BNL-114078-2017-JA

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Submitted to the Journal Applied Surface Science

July 17, 2017

Nuclear Sciences & Technology Department

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE Office of Science (SC),
Nuclear Physics (NP) (SC-26)**

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Accepted Manuscript

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PII: S0169-4332(17)31973-6
DOI: <http://dx.doi.org/doi:10.1016/j.apsusc.2017.06.318>
Reference: APSUSC 36518

To appear in: *APSUSC*

Received date: 15-3-2017
Revised date: 27-6-2017
Accepted date: 29-6-2017

Please cite this article as: Mohamed S.Elbakhshwan, Simerjeet K.Gill, Abdul K.Rumaiz, Jianming Bai, Sanjit Ghose, Raul B.Rebak, Lynne E.Ecker, High-temperature oxidation of advanced FeCrNi alloy in steam environments, Applied Surface Science <http://dx.doi.org/10.1016/j.apsusc.2017.06.318>

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High-temperature oxidation of advanced FeCrNi alloy in steam environments

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High-temperature oxidation of advanced FeCrNi alloy in steam environments using synchrotron methods

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Abstract

Alloys of iron-chromium-nickel are being explored as alternative cladding materials to improve safety margins under severe accident conditions. Our research focuses on non-destructively investigating the oxidation behavior of the FeCrNi alloy “Alloy 33” using synchrotron-based methods. The evolution and structure of oxide layer formed in steam environments was characterized using X-ray diffraction, hard X-ray photoelectron spectroscopy, X-ray fluorescence methods and scanning electron microscopy. Our results demonstrate that a compact and continuous oxide scale was formed consisting of two layers, chromium oxide and spinel phase (FeCr₂O₄) oxides, wherein the concentration of the FeCr₂O₄ phase decreased from the surface to the bulk-oxide interface.

Keywords: FeCrNi alloy, Alloy 33, steam oxidation, XRD, HAXPES, XRF, SEM

Highlights:

1. Synchrotron based methods provide a powerful approach to understand the oxidation of Alloy 33.
2. Superheated steam environment was used to assess Alloy 33 as an accident tolerant cladding.
3. Continuous oxide scale consisted of two layers, chromium oxide and spinel phase (FeCr₂O₄) oxides.
4. Concentration of the spinel phase decreased from the oxide surface to the alloy-oxide interface.
5. Increase in temperature from 800°C to 1000°C led to increase in surface oxidation.

1. Introduction

Following the accident at the Fukushima nuclear power plant, the U.S. Department of Energy is focusing on developing nuclear fuels and cladding with an enhanced tolerance of accidents. Accident tolerant claddings should withstand the loss of coolant for longer times compared to conventional zirconium-based reactor claddings [1]. Zirconium alloys are used as cladding materials for light water reactors (LWR) due to its low thermal neutron cross section, corrosion resistance, and structural integrity in normal operating conditions [1]. However, they fail under accident conditions, such as a loss-of-coolant accident (LOCA) due to their oxidation becoming self-catalytic, so engendering the complete oxidation of the cladding and hydrogen release in form of explosions, such as those seen in the Fukushima incident [1, 2].

Advanced steel alloys offer enhanced resistance to high-temperature oxidation in steam environments due to the formation of protective oxide layers of chromia (Cr_2O_3) and/or alumina (Al_2O_3) oxides on the surface of the alloy, which enhance their stability at high temperatures by acting as an effective diffusion barrier, so resulting in low rate of oxidation [3 - 5]. These passivating oxide layers, resistant to accelerated oxidation, offer an improvement over the current designs by reducing the production of hydrogen gas, and by delaying the release of fission products into the environment. Hence, these alloys present a great opportunity to explore alternative cladding materials with better accident tolerance for commercial light water reactors.

Austenitic steel alloys offer strength and oxidation resistance at high temperatures [6 - 10] due to their high concentrations of chromium and nickel. The presence of chromium leads to the formation of a chromium oxide layer on the surface that prevents further oxidation of the base metal, while nickel enhances the stability of the protective layer [10 - 12].

Alloy 33 (UNS R20033) is commercially available advanced austenitic steel alloy with nominal composition [wt%]: 33% Cr, 32% Fe, 31% Ni, 1.6% Mo, 0.6% Cu, 0.4% N, and 0.01% C. The addition of nitrogen ensures the stability of the austenite phase and delays the intermetallic compounds formation [13, 14], while copper and molybdenum were added to improve the alloy resistance to pitting corrosion [14], which makes it attractive for several applications in corrosive environments including mineral acids and chloride solutions [13-17]. Alloy 33 was also studied for nuclear applications; it was proposed as a potential candidate for storage casing for nuclear waste in underground repositories [18], and showed resistance to corrosion under the normal operation conditions (pure water at approximately 300°C) of light water reactors (LWR) [19]. These corrosion resistance properties make it attractive for using in accident tolerant cladding applications, and corrosive environments.

Several studies investigated the behavior of alloys with high Ni concentrations in corrosive environments [20 - 22], but few focused on such alloys with similar concentrations of Ni, Cr, and Fe. In this study, we undertook a structural investigation of the oxide layer formed on Alloy 33 under nuclear accident conditions using scanning electron microscopy (SEM) as well as high-resolution X-ray fluorescence (XRF), Grazing incidence X-ray diffraction (GIXRD), and Hard X-ray photoelectron spectroscopy (HAXPES) synchrotron-based techniques. Specimens were exposed to a steam environment at 800°C and 1000°C for 8, 24, and 48 hours. GIXRD was used to gain structural information on the surface oxide layer formed on Alloy 33 in steam environments. Low incidence angles were used to significantly increase the path length of the incident beam and the diffracted beams into the oxide layer,

so enhancing the sensitivity of the signal from the surface oxide layer, and enabling depth-dependent measurements of the oxide phases formed on Alloy 33. GIXRD structural measurements of the oxide phases were complemented by HAXPES measurements that provide information about the chemical composition of the elements and their oxidation states, while the XRF studies gave the 2D elemental distribution of various oxide phases present at the surface of Alloy 33. Such detailed structural analysis of the corrosion products and the oxide layer formed during accidents provide a fundamental understanding of the oxide interface of Alloy 33, and help in assessing its potential as an accident tolerant cladding for applications in LWRs.

2. Experimental Methods

Commercial Alloy 33 specimens were provided by Krupp VDM GmbH Company. The specimens were exposed to 100% steam at a flow rate of 2.5 g/min. The specimens were flat rectangles, measuring approximately 25 x 8 x 2.3 mm with a total surface area of about 5.3 cm². At the beginning, the specimen surfaces were ground on wet SiC paper up to a 320-grid finish, and then washed with solvents and dried. The weight of the specimens was measured directly reading from a microbalance at room temperature before and after each test; the change in mass due to exposure to steam was calculated. Specimens were exposed to steam at 800°C and 1000°C for 8, 24, and 48 hours.

Scanning Electron Microscopy (SEM) analyses were conducted using Analytical SEM JEOL 7600F instrument operating at an accelerating voltage of 5 kV. The cross-sectional samples were cut and polished through several stages up to 0.1 µm alumina powder solutions. The plane-view images were collected using SEI detector while the cross-sectional images were collected using the LBE detector to overcome the sample charging.

Grazing incidence X-ray diffraction (GIXRD) measurements were obtained at the X14A beamline at the National Synchrotron Light Source (NSLS) to maximize the signal from the Alloy 33 surface oxide layer, and to perform depth-dependent measurements of the oxide phases. The X-ray wavelength was 0.7792 Å with a beam size of 2.0 x 0.2 mm². The measurements were performed at a grazing incidence with a 2θ range from 10 to 60 degrees, and four samples with tilt angles (ω) of 0.3, 0.5, 1.0, and 2.0 degrees were used to probe different depths in the specimens [23]. The two-dimensional diffraction patterns were integrated and reduced to a 1D pattern using Fit2D software [24]. In addition, the MDI JADE X-ray diffraction database was used to identify the crystal phases present in the Alloy 33 specimens.

Hard X-ray photoelectron spectroscopy (HAXPES) is a high-resolution surface-sensitive quantitative spectroscopic technique that measures the elemental composition. The use of synchrotron-based HAXPES is advantageous due to its high photon flux, which can probe a thicker region than a bench-top XPS instrument. HAXPES was used to study the elemental composition at the surface of Alloy 33, both before and after steam oxidation. These studies, conducted at the X24A beamline at the NSLS using an ultra-high vacuum chamber; the specimens were analyzed at a pressure of 1x10⁻⁸ Pa. The data were collected using 4 keV X-rays with a 1x1 mm spot size. The sample stage was tilted 5 degrees relative to the beam, and at the estimated probe depth (for this energy) of 63 Å.

X-ray fluorescence (XRF) was used to obtain a 2D element map of Alloy 33 samples before and after exposure to steam. Measurements were taken at the F3 endstation at the Cornell High Energy

Synchrotron Source (CHESS). The energy of the incident beam was 17 keV, with the circular beam with cross section of 20 μm diameter. The experiment was performed using backscattering configuration with the MAIA detector. Specimens were placed 1 mm away from the detector, which has a hole through to pass the X-ray beam [25]. The backscattered signal was collected with 384 element detectors, and the data was reduced and analyzed using GeoPixe software. We scanned a total area of 3x3 mm^2 on the surface of Alloy 33.

3. Results

3.1. SEM analysis of oxide morphology, thickness, and oxidation rate:

The oxidation rate of Alloy 33 was studied as a function of the temperature and time under a superheated steam environment to simulate conditions during an accident at the plant. Alloy 33 exhibited a very uniform greenish black oxide scale, so evidencing the corrosion resistance of Alloy 33 under accident conditions. Figure 1 shows the surface morphology of Alloy 33 after the steam exposure. At 800°C, irregular faceted oxide grains with size range from 100 – 600 nm were found to cover the surface at all exposure times (as shown in Figure 1(a)-(c)). However, a network of fiber-like elongated oxide grains was found to cover the surface after exposure to steam at 1000°C for 8 and 24 hours (as shown in Figure 1(d) and (e)). The length of the fiber-like grains was found to be as long as 1 μm while the thickness was found to be as much as 200 nm. The surface morphology changed after exposure for 48 hours, the fiber-like grains were replaced by sharp needle-like grains in addition to irregular faceted grains that cover the whole surface (as shown in Figure 1(f)). Cross-sectional SEM images show that the oxide thickness increased with exposure time at both temperatures as shown in Figure 2. The scale thickness shows a significant difference between 800°C (as shown in Figure 2(a)-(c)) and 1000°C (as shown in Figure 2(d)-(f)), where the oxide layer was an order of magnitude higher at 1000°C ranging between 2.4 and 5 μm as compared to 1 μm or less oxide thickness for steam exposure at 800°C. This indicates that the oxidation kinetics is much faster at the 1000°C as compared to 800°C.

The initial oxidation of metals at high temperature occurs by the formation of an oxide monolayer on the surface, then further oxidation requires the transportation of either metal or oxygen ions through the oxide layer. This transport phenomenon is controlled by the diffusion rates of these ions and generally follows the Wagner's theory for oxidation which shows that the oxidation process is governed by a parabolic rate [26 - 30]. Therefore the experimental data for oxidation of Alloy 33 at 800°C and 1000°C temperatures were fit to a parabolic equation according to the equation [31 - 34]:

$$d = k_p t^n \quad (1)$$

where d is the oxide layer thickness, k_p is the growth rate of the oxide layer, n is the time exponent and t is the time. Figure 3 shows the change of the oxide thickness as a function of the temperature and exposure time. The thickness of the oxide increases with the time following a parabolic curve with time exponent close to 0.5 for both temperatures, suggesting that alloy is self-protective in these conditions [35]. These results are well aligned with corrosion studies for several advanced steel alloys reported previously [19, 35].

3.2. XRF studies for elemental analyses of surface oxide:

The surface morphology and uniformity of the oxide surface was studied using SEM as discussed in the previous section. Further, X-ray fluorescence (XRF) was used to study the elemental distribution in the oxide scale before and after steam oxidation. XRF analyses of control specimens and Alloy 33 specimens exposed to 100% steam was performed using an area of $3 \times 3 \text{ mm}^2$. As shown in Figure 4, the XRF spectra of Alloy 33 showed mainly iron, nickel, and chromium along, with a small Cu peak (peak G), that we attribute to the kapton tape used to mount the specimens.

Figures 5 and 6 show the Cr, Fe, and Ni-elemental maps on the surface of Alloy 33, where the normalized XRF intensities are scaled from red (maximum) to black (minimum). For Alloy 33 specimens exposed to steam at 800°C , no change in Ni concentration was observed, confirming the minimal diffusion of nickel. The concentration of Cr increased after exposure to steam, owing to the selective oxidation of Cr and the formation of chromium oxide as passivating layer. The Fe concentration increased after 8 and 24 hours of exposure to steam, representing the rapid diffusion of Fe and the formation of spinel as the surface layer. After exposing Alloy 33 to steam at 1000°C , we observed an increase in Cr and Fe concentration supporting the formation of an oxide layer with spinel and chromium oxide, although it was not uniformly distributed, with enhanced Ni diffusion [12].

3.3. GIXRD studies for structural characterization of surface oxide:

The GIXRD analysis of unexposed (control) Alloy 33 revealed that it is polycrystalline alloy with $\gamma\text{-FeNi}$ as the dominant phase, as shown in Figure 7(a). Specimens were exposed to a steam environment at 800°C for different times. After 8 hours of oxidation, we observed the development of a mixed oxide layer consisting of mainly Cr_2O_3 oxide (PDF# 38-1479) with small fraction of FeCr_2O_4 oxide (PDF# 34-0140). The oxide peak intensities continued to increase relative to the base metal with longer exposure times; 24 and 48 hrs. Further, the intensities of the Cr_2O_3 and FeCr_2O_4 oxide peak increased with rise in the steam temperature from 800°C to 1000°C . Specimens oxidized at 1000°C had well-developed oxide peaks after only 8 hours of exposure, as shown in Figure 7(b), compared to the specimen oxidized at 800°C , where more complete oxidation was observed after 48 hrs. This observation aligns with the formation of thicker oxide formed after exposure at 1000°C compared to 800°C as shown in Figure 2.

Depth-resolved GIXRD was used to reveal the development of the oxide layer as a function of the distance from base alloy. Depth-resolved GIXRD patterns for Alloy 33 exposed to steam at 800°C were collected at different tilt angles of the sample relative to the beam. It is clear that as the tilt angle increases (X-rays penetrate deeper into the specimen), the intensity of the Cr_2O_3 peaks increases relative to FeCr_2O_4 , demonstrating that Cr_2O_3 is formed near the metal/oxide interface while FeCr_2O_4 is more abundant at the oxide surface. This trend can be seen clearly in Figure 8 which illustrates the change in the relative intensities between the most intense reflections in both oxides as a function of the tilt angle. We observed that relative intensity of $\text{Cr}_2\text{O}_3/\text{FeCr}_2\text{O}_4$ rose with increasing depth in the specimen towards the Alloy 33 substrate.

3.4. HAXPES studies for analysis of oxidation states of the surface oxide:

HAXPES analysis of the control Alloy 33 specimen shows that elements Cr, Fe, and Ni exist on the surface of the Alloy 33 along with native oxides formed due to exposure to air. The spectrum of Cr $2p_{3/2}$ was fitted using four peaks; the metallic chromium peak at 572.4 eV, the substoichiometric

chromium oxide peak (CrO_x , $1 < x < 1.5$) at 573.1 eV, chromium hydroxide with broad peak at 575.3 eV [36], and small peak representing the stoichiometric Cr_2O_3 .

Exposure to steam at 800°C resulted in the oxidation of Alloy 33 and the formation of Cr_2O_3 oxide with time. The high resolution of HAXPES revealed that the Cr $2p_{3/2}$ spectrum contains the Cr_2O_3 and FeCr_2O_4 oxides along with the chromium hydroxide $\text{Cr}(\text{OH})_3$ after 8 hours of exposure as shown in Figure 9(a). The Fe $2p_{3/2}$ peak showed the presence of the FeCr_2O_4 oxide phase after 8 and 24 hours, which disappeared after 48 hours, as shown in Figure 10(a). This FeCr_2O_4 oxide phase was further confirmed by the presence of the doublet in the Cr $2p_{3/2}$ spectrum after 8 and 24 hours as shown in Figure 9(a). No nickel peaks were detected on the surface after oxidation at 800°C at all exposure times, as shown in Figure 11(a) and 11(b).

After steam exposure at 1000°C, the observation of Fe $2p_{3/2}$ at all exposure times confirmed the presence of the FeCr_2O_4 oxide, as shown in Figure 10(b). This is further supported by presence of the Cr $2p_{3/2}$ doublet seen consistently at all exposures as shown in Figure 9(b). A weak nickel signal was observed on the surface at all exposure times and can be attributed to enhanced diffusion of Ni through the chromium oxide scale and led to the formation of $\text{Ni}(\text{OH})_2$ on the surface, as shown in Figure 11(b).

4. Discussion

Recently after Fukushima incident, there is greater interest in understanding the oxidation mechanisms and qualifying new cladding materials being protective at higher temperature (600°C or above) to gain higher safety margins under accident scenarios and off-nominal conditions. Advanced steel alloys including ferritic steels T91 and HT9, Nanostructured ferritic Alloy, MA956, APMT and Alloy 33 are being extensively screened for accident tolerant applications due their superior corrosion resistance over conventional Zirconium based alloys [3-5, 19]. In this study, a combination of synchrotron methods (XRD, XRF and HAXPES) along with SEM was utilized to understand high temperature steam oxidation of Alloy 33 for fuel cladding applications. We demonstrate that during steam oxidation of Alloy 33 at 800C and 1000C, a protective, compact and continuous chromium oxide scale is formed at substrate/oxide interface which increases in thickness as function of both exposure time and temperature (Figure 2).

Further synchrotron based X-ray fluorescence studies of Alloy 33 confirmed the selective oxidation of Cr as compared to Fe and Ni, which lead to formation of chromium oxide as major phase in the oxide layer (Figure 5-6). Depth resolved XRD showed that oxide layer on Alloy 33 was formed of Cr_2O_3 and spinel FeCr_2O_4 phases, where latter phase is more abundant at the Alloy 33/oxide interface (Figures 7-8). The formation of Cr_2O_3 and spinel FeCr_2O_4 phases was further confirmed when surface oxide was probed using HAXPES. Also, peak shape of the Cr $2p_{3/2}$ in HAXPES analysis was found to be similar at all exposure times at 1000°C while that was not the case at 800°C, indicating that oxidation process has stabilized at 1000°C and composition of oxide scale is not expected to change with time at this temperature.

Our study demonstrates that the protective behavior of the Alloy 33 is due to the formation of the dominant chromium oxide phase that slows diffusion rates of Fe and Ni through the scale compared to the other oxides from the Fe-Cr-Ni system [37]. This observation agrees with previous studies which found, regardless of the Ni and Fe content, that when the concentration of Cr is more than 20%, a predominantly

continuous chromic-oxide scale is formed at the early stages of oxidation [4, 5]. The oxidation of Ni-Fe-Cr alloys can be explained as follows; in the initial stages of oxidation, the Cr_2O_3 oxide layer is formed by cation diffusion [38]. Both Fe and Ni ions enter the Cr_2O_3 layer by chemical substitution, reducing the number of cation vacancies, and hence, the oxidation rate. They are transported through the Cr_2O_3 scale, eventually emerging to form an outer layer with the Fe and Ni spinel phases [37, 38]. As the exposure time increases, Fe interacts with the Cr_2O_3 scale to form a thicker spinel oxide layer (FeCr_2O_4). As a result, the final oxide film consists of two layers; an inner layer of Cr_2O_3 , and outer one rich in spinel oxide [12, 37, 38]. The composition and thickness of the oxide film depend on the, temperature, and exposure time [36, 37 - 41].

Our studies showed that Alloy 33 forms a protective oxide layer after steam oxidation under off-nominal conditions (upto 1000°C). However, a more detailed investigation is needed at higher temperatures up to 1300°C and on effects of irradiation on Alloy 33 to evaluate its full potential as an accident tolerant cladding. Finally these results showed that employing micro-analytical methods in addition to synchrotron characterization techniques provide a deep and detailed understanding of the oxidation of advanced steel alloys in extreme conditions.

5. Conclusions

The application of synchrotron-based GIXRD, HAXPES, and XRF complemented by SEM to investigate the oxidation behavior of Alloy 33 provides a powerful approach to understand the structure of the surface oxide. Our study offers the fundamental knowledge needed to explain the enhanced corrosion resistance of Alloy 33 claddings under accident conditions, where temperatures in the order of 600°C and higher maybe expected. The resistance to corrosion of Alloy 33 can be attributed to formation of protective chromic oxide layer at the alloy-oxide interface.

The oxide surface morphology was found to change with the oxidation temperature such that irregular faceted grains formed after steam exposure at 800°C , while the exposure at 1000°C led to the formation of fiber/needle-like elongated oxide grains. In the same time, the temperature and exposure time led to the increase of the oxide thickness.

The surface oxide structure consisted of two layers in which: the inner chromic oxide as dominant phase at the alloy-oxide interface, and FeCr_2O_4 spinel phase that is more abundant closer to the oxide surface. It was observed that, the increase in temperature from 800°C to 1000°C led to increase in surface oxidation and enhanced the diffusion of Ni. On the other hand, an increase in surface oxide thickness and rise in formation of mixed oxides was observed with increase in exposure time. Such detailed structural characterizations of surface oxide at Alloy 33 in superheated steam environments have not been undertaken before and are crucial to deploying advanced steels as alternative cladding materials for severe accident conditions in advanced nuclear energy systems.

Acknowledgements

This work is supported by Laboratory Directed Research and Development (LDRD) Program (Project no. 13-027) at BNL. Work at the NSLS, BNL is supported under US DOE contract DE-AC02-CH10886. This research used resources of the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science Facility, at BNL under Contract No. DE-SC0012704. Alloy 33 specimens were obtained from GE. CHESS is supported by the NSF & NIH/NIGMS via NSF award DMR-1332208.

References

- [1] K.A. Terrani, S.J. Zinkle, L.L. Snead, Advanced oxidation-resistant iron-based alloys for LWR fuel cladding, *J. Nucl. Mater.* 448 (2014) 420–435.
- [2] M.S. Elbakhshwan, S.K. Gill, A.T. Motta, R. Weidner, T. Anderson, L.E. Ecker, Sample environment for in situ synchrotron corrosion studies of materials in extreme environments., *Rev. Sci. Instrum.* 87 (2016) 105122.
- [3] K.A. Terrani, C.M. Parish, D. Shin, B.A. Pint, Protection of zirconium by alumina- and chromia-forming iron alloys under high-temperature steam exposure, *J. Nucl. Mater.* 438 (2013) 64–71.
- [4] 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.
- [5] T. Cheng, J.R. Keiser, M.P. Brady, K.A. Terrani, B.A. Pint, Oxidation of fuel cladding candidate materials in steam environments at high temperature and pressure, *J. Nucl. Mater.* 427 (2012) 396–400.
- [6] H. Abe, S.M. Hong, Y. Watanabe, Oxidation behavior of austenitic stainless steels as fuel cladding candidate materials for SCWR in superheated steam, *Nucl. Eng. Des.* 280 (2015) 652–660.
- [7] N. Otsuka, H. Fujikawa, Scaling of Austenitic Stainless Steels and Nickel-Based Alloys in High-Temperature Steam at 973K, *Corrosion.* 47 (1991) 240–248.
- [8] C. Sun, R. Hui, W. Qu, S. Yick, Progress in corrosion resistant materials for supercritical water reactors, *Corros. Sci.* 51 (2009) 2508–2523.
- [9] A.R. Paul, K.N. Kaimal, M.C. Naik, S.R. Dharwadkar, Lattice and grain boundary diffusion of chromium in superalloy Incoloy-800, *J. Nucl. Mater.* 217 (1994) 75–81.

- [10] L. Tan, K. Sridharan, T.R. Allen, The effect of grain boundary engineering on the oxidation behavior of INCOLOY alloy 800H in supercritical water, *J. Nucl. Mater.* 348 (2006) 263–271.
- [11] M. Fulger, M. Mihalache, D. Ohai, S. Fulger, S.C. Valeca, Analyses of oxide films grown on AISI 304L stainless steel and Incoloy 800HT exposed to supercritical water environment, *J. Nucl. Mater.* 415 (2011) 147–157.
- [12] F. Huang, J.Q. Wang, E.H. Han, W. Ke, Short-time Oxidation of Alloy 690 in High-temperature and High-pressure Steam and Water, *J. Mater. Sci. Technol.* 28 (2012) 562–568.
- [13] M. V. Cardoso, S.T. Amaral, E.M.A. Martini, Temperature effect in the corrosion resistance of Ni-Fe-Cr alloy in chloride medium, *Corros. Sci.* 50 (2008) 2429–2436.
- [14] A. Munoz, J. Anton, J. Guinon, V. Herranz, Effects of solution temperature on localized corrosion of high nickel content stainless steels and nickel in chromated LiBr solution, *Corros. Sci.* 48 (2006) 3349–3374.
- [15] S. Nagarajan, M. Karthega, N. Rajendran, Pitting corrosion studies of super austenitic stainless steels in natural sea water using dynamic electrochemical impedance spectroscopy, *J. Appl. Electrochem.* 37 (2006) 195–201.
- [16] A. Gildenpfennig, U. Gramberg, G. Hohlneicher, Passivation and corrosion of the metallic high performance materials Alloy 33 and MC-Alloy in different environments, *Corros. Sci.* 45 (2003) 575–595.
- [17] A. Munoz, J. Anton, J. Guinon, V. Herranz, Galvanic studies of copper coupled to alloy 33 and titanium in lithium bromide solutions, *Corrosion.* 58 (2002) 995–1003.
- [18] V. Kain, P. Sengupta, P.K. De, S. Banerjee, Case Reviews on the Effect of Microstructure on the Corrosion Behavior of Austenitic Alloys for Processing and Storage of Nuclear Waste, *Metall. Mater. Trans.* 36A (2005) 1075–1084.
- [19] R.B. Rebak, Alloy Selection for Accident Tolerant Fuel Cladding in Commercial Light Water Reactors, *Metall. Mater. Trans. E.* 2 (2015) 197–207.
- [20] L.F. He, P. Roman, B. Leng, K. Sridharan, M. Anderson, T.R. Allen, Corrosion behavior of an alumina forming austenitic steel exposed to supercritical carbon dioxide, *Corros. Sci.* 82 (2014) 67–76.
- [21] L. Tan, X. Ren, K. Sridharan, T.R. Allen, Effect of shot-peening on the oxidation of alloy 800H exposed to supercritical water and cyclic oxidation, *Corros. Sci.* 50 (2008) 2040–2046.
- [22] L. Tan, T.R. Allen, Y. Yang, Corrosion behavior of alloy 800H (Fe-21Cr-32Ni) in supercritical water, *Corros. Sci.* 53 (2011) 703–711.
- [23] M. Birkholz, *Thin Film Analysis by X-Ray Scattering*, Wiley-VCH Verlag GmbH & Co. KGaA, 2006.
- [24] A. Hammersley, ESRF Internal Report, ESRF97HA02T, FIT2D: An Introduction and Overview, 1997.

- [25] C.G. Ryan, R. Kirkham, R.M. Hougha, G. Moorhead, D.P. Siddons, M.D. De Jonge, D.J. Paterson, G. De Geronimo, D.L. Howarde, J.S. Cleverley, Elemental X-ray imaging using the Maia detector array: The benefits and challenges of large solid-angle, Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip. 619 (2010) 37–43.
- [26] A. Khanna, “Introduction to high temperature oxidation and corrosion,” ASM international, 2002.
- [27] A. Batchelor, L. Lam, M. Chandrasekaran, Materials Degradation and its Control by Surface Engineering, third ed., Imperial College Press, 2011.
- [28] P. Berthod, Kinetics of high temperature oxidation and chromia volatilization for a binary Ni-Cr alloy, Oxid. Met. 64 (2005) 235–252.
- [29] C. Badini, F. Laurella, Oxidation of FeCrAl alloy: Influence of temperature and atmosphere on scale growth rate and mechanism, Surf. Coatings Technol. 135 (2001) 291–298.
- [30] S. Mrowec, A. Stokłosa, Calculations of parabolic rate constants for metal oxidation, Oxid. Met. 8 (1974) 379–391.
- [31] B.P. Mohanty, D.A. Shores, Role of chlorides in hot corrosion of a cast Fe-Cr-Ni alloy. Part I: Experimental studies, Corros. Sci. 46 (2004) 2893–2907.
- [32] N. qiang Zhang, H. Xu, B. rang Li, Y. Bai, D. yu Liu, Influence of the dissolved oxygen content on corrosion of the ferritic-martensitic steel P92 in supercritical water, Corros. Sci. 56 (2012) 123–128.
- [33] D. Laverde, T. Gómez-Acebo, F. Castro, Continuous and cyclic oxidation of T91 ferritic steel under steam, Corros. Sci. 46 (2004) 613–631.
- [34] J.Y. Lee, H.G. Kim, M.R. Choi, C.W. Lee, M.H. Park, K.H. Kim, S.H. Lim, Microstructural evaluation of oxide layers formed on Fe-22Cr-6Al metallic foam by pre-oxidization, Appl. Surf. Sci. 293 (2014) 255–258.
- [35] W.J. Quadackers, J. Zurek, 1.17 Oxidation in Steam and Steam / Hydrogen Environments, Shreir’s Corros. 1 (2010) 407–456.
- [36] 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.
- [37] J.M. Francis, J.A. Jutson, J.H. Buddery, An oxidation study of Ni-Cr-Fe alloys in carbon dioxide at 800 to 1000°C, J. Mater. Sci. 2 (1967) 78–87.
- [38] G.R. Wallwork, The oxidation of alloys, Reports Prog. Phys. 39 (1975) 401–485.
- [39] X. Zhong, E.H. Han, X. Wu, Corrosion behavior of Alloy 690 in aerated supercritical water, Corros. Sci. 66 (2013) 369–379.
- [40] X. Zhong, X. Wu, E.H. Han, Effects of exposure temperature and time on corrosion behavior of a ferritic-martensitic steel P92 in aerated supercritical water, Corros. Sci. 90 (2015) 511–521.

[41] H. Bittner, J. Bell, J. Land, Steam Oxidation of Fe-32 % Ni-23 % Cr Alloys with Manganese and Carbon, *Electrochim. Soc.* 127 (1980) 902–906.

Figure 1: Plane-view SEM images of Alloy 33 samples exposed to steam at 800°C for A) 8, B) 24, C) 48 hours and 1000°C for D) 8, E) 24, and F) 48 hours.

Figure 2. Cross-sectional SEM images of Alloy 33 after exposure to steam at 800°C for A) 8, B) 24, C) 48 hours and 1000°C for D) 8, E) 24, and F) 48 hours.

Figure 3. Thickness of the oxide layer developed on Alloy 33 surface after exposure to steam at 800°C and 1000°C.

Figure 4. X-ray fluorescence spectrum of control Alloy 33 specimen. The spectrum shows the elemental constituents, pile up peaks, the Compton peaks, and the elastic scattering peaks.

Figure 5. 3x3 mm² elemental mapping for A) Chromium, B) Iron, and C) Nickel in Alloy 33 specimens exposed to steam at 800°C for 1) control, 2) 8 hours, 3) 24 hours, and 4) 48 hours. Red color represents the highest concentration, while black represents the lowest.

Figure 6. 3x3 mm² elemental mapping for A) Chromium, B) Iron, and C) Nickel in Alloy 33 specimens exposed to steam at 1000°C for 1) control, 2) 8 hours, 3) 24 hours, and 4) 48 hours. Red color represents the highest concentration, while black represents the lowest.

Figure 7. GIXRD patterns for (a) control and oxidized Alloy 33 at 800°C Alloy 33 specimens for 8, 24, and 48 hours and (b) at 800°C and 1000°C for Alloy 33 for 8 hours at a tilt angle of 0.3 degrees. The arrows point to the Cr_2O_3 (1 0 4) and FeCr_2O_4 (3 1 1) reflections.

Figure 8. Relative intensity of between Cr_2O_3 (1 0 4) and FeCr_2O_4 (3 1 1) reflections as a function of the specimen tilt angle. Specimens were exposed to steam at 800°C for 48 hours.

Figure 9. HAXPES spectra of Cr $2p_{3/2}$ electron binding energy for Alloy 33 samples exposed to steam at (a) 800°C and (b) 1000°C versus normalized intensity.

Figure 10. HAXPES spectra of Fe $2p_{3/2}$ electron binding energy for control and ones exposed to steam at (a) 800°C and (b) 1000°C versus normalized intensity.

Figure 11. HAXPES spectra of Ni 2p_{3/2} electron binding energy for (a) control and (b) samples exposed to steam at 800°C and 1000°C for 48 hours. The noisy data indicates that the amount of Ni on the surface is very small.