attributed to preferential diffusion of Cr via grain boundaries to the surface in both steam and air environment [39]. These initial Cr_2O_3 nucleation sites near grain boundaries then coalesce into a continuous Cr_2O_3 layer. Such initial formation of Cr_2O_3-based surface oxide layer has been observed in early stages of oxidation, both in a high-temperature aqueous environment [49] as well as oxygen containing environment [38,39].

In our work, one distinctive characteristic of steam oxidation is the lack of an enriched Ni-Fe-based oxide surface layer. A question that arises here is – what phenomenon is responsible for such lack of Ni-Fe-based oxide in steam environment under LOCA conditions studied? We attribute this lack of an outer layer enriched with a Ni- or Fe-based oxide in steam to the significant difference in partial pressure of oxygen between steam and air environment.

As discussed above, initially Cr_2O_3 is formed as surface oxide layer in both air and steam environments. However, in steam environment H_2O is preferentially absorbed near the surface while O_2 diffuses into the sub-surface region to react with alloying elements [41]. Accordingly, the partial pressure of O_2 adsorbed into the alloy is further diminished compared to the minimal amount of oxygen available in the atmospheric steam**.** The laboratory air used in this investigation was near ambient pressure, meaning the partial pressure of O_2 is ~0.21 atm. In contrast, in 100% steam at ambient pressure Jung, et al. calculated at 1200 °C that the partial pressure of O_2 is only ~9.2E-5 atm [50]. Such low availability of oxygen in steam favors the formation of Cr_2O_3 over Ni- or Fe-based oxides given that Cr_2O_3 is thermodynamically more stable, hence requiring a lower dissociation partial pressure of O_2 [41]. Lower partial pressure and, hence, availability of oxygen in steam environment has been reported previously to result in lack of Ni-based surface oxide. For instance, Alstrup et al. [20] attributed the lack of NiO

formation in H_2O/H_2 atmospheric mixtures to the partial pressure of O_2 being too low to form NiO. A follow-up mechanistic study under the conditions explored in this investigation would be needed to verify this hypothesis.

5. Conclusions

In this work, a multi-modal approach was employed to investigate oxidation products and compare the extent of oxidation of A600 when exposed to superheated air and steam under LOCA conditions, and a mechanism for oxide growth in air and steam environments is proposed. We demonstrate that surface oxide layer comprised of a $NiFe_2O_4$-enriched outer region followed by a Cr_2O_3-enriched sub-surface layer after exposure to air while only a Cr_2O_3-enriched layer was observed after exposure to steam. The lack of Ni-Fe-enriched oxidation products after exposure to steam is attributed to the lower partial pressure of O_2 in steam as compared to air environment. The extent of oxidation in both environments was estimated to be ≤ 10 μm thick, 8.8 ± 0.1 μm in air and 6.1 ± 0.3 μm in steam, consuming a minimal amount of the specimen. However, oxide spallation was observed in both air and steam environments, which may indicate that the mechanical integrity of the passivated surface is variable. Based on oxidation products and extent of oxidation, the performance of A600 shows its superior potential as compared to Zircaloy and as a candidate for constructing ATCs, but additional analysis is needed to assess the spallation of the surface oxide layer and determine pathways to improving the alloy's passivating capabilities under LOCA conditions.

6. Acknowledgements

The authors thank the National GEM Consortium and Brookhaven National Laboratory, especially the supporting staff at the Center for Functional Nanomaterials (CFN), including Fernando Camino, Gwen Wright, and Kim Kisslinger, and staff at National Synchrotron Light Source II (NSLS-II), including Jianming Bai, for their support.

This research used resources at the XPD beamline of the NSLS-II and CFN, a U.S. Department of Energy (DOE) Office of Science User Facility operated by Brookhaven National Laboratory under Contract No. DE-SC0012704. Raman spectroscopy measurements acquired with the HORIBA XploRa microscope were performed at the Ames Laboratory, which is operated for the DOE by Iowa State University [Contract No. DE-AC02-07CH11358].

7. References

[1] American Nuclear Society, Fukushima Daiichi: ANS Committee Report, LaGrange Park, IL, 2012. http://fukushima.ans.org/report/Fukushima_report.pdf.

[2] K.L. Murty, I. Charit, Overview of Nuclear Reactor Systems and Fundamentals, in: An Introd. to Nucl. Mater., 1st ed., Wiley-VCH, Berlin, 2012: pp. 1–42. http://www.wiley-vch.de/en/?option=com_eshop&view=product&isbn=3-527-41201-8.

[3] D. Féron, Nuclear corrosion science and engineering, Woodhead Publishing Limited, Oxford, 2012. doi:10.1533/9780857095343.

[4] C.R.F. Azevedo, Selection of fuel cladding material for nuclear fission reactors, Eng. Fail. Anal. 18 (2011) 1943–1962. doi:10.1016/j.engfailanal.2011.06.010.

[5] I.G. Wright, R.B. Dooley, A review of the oxidation behaviour of structural alloys in steam, Int. Mater. Rev. 55 (2010) 129–167. doi:10.1179/095066010X12646898728165.

[6] B.A. Pint, K.A. Terrani, M.P. Brady, T. Cheng, J.R. Keiser, High temperature oxidation of fuel cladding candidate materials in steam–hydrogen environments, J. Nucl. Mater. 440 (2013) 420–427. doi:10.1016/j.jnucmat.2013.05.047.

[7] R.B. Rebak, Alloy Selection for Accident Tolerant Fuel Cladding in Commercial Light Water Reactors, Metall. Mater. Trans. E. 2 (2015) 197–207. doi:10.1007/s40553-015-0057-6.

[8] M.S. Elbakhshwan, S.K. Gill, A.K. Rumaiz, J. Bai, S. Ghose, R.B. Rebak, L.E. Ecker, High-temperature oxidation of advanced FeCrNi alloy in steam environments, Appl. Surf. Sci. 426 (2017) 562–571. doi:10.1016/j.apsusc.2017.06.318.

[9] R.B. Rebak, V.K. Gupta, M. Larsen, Oxidation Characteristics of Two FeCrAl Alloys in Air and Steam from 800°C to 1300°C, Jom. 70 (2018) 1484–1492. doi:10.1007/s11837-018-2979-9.

[10] T.M. Copeland-Johnson, C.K.A. Nyamekye, S.K. Gill, L. Ecker, N. Bowler, E.A. Smith, R.B. Rebak, Characterization of Kanthal APMT and T91 oxidation at beyond design-basis accident temperatures, Corros. Sci. 171 (2020) 108598. doi:10.1016/j.corsci.2020.108598.

[11] S.J. Zinkle, K.A. Terrani, J.C. Gehin, L.J. Ott, L.L. Snead, Accident tolerant fuels for LWRs: A perspective, J. Nucl. Mater. (2014). doi:10.1016/j.jnucmat.2013.12.005.

[12] I. Charit, Accident Tolerant Nuclear Fuels and Cladding Materials, Jom. 70 (2018) 173–175. doi:10.1007/s11837-017-2701-3.

[13] K.A. Terrani, Accident tolerant fuel cladding development: Promise, status, and challenges, J. Nucl. Mater. 501 (2018) 13–30. doi:10.1016/j.jnucmat.2017.12.043.

[14] G.Y. Lai, High-Temperature Corrosion and Materials Applications., ASM International, 2007.

[15] ASTM International, SAE International, Metals and Alloys in the Unified Numbering System (11th Edition), ASTM International, 2008. https://app.knovel.com/hotlink/toc/id:kpMAUNSE01/metals-alloys-in-unified/metals-alloys-in-unified.

[16] C. Farrar, The Alloy Tree: A Guide to Low-Alloy Steels, Stainless Steels and Nickel-Base Alloys, Elsevier Science, 2004.

[17] N. Birks, H. Rickert, Oxidation Mechanism of Some Nickel-Chromium Alloys, J. Inst. Met. 91 (1963) 308–311.

[18] C.S. Giggins, F.S. Pettit, Oxidation of Ni-Cr Alloys Between 800 Degrees and 1200 Degrees C, Trans. Am. Inst. Mining, Metall. Pet. Eng. 245 (1969) 2495–2507.

[19] F. Abe, H. Araki, H. Yoshida, M. Okada, R. Watanabe, The effect of grain size on the corrosion behaviour of inconel 600 in high-temperature steam, Corros. Sci. 21 (1981) 819–842. doi:10.1016/0010-938X(81)90024-X.

[20] N.C. Alstrup, N. Langvad, I. Chorkendorff, AES and SAM studies of oxide formation on Inconel 600 at high temperatures, Surf. Interface Anal. 22 (1994) 441–444. doi:10.1002/sia.740220194.

[21] F. Hamdani, H. Abe, B. Ter-Ovanessian, B. Normand, Y. Watanabe, Effect of Chromium Content on the Oxidation Behavior of Ni-Cr Model Alloys in Superheated Steam, Metall. Mater. Trans. A[1] F. Hamdani, H. Abe, B. Ter-Ovanessian, B. Normand, Y. Watanabe, Eff. Chromium Content Oxid. Behav. Ni-Cr Model Alloy. Superheated Steam, Met. Mater. Trans. A. 46 2285–2293. Do. 46 (2015) 2285–2293. doi:10.1007/s11661-015-2786-7.

[22] A.A. Hashim, A.S. Hammood, N.J. Hammadi, Evaluation of High-Temperature Oxidation Behavior of Inconel 600 and Hastelloy C-22, Arab. J. Sci. Eng. 40 (2015) 2739–2746. doi:10.1007/s13369-015-1766-y.

[23] D.-S. Li, G. Chen, D. Li, Q. Zheng, P. Gao, L.-L. Zhang, Oxidation resistance of nickel-based superalloy Inconel 600 in air at different temperatures, Rare Met. (2018). doi:10.1007/s12598-018-1148-1.

[24] United States Nuclear Regulatory Commission, Acceptance criteria for emergency core cooling systems for light-water nuclear power reactors, NRC Regulations, n.d. https://www.nrc.gov/reading-rm/doc-collections/cfr/part050/part050-0046.html.

[25] ASTM International, Standard Test Method for Measurement of Metal and Oxide Coating Thickness by Microscopical Examination of Cross Section, Untied States, 2013.

[26] K. Eliceiri, C.A. Schneider, W.S. Rasband, K.W. Eliceiri, NIH Image to ImageJ : 25 years of image analysis HISTORICAL commentary NIH Image to ImageJ : 25 years of image analysis, Nat. Methods. 9 (2012) 671–675. doi:10.1038/nmeth.2089.

[27] S.N. Lafuente B, Downs R T, Yang H, The power of databases: the RRUFF project, W. De Gruyter, Berlin, 2015.

[28] A.K. Cheetham, A.P. Wilkinson, Synchrotron X-ray and Neutron Diffraction Studies in Solid-State Chemistry, Angew. Chemie Int. Ed. English. 31 (1992) 1557–1570. doi:10.1002/anie.199215571.

[29] P. Colomban, Potential and Drawbacks of Raman (Micro)spectrometry for the Understanding of Iron and Steel Corrosion, in: New Trends Dev. Automot. Syst. Eng., InTech, 2011. doi:10.5772/13436.

[30] H.H. Landolt, R. Börnstein, Chromium sesquioxide (Cr2O3): phonon wavenumbers, elastic moduli, in: O. Madelung, U. Rössler, M. Schulz (Eds.), Non-Tetrahedrally Bond. Bin. Compd. II, Springer-Verlag, Berlin/Heidelberg, 1998: pp. 1–2. doi:10.1007/10681735_653.

[31] B.D. Hosterman, Raman Spectroscopic Study of Solid Solution Spinel Oxides, (2011) 151.

[32] K.F. McCarty, D.R. Boehme, A Raman study of the systems Fe3-xCrxO4 and Fe2-xCrxO3, J. Solid State Chem. 79 (1989) 19–27. doi:10.1016/0022-4596(89)90245-4.

[33] D. Bartels, Assessment of Corrosion Resistance of Candidate Alloys for Accident Tolerant Fuel Cladding Under Reactor Conditions, 2018. https://neup.inl.gov/SiteAssets/Final Reports/FY

2014/14-6317 NEUP Final Report.pdf.

[34] W. Wei, G. Shujiang, C. Gang, W. Fuhui, Growth mechanism of surface scales on Ni–Fe–Cr alloys at 960 °C in air, Corros. Sci. 173 (2020). doi:10.1016/j.corsci.2020.108737.

[35] I.A. Alkadir, M.N. at Jawhar, Improvement of Oxidation Resistance of Inconel 600 Alloy by Pack Cementation Process, Int. J. Adv. Technol. 09 (2018) 3–6. doi:10.4172/0976-4860.1000208.

[36] H. Lefaix-Jeuland, L. Marchetti, S. Perrin, M. Pijolat, M. Sennour, R. Molins, Oxidation kinetics and mechanisms of Ni-base alloys in pressurised water reactor primary conditions: Influence of subsurface defects, Corros. Sci. 53 (2011) 3914–3922. doi:10.1016/j.corsci.2011.07.024.

[37] J. Robertson, The mechanism of high temperature aqueous corrosion of stainless steels, Corros. Sci. 32 (1991) 443–465. doi:10.1016/0010-938X(91)90125-9.

[38] N.S. McIntyre, D.G. Zetaruk, D. Owen, XPS study of the initial growth of oxide films on Inconel 600 alloy, Appl. Surf. Sci. 2 (1978) 55–73. doi:10.1016/0378-5963(78)90006-5.

[39] F.H. Stott, G.C. Wood, J. Stringer, The influence of alloying elements on the development and maintenance of protective scales, Oxid. Met. 44 (1995) 113–145. doi:10.1007/BF01046725.

[40] J. Xiao, N. Prud'homme, N. Li, V. Ji, Influence of humidity on high temperature oxidation of Inconel 600 alloy: Oxide layers and residual stress study, Appl. Surf. Sci. 284 (2013) 446–452. doi:10.1016/j.apsusc.2013.07.117.

[41] D.J. Young, High Temperature Oxidation and Corrosion of Metals, 2nd ed., Elsevier, Boston, MA, 2016. doi:10.1016/C2014-0-00259-6.

[42] V.B. Trindade, U. Krupp, P.E.G. Wagenhuber, H.-J. Christ, Oxidation mechanisms of Cr-containing steels and Ni-base alloys at high-temperatures -. Part I: The different role of alloy grain boundaries, Mater. Corros. 56 (2005) 785–790. doi:10.1002/maco.200503879.

[43] B.A. Pint, S. Dryepondt, K.A. Unocic, Oxidation of Superalloys in Extreme Environments, in: 7th Int. Symp. Superalloy 718 Deriv., 2012: pp. 859–875. doi:10.1002/9781118495223.ch66.

[44] F.S. Pettit, G.H. Meier, Oxidation and Hot Corrosion of Superalloys, in: Superalloys 1984 (Fifth Int. Symp., TMS, Pittsburgh, 1984: pp. 651–687. doi:10.7449/1984/Superalloys_1984_651_687.

[45] S.Y. Persaud, R.C. Newman, A Review of Oxidation Phenomena in Ni Alloys Exposed to Hydrogenated Steam Below 500°C, Corrosion. 72 (2016) 881–896. doi:10.5006/1957.

[46] L. Volpe, M.G. Burke, F. Scenini, Correlation between Grain Boundary Migration and Stress Corrosion Cracking of Alloy 600 in Hydrogenated Steam, Acta Mater. 186 (2020) 454–466. doi:10.1016/j.actamat.2020.01.020.

[47] B. Langelier, S.Y. Persaud, R.C. Newman, G.A. Botton, An atom probe tomography study of internal oxidation processes in Alloy 600, Acta Mater. 109 (2016) 55–68. doi:10.1016/j.actamat.2016.02.054.

[48] M. Sennour, L. Marchetti, F. Martin, S. Perrin, R. Molins, M. Pijolat, A detailed TEM and SEM study of Ni-base alloys oxide scales formed in primary conditions of pressurized water reactor, J. Nucl. Mater. 402 (2010) 147–156. doi:10.1016/j.jnucmat.2010.05.010.

[49] A. Machet, A. Galtayries, S. Zanna, L. Klein, V. Maurice, P. Jolivet, M. Foucault, P. Combrade, P.

Scott, P. Marcus, XPS and STM study of the growth and structure of passive films in high temperature water on a nickel-base alloy, Electrochim. Acta. 49 (2004) 3957–3964. doi:10.1016/j.electacta.2004.04.032.

[50] T.S. Jung, Y.S. Na, M.J. Joo, K.Y. Lim, Y.H. Kim, S.J. Lee, Thermodynamic and experimental analyses of the oxidation behavior of UO2 pellets in damaged fuel rods of pressurized water reactors, Nucl. Eng. Technol. 52 (2020) 2880–2886. doi:10.1016/j.net.2020.05.007.

8. Figure Captions

Figure 1: Photographs of a) control (thickness (t) = 2.37 mm), b) air-oxidized (t = 2.33 mm), and c) steam-oxidized A600 (t = 2.39 mm). Lighter regions correspond to exposed alloy due to spallation. Note all displayed sample dimension tolerances are ± 0.01 mm.

Figure 2: a) SEM backscattered electron image of the surface of A600 after exposure to air, with enriched regions labeled accordingly. EDS false coloring of this site of interest illustrates distribution of elements, b) overlaid, and c) featured individually based on their respective color.

Figure 3: a) SEM backscattered electron image of a cross-sectioned segment of A600 after exposure to air with enriched regions labeled accordingly. EDS false coloring of this site of interest illustrates distribution of elements, b) overlaid, and c) featured individually based on their respective color.

Figure 4: SEM backscattered electron image of A600 a) before and b) after exposure to steam, showing regions of Cr-enrichment and exposed alloy (Ni-Cr superalloy) after spallation, labeled accordingly. EDS false coloring of this site of interest illustrates distribution of elements, c) overlaid, and d) featured individually based on their respective color.

Figure 5: a) SEM backscattered electron image of a cross-sectioned segment of A600 after exposure to steam. Again, regions of notable enrichment are labeled. b) and c) EDS maps organized in a similar format as presented in Figure 3.

Figure 6: Raman spectra acquired from the surface of air-oxidized A600, alongside spectra reported in the literature for $NiFe_2O_4$ [31] and Cr_2O_3 [27].

Figure 7: Raman spectra acquired from a cross-section of air-oxidized A600 specimen, alongside spectra reported in literature for $Fe_{(3-x)}Cr_xO_4$ [32] and Cr_2O_3 [27]. The arrows indicate the location of two notable Raman shifts at 552 cm^{-1} and 689 cm^{-1}.

Figure 8: a) Optical microscopy image captured at a) surface of air-oxidized A600. Corresponding Raman filter images illustrate the distribution of Raman shifts at b) 552 ± 2 cm^{-1} and c) 694 ± 3 cm^{-1} in the in the area bordered by the thein white-dashed line.

Figure 9: a) Optical microscopy image captured a) on cross-sectioned air-oxidized A600. Corresponding Raman filter images illustrate the distribution of Raman shifts at b) 553 ± 1 cm^{-1} and c) 691 ± 5 cm^{-1} in the area bordered by the white-dashed line.

Figure 10: Representative Raman spectra acquired at the surface of a steam-oxidized A600 specimen and compared with reported spectra of oxide species $Fe_{(3-x)}Cr_xO_4$ [32], Fe_3O_4 [27], and Cr_2O_3 [27]. The arrows indicate the location of two notable Raman shifts at 550 cm^{-1} and 683 cm^{-1}.

Figure 11: Optical images captured on the surface of steam-oxidized A600 a) before and b) after oxidation. The Raman images shifts at c) 555 ± 2 and d) 684 ± 4 cm^{-1} wavenumbers are shown in b) the region bordered in by a pink-dashed square line in b). The color scale represents the Raman scattering intensity.

Figure 12: Optical image captured from a) cross-sectioned segment of steam-oxidized A600. The Raman images b) 553 ± 2 cm^{-1} and c) 684 ± 2 cm^{-1} were collected in the area bordered in a) by a white-bordered rectangle. The color scale represents the Raman scattering intensity.

Figure 13: XPD patterns comparing A600 before and after steam oxidation. Phases shared amongst multiple patterns are usually only labeled once.

Figure 14: Schematics illustrating oxidation species detected at surface and within cross-sections of a) air-oxidized A600 and b) steam-oxidized A600

Figure 15: Schematic illustrating the proposed molecular diffusion mechanism of A600 when exposed to a) air, Cr-,Fe-, and Ni-oxides corresponding to $NiFe_2O_4$, Cr_2O_3, Fe_3O_4 and $Fe_{(3-x)}Cr_xO_4$ versus that of b) steam, with only Cr-oxides corresponding to Cr_2O_3. Major oxide phases are labeled in the schematic.