Project Number and Title: Improving Corrosion Behavior in SCWR, LFR and VHTR Reactor Materials by Formation of a Stable Oxide.

Project Number: DE-FC-07-06ID14744

Lead US Investigating Organization: The Pennsylvania State University
US Principal Investigator: Prof. Arthur Motta

Lead Collaborating Investigating Organization: Westinghouse Electric Co.

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Executive Summary

The high temperature and corrosive environments of Generation IV reactors cause uniform corrosion to be a major challenge for the materials to be used in the reactor cores and balance of plant. For three different reactor environments (supercritical water reactor (SCWR), lead fast reactor (LFR) and very high temperature reactor (VHTR)) the uniform corrosion rate of cladding and structural materials is a significant concern. The corrosion rate depends strongly on the environment (temperature, pressure, chemistry), but, importantly, the corrosion rate also depends strongly on the alloy composition and microstructure.

A study was conducted of the influence of the alloy microstructure and composition on the formation of a stable, protective oxide in the environments relevant to the SCWR and LFR reactor concepts. Oxide layers formed during various time exposures of samples of ferritic-martensitic alloys (one of which an oxide dispersion strengthened alloy) to 500 and 600°C supercritical water and to 500 and 550°C lead-bismuth eutectic for various times were studied using Microbeam synchrotron radiation diffraction and fluorescence, and cross-sectional transmission electron microscopy. These techniques were used to study the fine structure of these oxides to identify the structural differences between stable and unstable oxide layers.

The examination of the oxides formed both in supercritical water and in lead-bismuth eutectic showed that the oxide structure varied considerably between alloys and, for a given alloy, during the corrosion process. The structure and phase composition of the alloys and the relative thicknesses of the sub-layers of oxide could be correlated well with the corrosion kinetics.

The oxides formed in SCW all have a similar three-layer structure with Fe_3O_4 in the outer layer, a mixture of FeCr_2O_4 and Fe_3O_4 in the inner layer and a diffusion layer containing a mixture of metal grains and oxide precipitates. Large columnar grains form the outer layer while the inner layer contains small equiaxed grains. The main difference between alloys concerns the presence or absence of smaller phases such as Cr_2O_3 , which is observed for certain alloys or at the inner-diffusion layer interface or at the diffusion layer-metal interface. The presence of this Cr_2O_3 phase is suggested to influence strongly the corrosion behavior of the alloy. In all cases, the oxide formed is adherent and protective but the higher chromium and oxide dispersion strengthened alloys exhibit the slowest corrosion rates, which is linked to the presence of Cr_2O_3 at the interfaces.

In both SCW and in lead-bismuth the corrosion mechanism of the F-M steels studied involves preferential grain boundary attack, so that it is possible that using appropriate grain boundary engineering to properly orient the laths, alloys with greater corrosion resistance could be developed.

Project Objectives:

The objective of this study is to understand the influence of the alloy microstructure and composition on the formation of a stable, protective oxide in the environments relevant to the SCWR and LFR reactor concepts, as well as to the VHTR. It is proposed to use state-of-the art techniques to study the fine structure of these oxides to identify the structural differences between stable and unstable oxide layers. The techniques to be used are microbeam synchrotron radiation diffraction and fluorescence, and cross-sectional transmission electron microscopy on samples prepared using focused ion beam. Both as-fabricated and engineered alloys (grain boundary engineered or surface modified) will be studied. The different corrosion rates observed for alloys tested in the same environment are attributed to the different oxide microstructures the oxides formed on the alloys. These techniques can provide detailed structural and chemical composition information on the oxide layer on a sub-micron scale, distinguishing the various sub-layers formed during oxidation. This will allow an understanding of the mechanisms that lead to stable oxide growth, including the effect of surface modification and grain boundary engineering on oxide structure.

The high temperature and corrosive environments of Generation IV reactors cause uniform corrosion to be a major challenge for the materials to be used in the reactor cores and balance of plant. For three different reactor environments (supercritical water reactor (SCWR), lead fast reactor (LFR) and very high temperature reactor (VHTR)) the uniform corrosion rate of cladding and structural materials is a significant concern. The corrosion rate depends strongly on the environment (temperature, pressure, chemistry), but, importantly, the corrosion rate also depends strongly on the alloy composition and microstructure.

High temperature corrosion tests of various alloys are currently being conducted in the environments of relevance to these reactor concepts. In particular, corrosion tests in supercritical water are being conducted on several alloys at the University of Wisconsin. Tests of the same alloys are continuing in a lead-bismuth environment at Los Alamos to select materials for the lead fast reactor. Finally, tests in high temperature helium with controlled levels of impurities will be conducted at the University of Michigan on materials for use in the very high temperature reactor.

The alloys that resist corrosion do so by virtue of their development of a protective oxide layer that limits the access of corrosion species to the underlying metal, leading to stable oxide growth. The differences between a protective and a non-protective oxide lie in the oxide structure, which for a given environment, is determined by the alloy chemistry and microstructure. Indeed, very small changes in alloy microstructure can cause significant differences in corrosion rate [1]. Thus, to design corrosion resistant alloys from a fundamental perspective, it is necessary to understand the mechanisms of formation of a protective oxide and their relationship to the microstructure of the alloy.

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1. Experimental Procedures

1.1 Procurement of initial set of alloy oxides (Task 1)

The initial set of alloys that was envisioned for this study included ferritic-martensitic alloys as well as austenitic steels, oxide dispersion strengthened alloys and some nickel-base alloys. Additionally, several types of environments were also considered as a corrosion medium: supercritical water, lead-bismuth eutectic, pure lead, and helium. Nevertheless, as the project went on *the focus was set primarily on the ferritic-martensitic alloys corroded in supercritical water and lead-bismuth eutectic because the VHTR did not develop protective oxides similar to those in LBE and SCW.* Table 1 shows the elemental composition of the alloys studied.

Table1: Element composition of the alloys studied in wt%, (balanced iron)

Elements	9CrODS (SCW)	HCM12A (SCW)	NF616 (SCW)	T91 (SCW)	HT9 (SCW)	HT9 (LBE)	Model Alloy #3 (LBE)
Cr	8.6	10.83	8.82	8.37	11.94	11.5	9
Si	0.048	0.27	0.102	0.28	0.3	0.4	
Ni	0.06	0.39	0.174	0.21	0.62	0.5	
Mn	0.05	0.64	0.45	0.45	0.69	0.6	
C	0.14	0.11	0.109	0.1	0.21	0.1	
O	0.14						
P	<0.05	0.009	0.012	0.009	0.013		
S	0.003	0.002	0.003	0.003	0.005		
Ti	0.21				<0.01		
Y	0.28						
W	2	1.89	1.87		0.48		
N		0.063		0.048	0.005		
Al		0.001	0.005	0.022	<0.01		
V		0.19	0.194	0.219	0.3		
Co					0.03		
Cu		1.02		0.17	0.02		
Mo		0.3	0.468	0.9	1.03		
Nb		0.054	0.064	0.076			

The corrosion experiments in supercritical water were performed in the supercritical water corrosion loop at the University of Wisconsin. The supercritical loop is described in more detail in other articles [2, 3]. Samples were corroded at both 500°C and 600°C for 2, 4 and 6 weeks, except HT9 which was only corroded at 500°C for 1 and 3 weeks.

The corrosion experiments in lead-bismuth eutectic (44.8 wt% lead and 55.2 wt% bismuth) were performed in two different flowing Lead-Bismuth Eutectic (LBE) loops: the DELTA loop located at Los Alamos National Laboratories (LANL) [4], and another loop located at the Institute of Physics and Power Engineering (IPPE) in Russia. The flow velocities and dissolved oxygen concentrations for both loops are the same, but the temperature in the IPPE loop was higher and the samples were corroded for a longer time than those in the DELTA loop. This means that the oxide layers from samples corroded in the IPPE loop should be more advanced than those corroded in the DELTA loop. The other major difference between the two loops is that the LBE is removed for cleaning from the DELTA loop every 2 weeks, whereas it is not in the IPPE loop. This means that the LBE in the IPPE loop should have higher concentrations of impurities not only from the samples being studied, but from the internal components of the loop itself. Because of this, it is believed that the oxide dissolution rates in the IPPE loop are lower than those experienced in the DELTA loop.

1.2 Sample preparation

The characterization of the oxide layers was performed using two methods: synchrotron X-ray microbeam diffraction and fluorescence, and electron microscopy (both scanning (SEM) and transmission (TEM)). For both these techniques cross sectional samples were prepared in order to study the oxide microstructure as a function of the oxide position from the oxide-solution interface to the oxide-metal interface. The cross sectional samples are 3 mm discs with a thickness of about 1-2 mm and were prepared in manner described in detail in previous students' theses [5, 6]. The samples received from the corrosion tests consisted of small portions of rectangular shaped with an oxide layer on both sides of the coupon. The process of obtaining the characterization-ready cross sectional samples from these coupon parts is described schematically in Figure 1.

Figure 1: Schematic of the process of mounting cross-sectional samples and a schematic of a cross sectional sample.

The coupon parts are cut using a diamond saw to obtain small rectangular strips of about 2 mm in width. This strip contains two oxide surfaces but one of the two was sacrificed as the strip was mechanically thinned in order to obtain a thickness of about 0.3 mm. The mechanical thinning was achieved by using crystal bond to protect the oxide layer studied, while the other side was mechanically polished using 400 grit silicon paper. Once the strip was thin enough, it was placed inside the slot of the molybdenum rod, which was itself placed in a 3mm brass tube. Everything was then glued together using Gatan G-1 epoxy.

The molybdenum rod maintains mechanical stability of the sample and decreases the volume fraction of epoxy used. The molybdenum rod has a diameter of 2.26 mm and a length of about 40 mm. The slit in the rod is about 0.4-0.5 mm wide. The brass tubes have an external diameter of 3 mm and an internal diameter of 2.3 mm and about the same length as the molybdenum rods. The Gatan G-1 epoxy was cured at 80°C for 15-20 minutes. Once the sample has been mounted in such a way, the rods are cut into small discs that are about 1-2 mm thick using a diamond saw.

The small cross sectional discs are polished to obtain a mirror polish. 400 and 600 grit silicon carbide paper was used first on both sides in order to obtain two parallel surfaces. Then one side was polished further using Allied 8" 1200 grit silicon carbide adhesive discs followed by 1 micron diamond paste and 0.05 colloidal silica solution. These mirror polished samples were then used directly for the synchrotron experiments and were subsequently mounted on SEM stubs with silver paint for SEM observation.

1.3 Synchrotron X-ray diffraction and fluorescence

Description of the Advanced Photon Source Synchrotron:

The main characterization technique used to study the microstructure of the oxide layers formed on the samples was synchrotron radiation microbeam X-ray diffraction and fluorescence at the Advanced Photon Source (APS) located at the Argonne National Laboratory near Chicago, Illinois. The APS is a third generation synchrotron whose brilliance is orders of magnitudes higher than conventional Cu-K α and Mo-K α X-ray diffraction machines. Figure 2 shows a comparison of the brilliance between different X-Ray sources.

Figure 2: Comparison of X-Ray brilliances from different X-Ray sources in the United-States: Advanced Light Source (ALS), Berkeley, CA; Advanced Photon Source (APS), Argonne, IL; National Synchrotron Light Source (NSLS), Upton, NY; and Stanford Synchrotron Research Laboratory (SSRL), Stanford, CA. [<http://www.aps.anl.gov/>]

Synchrotron radiation as an X-ray source is unique in that it produces very high brilliance over a range of energies or wavelengths. The high photon flux enables us to detect small volume fractions of phases that would otherwise not be detected. Moreover, at the APS the beamline used was the 2-ID-D beamline, which can be focused to a 0.2 μ m spot.

Description of the experiments:

Figure 3 shows a schematic of the experimental setup. One of the major advantages of this experiment and the beamline facility is the simultaneous capture of chemical and elemental data by X-ray fluorescence, and of microstructural and phase information by X-ray diffraction. The experiment consists in scanning step by step through the oxide layer, and we simultaneously obtain both the elemental and phase information as a function of the position in the oxide layer. For this study, these elements followed using the fluorescence were: iron (Fe), chromium (Cr), aluminum (Al), silicon (Si), yttrium (Y), molybdenum (Mo), lead (Pb), argon (Ar), titanium (Ti), vanadium (V), manganese (Mn), cobalt (Co), nickel (Ni), and copper (Cu).

Table 2: Two-theta diffraction angles for Fe₃O₄, FeCr₂O₄, Cr₂O₃ and Fe bcc with their relative intensities for an energy of 9.5 keV.

Fe ₃ O ₄		FeCr ₂ O ₄		Cr ₂ O ₃		Fe bcc	
<i>2-theta</i>	<i>Intensity</i>	<i>2-theta</i>	<i>Intensity</i>	<i>2-theta</i>	<i>Intensity</i>	<i>2-theta</i>	<i>Intensity</i>
(220): 25.41	30	(220): 25.45	33	(104): 28.34	100	(110): 37.38	100
(311): 29.87	100	(311): 29.94	100	(110): 30.51	93		
(222): 31.23	8	(222): 31.32	7	(006): 33.47	7		
(400): 36.225	20	(400): 36.31	22	(113): 34.91	35		
				(202): 37.17	6		

1.4 Scanning Electron Microscopy (SEM)

Although unique information can be obtained using synchrotron X-ray diffraction and fluorescence to analyze the microstructure of oxide layers, the positioning of the microbeam would be done blindly. Without additional information, it is not possible to know where on the sample the scan was acquired and to relate the information obtained to particular features in the oxide layer. Consequently, the microbeam synchrotron analysis has to be complemented by scanning electron microscopy, which gives “eyes” to the X-ray data.

The SEM used was a FEI Quanta 200 ESEM (environmental scanning electron microscope). The scanning electron microscope (SEM) was equipped with an energy dispersive spectroscopy (EDS) system, which enabled the acquisition of elemental data which could confirm the fluorescence data. As stated in the sample preparation section, the samples analyzed with the SEM were prepared in the same way as the microbeam X-ray diffraction and fluorescence samples, but they were additionally mounted upon SEM stubs using carbon tape. The samples were examined under high vacuum (10⁻⁷ bars) using backscattered electron (BSE) imaging at an energy of 20 kV. BSE imaging is highly dependent on the atomic number Z of the material since the primary electrons coming from the beam are reflected or backscattered out of the material. The higher the atomic

number Z the brighter the resulting image. Thus, the contrast is essentially a chemical contrast dependent on the atomic number Z.

Conventional SEM imaging was also accompanied by the use of EDS and especially EDS-mapping. EDS-mapping creates an elemental image of the conventional SEM image. A region where an element is abundant will correspond to a bright area in the EDS-map and vice-versa. This creates a distribution of the main elements throughout the oxide layer but can also be used by zooming on a special feature and determining its chemical composition. This is the equivalent for the SEM image of what the fluorescence data was for the X-ray diffraction.

1.5 Transmission Electron Microscopy (TEM)

Focused Ion Beam preparation:

The TEM samples were prepared using a Focused Ion Beam (FIB). The model is a FEI Company Quanta 200 3D Dual Beam FIB. The FIB was used instead of traditional mechanical thinning with ion milling, primarily because the FIB allows for the production of site-specific specimens, a greater viewing area, and a greater degree of reproducibility. This means that if the oxide layer to be examined is small enough ($\sim 10\mu\text{m}$) a specimen can be produced that will include electron transparency of the entire oxide layer, the interface between the oxide and the metal, as well as part of the metal layer with lateral electron transparency up to 10 microns or more. Preparing samples with the FIB also allowed us to have a much larger viewing area than previous methods, ensuring consistency throughout the specimen.

The FIB uses Ga^+ ions to mill samples as well as to deposit a layer of tungsten or platinum to protect the sample during milling and also to use the tungsten/platinum deposition to attach the milled sample to a sample holder. The Ga^+ ions are extracted from the source much in the same way as the SEM extracts electrons from its source.

The method used to prepare the samples in this study has been termed the FIB *in-situ* lift-out (INLO) and was chosen for convenience, reproducibility, and versatility. The benefit of using the lift-out technique is that it requires no initial specimen preparation. The INLO method employed in this study removes the specimen first then thins it. Removing the sample and attaching it to a sample holder with tungsten before thinning allows for the sample to relieve itself of stress during thinning as well as to have a heat sink during TEM examination. This method also has the advantage of full range of tilt during examination in the TEM and the sample can be returned to the FIB for additional thinning if necessary.

Removing the sample and attaching it to a sample holder with tungsten before thinning allows for the sample to relieve itself of stress during thinning as well as to have a heat sink during TEM examination. This method also has the advantage of full range of tilt during examination in the TEM and the sample can be returned to the FIB for additional thinning if necessary.

The step-by-step process for producing a TEM specimen using the FIB is as follows:

First, a layer of tungsten or platinum approximately 1 μm wide x 10 μm long x 3 μm high is deposited to the area of interest to protect the sample during the milling and thinning processes.

After the protective layer is deposited, the region of interest is milled at an angle of 22° using a horseshoe shape (with an approximate thickness of 1.5 μm), rotated 180° , and milled again to produce a wedge-shaped sample as illustrated in Figure 4. The sample is trench-milled at the maximum current of 7 nA in order to limit the amount of time spent on this step. The milling time is determined by considering the major elements of the sample and their respective sputtering yields (the number of ejected ions divided by the number of incident ions). The FIB/SEM system has already been preset for silicon and the corrected sample milling depth is calculated by multiplying the desired depth by the ratio of silicon's sputtering yield and the sample's sputtering yield. Because all of the major elements within our samples have higher sputtering yields than silicon, correcting the milling depth ends up reducing the total milling time.

Figure 4: Illustration of trench-milling a sample in the FIB

After the sample is milled free from the substrate, it is attached to a tungsten microprobe by tungsten deposition, transferred to a FIB/TEM sample holder where the sample is also attached by tungsten deposition, and then the microprobe is detached from the sample by milling it with the FIB. All milling steps were completed at a voltage of 30 keV.

The sample then undergoes several steps of thinning in which decreasing currents are used (1 nA-30 pA) until the sample has reached electron transparency or an approximate thickness of 100 nanometers or less. Electron transparency is determined approximately by dropping the voltage of the SEM to 5 keV, and thinning the sample until it appears bright. At this point of maximum brightness, not only are the electrons reflecting from the viewable surface of the sample back to the SEM detector but the electrons are also reflecting from the back surface of the sample as well.

This method has been used to produce TEM specimens from the cross-sectional samples prepared for the synchrotron. The cross-sectional samples were used when the oxide layers, which had thickness in excess of 10 microns, proved to be too thick to be prepared from the bulk samples. This allowed the examination of a sample with an oxidation layer of approximately 80 microns by preparing several specimens from the cross-sectional samples as shown in Figure 5. From this image, the locations of some TEM samples that were fabricated for this study can be seen.

Figure 5: Trench-milled samples from 3 mm cross-sectional disks.

Transmission Electron Microscope:

TEM imaging, diffraction analysis, and chemical analysis using Energy Dispersive Spectroscopy spectra were obtained using a Philips 420, 120 keV TEM with a tungsten filament with the aid of a Gatan double tilt sample holder. Electron energy loss spectroscopy was performed on a JEOL, LaB₆ filament based 200 keV TEM, with the aid of a Gatan Imaging Filter (GIF). The energy filtered images were acquired by selecting peaks for each desired element and integrating the intensity under the peaks. It is important to select peaks that do not overlap, in order to provide individual images of each selected element.

2. Alloys exposed to supercritical water (SCW)

2.1 Corrosion of 9CrODS alloy

2.1.1 Introduction

9CrODS is a ferritic steel containing a fine dispersion of yttrium-titanium rich oxide nano-particles dispersed in the alloy matrix. This alloy was developed by Japan Atomic Energy Agency for application in sodium cooled fast reactors [8, 9]. The ODS Y₂O₃ particles were mechanically mixed with the other elements before being sealed in cans under vacuum of 0.1 Pa at 400°C, and then hot-extruded and forged at 1150°C. The alloy was normalized for one hour at 1050°C, air-cooled, and then tempered at 800°C for one hour. The details of the manufacturing process are described elsewhere [9]. It exhibits higher creep strength and radiation damage resistance than conventional ferritic-martensitic steels [8, 9]. This alloy also exhibits good corrosion resistance, which has

been suggested to be caused by the enhanced chromium segregation at the grain boundaries to form Cr_2O_3 [10, 11].

The corrosion experiments were performed in the natural circulation supercritical water corrosion loop at the University of Wisconsin. The supercritical loop is described in more detail in other articles [2, 3]. The pressure was 25 MPa, the dissolved oxygen content was ~25ppb, and the temperature and exposure time depended on the sample: 500 or 600°C for 2, 4 or 6 weeks.

The oxide layers formed on these samples were characterized using microbeam synchrotron X-Ray diffraction and fluorescence, and scanning electron microscopy (SEM). Preliminary results on 9CrODS corroded at 600°C for 4 weeks have already been described in a previous article [12]. This paper reports expanded analysis of this alloy to include the influence of exposure time and temperature on the oxide microstructure.

2.1.2 Characterization of the oxide layer

2.1.2.1 Samples oxidized at 600°C

Figure 6 shows SEM images and fluorescence data for samples oxidized at 600°C for 2, 4 and 6 weeks. The SEM images showed that all samples exhibited a three-layer oxide structure: outer, inner and diffusion layers. As observed previously, the outer oxide contained only Fe_3O_4 , the inner oxide contained a mixture of Fe_3O_4 and FeCr_2O_4 , and the diffusion layer contained a mixture of oxide precipitates (FeCr_2O_4) and iron bcc metal grains. Additionally, the SEM images of the inner layer showed periodic lines of pores suggesting some periodicity in the oxidation process.

In all samples, the outer-inner oxide interface was distinct and is thought to be the original metal-water interface [11]. This is in agreement with an overall oxidation mechanism of an outer oxide formed by outward diffusion of the iron cations (Fe^{2+}) produced by the oxidation of the base metal, and inner oxide formation by inward diffusion of oxygen anions (O^{2-}) [10, 11]. Figure 7 shows a schematic of this oxidation mechanism. Both the outer and the inner oxide of the 4 and 6-week samples shown in Figure 6 were divided into two sub-layers, one porous and one non-porous. In the outer oxide, the porous sub-layer was observed near the coolant whereas in the inner oxide it was observed near the inner oxide-diffusion layer interface.

The fluorescence data in Figure 6 show both the iron $K\alpha$ (top line) and the Cr $K\alpha$ lines (bottom line). The fluorescence plots clearly showed the three layers. The outer layer contained only iron (and oxygen), while the inner layer was enriched in chromium compared to the base metal and the diffusion layer. The chromium content of the diffusion layer was intermediate to that of the metal and the inner layer. Additionally, a chromium enrichment peak (circled) was observed at the inner oxide-diffusion layer interface for the 2-week sample but at the diffusion layer-metal interface for both the 4 and 6-week samples.

Figure 6: SEM images and fluorescence data for 9CrODS 600°C 2, 4 and 6-week samples.

Figure 7: Schematic of the oxidation mechanism in supercritical water

A major change occurred between 2 and 4 weeks, with the formation of a relatively thick oxide film at the diffusion layer-metal interface. The beginning of the formation of this film was observed in the SEM image of the 2-week sample in the region labeled "A". The fact that no oxide precipitates were observed beyond this film suggested that this film may have a significant role in the corrosion resistance of 9CrODS. The formation of this film, between the 2 and 4-week samples, was accompanied by a shift of the chromium enrichment peak observed in the fluorescence data from the inner oxide-diffusion layer interface to the diffusion layer-metal interface. Consequently, the film was formed by a chromium rich oxide, which the diffraction data showed was Cr_2O_3 .

The 9CrODS 600°C 2-week sample had a diffusion layer three times larger than the inner layer, which suggested oxygen had diffused deep into the alloy relatively fast. The diffusion layer ended at a uniform distance from the inner oxide-diffusion layer interface, which likely represents the location where the solubility limit of oxygen in the metal was exceeded. Oxide precipitates formed when the oxygen concentration was above that limit. The diffraction data for the 2-week sample showed that the outer layer was Fe_3O_4 , the inner layer was a mixture of Fe_3O_4 and FeCr_2O_4 , and the diffusion layer only contained FeCr_2O_4 . Moreover, Cr_2O_3 was observed at the inner oxide-diffusion layer interface, where the fluorescence data showed chromium enrichment. The presence of

Cr_2O_3 along with chromium enrichment at the inner oxide-diffusion layer interface makes this interface play an active role in the corrosion resistance since Cr_2O_3 is known to hinder diffusion of oxygen and iron ions [13, 14]. Figure 8 shows the diffraction data for 9CrODS 600°C 2 weeks acquired with a 0.2 μm step-size.

Figure 8: Diffraction data of the inner and diffusion layers for 9CrODS 600°C 2 weeks acquired using a 0.2 μm step-size.

The 9CrODS 600°C 4-week sample showed a shift of the main peak associated with Fe_3O_4 - FeCr_2O_4 from 29.94° (FeCr_2O_4) in the diffusion layer to 29.87° (Fe_3O_4) in the middle of the inner layer. Figure 9 shows a close-up of the diffraction data on the peak associated with the Fe_3O_4 - FeCr_2O_4 (311) plane where this shift is seen.

Figure 9: Close-up of the diffraction data for 9CrODS 600°C 4-weeks on the peak associated with the (311) plane of both Fe_3O_4 and FeCr_2O_4 .

Figure 10 shows the diffraction data for 9CrODS 600°C 4 weeks acquired using a 0.2 μm step-size. Apart from thicker oxide layers, the main difference between the 2-week and the 4-week samples was the presence of the continuous Cr_2O_3 film. This film

was a few microns thick and is composed of both Cr_2O_3 and FeCr_2O_4 . However, immediately next to the interface with the metal, the film was a continuous layer of Cr_2O_3 with no FeCr_2O_4 . Peaks associated with FeCr_2O_4 were observed in the region of the film nearer to the diffusion layer. This phase layout is in agreement with thermodynamic data since Cr_2O_3 forms at the lowest oxygen potential, followed by FeCr_2O_4 and then at higher oxygen potentials by Fe_3O_4 [15]. Figure 11 shows the analysis of diffraction data taken in the film at the diffusion layer-metal interface. It is likely this continuous Cr_2O_3 present at the film-metal interface was responsible for almost stopping the diffusion of oxygen beyond the film, thus inhibiting further oxidation of the metal [13]. Cr_2O_3 has been shown to serve both as a kinetic and thermodynamic oxidation barrier since the diffusion of species is slow through Cr_2O_3 but it also decreases the oxygen potential on the inner interface, thus hindering oxidation of the metal [14]. Additionally, a TEM investigation confirmed the presence of this Cr_2O_3 film [16].

Figure 10: Diffraction data for 9CrODS 600°C 4 weeks acquired using a step-size of 0.2 μm .

Diffraction peaks associated with Cr_2O_3 (full circles) were still observed at the inner oxide-diffusion layer interface. Since Cr_2O_3 hinders the diffusion of oxygen, this may explain the slow advancement of the inner oxide in the diffusion layer. Additionally, a large peak (circled with dotted line and labeled FeO) was observed in the inner oxide at a diffraction angle of about 35.2° . This peak was thought to be associated with the FeO (200) plane which diffracts at an angle of 35.29° .

Figure 11: Detailed PeakFit analysis of the oxide ribbon at the diffusion layer-metal interface.

The 9CrODS 600°C 6-week sample appeared to be similar to the 4-week sample, in particular because of the presence of the Cr_2O_3 film. However, the microstructure of this sample differed from the 4-week sample. First, almost no FeCr_2O_4 was observed and Fe_3O_4 was present throughout the oxide layers including the diffusion layer. Figure 12 shows the diffraction data for 9CrODS 600°C 6 weeks.

In the 6-week sample, the Cr_2O_3 present for shorter exposure times at the inner oxide-diffusion layer had disappeared, which could also explain the disappearance of the line of pores observed at that interface in the 2 and 4-week samples. The 6-week sample showed a non-linear inner oxide-diffusion layer interface and a greater interpenetration of the inner oxide into the diffusion layer (observed on the SEM image) suggesting advancement of the inner oxide into the diffusion layer. This is thought to be linked with the absence of Cr_2O_3 at this interface.

Additionally, a strong peak at an angle of 31.9° (circled with dotted line and labeled $\text{Fe}_{0.98}\text{O}$) was observed right before the Cr_2O_3 film in the diffusion layer. This peak may possibly be associated with the (101) plane of $\text{Fe}_{0.98}\text{O}$ normally located at 31.88° . Moreover, a remnant of the possible FeO peak that was observed in the 4-week sample was seen in the middle of the inner oxide.

Figure 12: Diffraction data for 9CrODS 600°C 6 weeks acquired using a 0.2 μm step-size

2.1.2.2 Samples oxidized at 500°C

Three samples were oxidized at 500°C for the same exposure times as for the 600°C samples: 2, 4 and 6 weeks. Only the 4 and 6 week samples were characterized using microbeam synchrotron radiation diffraction and fluorescence. Figure 13 shows the SEM images of the three samples.

Figure 12: SEM images for 9CrODS 500°C exposed to supercritical water for 2, 4 and 6 weeks.

The oxide layers formed at 500°C were different from the samples oxidized at 600°C in several aspects. First, the oxide layers were much thinner. Whereas the outer

layer thickness for the 600°C 4-week sample was about 38 μm , it was only 6.5 μm for the 500°C 4-week sample. Consequently, the oxidation is significantly slower at 500°C. The diffusion layer-metal interface on the 6-week sample suggested that the diffusion of oxygen occurred by a grain boundary process, since oxides preferentially precipitated at the metal grain boundaries. In the 600°C samples the oxide precipitates in the diffusion layer had not seemed to be formed by a grain boundary process since they had not outlined the metal grains.

Second, no distinct diffusion layer similar to that seen in the 600°C oxide layer samples was observed. A slight difference in contrast (the diffusion layer appeared darker than the metal) showed the presence of a diffusion layer. This is also observed in the fluorescence data, which show only a gradual decrease in the chromium content from its level in the inner layer to that in the metal. Figure 13 shows the fluorescence data for the 500°C 4 week sample (left) and that for the 500°C 6-week sample (right). The 500°C 6-week sample was different from the two other 500°C samples in that respect, since its diffusion layer appeared similar to its inner oxide except with slightly lighter contrast. Nevertheless, the diffraction data showed very few oxide peaks in the diffusion layer of all the samples. This suggests that the diffusion layer in the 500°C samples consists of a solid solution of oxygen containing few oxide precipitates.

Figure 13: Fluorescence data for the 9CrODS 500°C 4-week sample (left) and for 9CrODS 500°C 6-week sample (right).

Finally, the diffraction data showed that the main oxide phase formed throughout the oxide layers was Fe_3O_4 . FeCr_2O_4 appeared mainly at the outer-inner oxide interface. Figure 14 shows the 3D diffraction plot for the 9CrODS 500°C 4-week sample and Figure 15 that for the 9CrODS 500°C 6-week sample. Figure 16 shows a close-up of the diffraction data on the main peak associated with Fe_3O_4 - FeCr_2O_4 showing the presence of FeCr_2O_4 at the outer-inner oxide interface. Little Cr_2O_3 was observed but few peaks associated with that phase were seen both in the middle of the inner oxide and in the diffusion layer near the diffusion layer-metal interface. No chromium enrichment was observed in the fluorescence data at the locations where Cr_2O_3 was observed. Consequently, it appears that insufficient Cr_2O_3 formed (due to a low diffusion coefficient of chromium at 500°C) to be able to serve as a barrier for oxidation, in

contrast to the 600°C samples. Several studies have shown that chromium diffuses much slower in ferritic steel at 500°C than at 600°C by about two orders of magnitude (about $8 \times 10^{-20} \text{ m}^2 \cdot \text{s}^{-1}$ at 600°C and $3.5 \times 10^{-22} \text{ m}^2 \cdot \text{s}^{-1}$ at 500°C) [17, 18]. Thus at 500°C the diffusion of chromium in ferritic steel is too low for chromium to diffuse enough to form Cr_2O_3 .

Figure 14: 3D Matlab plot of the diffraction peaks for the 9CrODS 500°C 4-week sample.

Figure 15: 3D Matlab plot of the diffraction peaks for the 9CrODS 500°C 6-week sample.

Figure 16: Close up of the diffraction data centered on the 29.9° peak for 9CrODS 500°C 4 and 6 weeks

2.1.3 TEM analysis of the oxide layers formed on the 9CrODS alloy

A TEM specimen was prepared from the metal/diffusion layer interface in the 2-week sample as shown in Figure 17. TEM specimens were also prepared from the 4-week sample as shown in Figure 18.

Figure 17: SEM backscattered electron image of the oxide sub-layers on 9Cr ODS, after 2 week exposure to 600°C SCW showing the location of the TEM sample.

Figure 18: SEM secondary electron image of 9Cr ODS, after 4 weeks exposure to 600°C showing the locations for TEM samples.

2.1.3.1 9Cr ODS 4 weeks

Figures 19 to 22 show the 4 different TEM samples that we made and studied for the 9CrODS 4-week sample as was shown in Figure 18. Figure 19 corresponds to the outer-inner layer interface, Figure 20 to the inner-diffusion layer interface and Figures 21 and 22 to the diffusion layer-metal interface.

Figure 19: TEM bright field image of the outer-inner layer interface of the 9CrODS 4-week sample.

Figure 20: TEM bright field image of the inner-diffusion layer interface of the 9CrODS 4-week sample.

Figure 21: TEM bright field image of the diffusion layer-metal interface of the 9CrODS 4-week sample.

Figure 22: TEM bright field image of the diffusion layer-metal interface of the 9CrODS 4-week sample.

Figure 23 (a) is a cross-sectional bright field image of the large grains of the outer oxide layer (a few microns in width). The corresponding diffraction pattern is consistent with the Fe_3O_4 [011] zone axis. It should be noted that the phases FeCr_2O_4 and Fe_3O_4 are often reported in oxide layers formed on ferritic-martensitic alloys, and they have the same crystal structure with only a small difference in lattice parameter, which is nearly indistinguishable via electron diffraction. In this case we distinguish between the two phases via elemental information from EDS.

Figure 22: TEM BF images and corresponding DPs indexed as (a) the Fe_3O_4 zone axis [011], from an outer oxide grain and (b) the FeCr_2O_4 zone axis [001], from the inner oxide of the 4 week 9Cr ODS sample.

Figure 23 (b) shows a bright field image of the small grains of the inner oxide layer and the corresponding diffraction pattern indexed as the FeCr_2O_4 [001] zone axis.

Although the inner oxide grains are smaller than the diffraction aperture, a single pattern is formed, indicating that many grains have similar orientations. EDS spectra, taken from the outer oxide layer and the inner oxide layer, confirm that the inner oxide is rich in Cr (via Cr-K) while the outer oxide is formed from only Fe.

The elemental distribution in the diffusion layer is considerably more complex than in the other layers. As a result, energy filtered and EDS maps were employed. Figure 24 shows a bright field TEM image of the diffusion layer/metal interface and corresponding Fe (EFTEM), O (EFTEM), and Cr (EDS) maps. The bright field image shows the sample to be thicker on one side and shows damage caused by sample preparation. The Cr_2O_3 band corresponds to the bracketed region marked "B" (it is clear that this region contains Cr and O and little Fe), while the remainder of the diffusion layer is marked "A". The chromium and oxygen are strongly correlated, whereas the iron appears to be anticorrelated to the chromium and oxygen. This indicates that the chromium oxidizes preferentially to iron as would be expected. The elemental maps also reveal that there is a band rich in all three elements below the diffusion layer; hence, this band appears to be a two-phase mixture of small Fe-rich regions (likely Fe metal) and Cr oxide. Figure 25(a)(inset) is a diffraction pattern, which reveals that the band contains Cr_2O_3 . Figure 25(b)(inset) is a diffraction pattern from the region in the diffusion layer, immediately adjacent to the Cr_2O_3 grains at the oxide front, which was indexed as FeCr_2O_4 . This FeCr_2O_4 grain was one of many found trailing the Cr_2O_3 band. Cr_2O_3 and FeCr_2O_4 diffraction peaks were also found in the same locations in this sample during previous microbeam synchrotron diffraction analysis [5]. In the rest of the diffusion layer, a mixture of Cr-rich oxides and Fe metal are seen.

EDS confirms the diffraction analysis. Figure 26 is an EDS spectrum taken from the region at the oxide front identified as Cr_2O_3 , compared to a spectrum taken from the metal. The spectrum from the oxide band reveals chromium and oxygen peaks with little iron present; whereas, the reference spectrum from deep inside the metal layer reveals this region is predominantly iron with a small fraction of chromium and no detectable oxygen, which agrees with the diffraction analysis.

Figure 24: TEM bright field image and corresponding Fe, O, and Cr elemental maps of diffusion layer from 9Cr ODS 600°C, 4 weeks.

Figure 25: TEM bright field images and corresponding diffraction patterns of (a) Cr_2O_3 with zone axis of $[210]$ and (b) FeCr_2O_4 , with zone axis $[013]$, within the diffusion layer from 9Cr ODS 4-weeks sample.

Figure 26: EDS spectra of reference metal and region determined to be Cr_2O_3 in the diffusion layer of 9Cr ODS, 4-week sample.

2.1.3.2 9Cr ODS 2-weeks

Figure 27 shows the TEM bright field image of the diffusion layer of the 9CrODS 2-week sample.

Figure 27: TEM bright field image of diffusion layer at the diffusion layer/metal interface of 9Cr ODS, 2-week sample. Arrows indicate the metal/diffusion layer interface.

A cross-sectional sample of the diffusion layer-metal interface was examined. Iron (EF), oxygen (EF), and chromium (EDS) elemental maps were also obtained for the 2-week sample (Figure 28). As in the 4-week sample, chromium and oxygen are strongly correlated within the diffusion layer. Chromium and oxygen-rich filaments are also observed in the maps, which correspond to the dark features seen in the diffusion layer in the SEM image in Figure 1.

Figure 28: Elemental maps of iron, oxygen, and chromium for the diffusion layer of 9Cr ODS, 2-week sample.

Figure 29(a) is a bright field image of an iron-containing grain in the diffusion layer, indexed as Fe-bcc. Figure 29(b) is a bright field image and corresponding diffraction pattern of a grain with high oxygen content. This diffraction pattern was indexed as FeCr_2O_4 . These and several other diffraction patterns indicate that the chromium and oxygen-rich regions in the diffusion layer are FeCr_2O_4 and that the iron-rich regions are bcc Fe.

In order to confirm these conclusions, the composition of these regions was analyzed using EDS. Figure 30 is the EDS spectrum from the FeCr_2O_4 grain shown in Figure 29(b). The spectrum reveals strong chromium peaks, and smaller iron peaks. It can be seen from the spectrum that the intensity of the chromium $K_{\alpha 1}$ peak is approximately twice that of the iron $K_{\alpha 1}$ peak. Coupled with the diffraction analysis this indicates that the grain is FeCr_2O_4 .

The FeCr_2O_4 filament-like grains found within the diffusion layer were shorter than $1.5\ \mu\text{m}$ in their longest dimension, indicating that the finger-like structure consists of several grains. The Fe grains were also small, in general $1\ \mu\text{m}$ or less in their longest dimension and irregular in shape, as seen in Figure 29(a).

While FeCr_2O_4 and bcc Fe were found within the diffusion layers of both the 2- and 4-week samples, Cr_2O_3 was also found within the diffusion layer at the diffusion layer/metal interface of the 4-week sample. Between these two stages of corrosion, the thickness of the diffusion layer is reduced by a third while that of the inner oxide layer approximately doubles. This suggests that the corrosion has slowed down, and that internal layer restructuring is taking place between the inner and diffusion layers, likely due to the development of the Cr_2O_3 band at the diffusion layer-metal interface. These observations largely agree with the microbeam synchrotron radiation fluorescence and diffraction examination of the same sample [5,8].

Figure 29: TEM bright field images and corresponding diffraction patterns of (a) Fe-bcc, with a zone axis of [001] and (b) FeCr_2O_4 , with a zone axis of [101], within the diffusion layer of 9Cr ODS, 2-week sample.

Figure 30: EDS spectrum of FeCr_2O_4 grain within the diffusion layer of 9Cr ODS, 2 week sample.

2.2 Corrosion of HCM12A

2.2.1 The structure of the base HCM12A alloy

HCM12A is a ferritic-martensitic steel alloy containing about 11 wt% of chromium. The samples studied were normalized at 1050°C for 1 hour then air-cooled before being tempered at 770°C for 7 hours and air-cooled. The corrosion experiments were performed in the supercritical water corrosion loop at the University of Wisconsin. The supercritical loop is described in more detail in other articles [2, 3]. The pressure used was 25 MPa, the temperature was 600°C and the dissolved oxygen content was ~25ppb. Three exposure times were used: 2, 4 and 6 weeks.

The oxide layers formed on HCM12A exposed to supercritical water have been previously studied using scanning electron microscopy (SEM), X-ray diffraction (XRD), and electron backscatter diffraction (EBSD) [15, 19, 20]. These studies have shown that HCM12A forms a dual layer structure at 500°C with Fe_3O_4 in the outer layer and spinel $(\text{Fe,Cr})_3\text{O}_4$ in the inner layer with some evidence of Cr_2O_3 [15]. At 600°C an internal oxidation layer or diffusion layer is also observed, showing evidence of FeO [19]. The implantation of an yttrium coating prior to oxidation appears to enhance the corrosion resistance of the alloy [19].

In the present study, HCM12A samples were exposed to 600°C SCW for three different exposure times: 2, 4 and 6 weeks. The 4-week sample was implanted with an yttrium surface coating prior to oxidation to investigate the influence of this coating on the corrosion resistance. The oxide layers formed on HCM12A samples were characterized using scanning and transmission electron microscopy (SEM and TEM), and microbeam synchrotron radiation diffraction and fluorescence. The focus is on determining the phases during the formation and evolution of the oxide layer and to understand the influence of the ferritic-martensitic lath structure of the base metal on the advancement of the oxide layer.

2.2.2 Characterization of the oxide layers

2.2.2.1 Samples oxidized at 600°C

Figure 31 shows SEM images and fluorescence spectra of the HCM12A samples oxidized at 600°C for 2, 4 and 6 weeks. The yttrium coating is observed as the white line in the outer layer. The oxide layers formed on HCM12A are similar to the ones observed for other candidate ferritic-martensitic alloys. The SEM images show that in 600°C SCW HCM12A forms a three-layer structure including a non-uniform diffusion layer unlike the one formed for the 9CrODS alloy. The porosity increases in the outer layer and decreases

in the inner layer with increasing exposure time. Additionally, oxides form preferentially at lath boundaries in the diffusion layer, which suggests that the oxide advancement is strongly influenced by the base metal microstructure since. The fluorescence data show that the inner layer is enriched in chromium and that the outer layer contains no chromium. Local chromium enrichments are observed at the inner layer-metal interface in the 4-week sample and at the diffusion layer-metal interface (about 16 μm from the outer-inner layer interface) for the 2-week sample. In both cases the associated diffraction data shows peaks consistent with the presence of Cr_2O_3 .

Figure 31: SEM images and fluorescence data for HCM12A 600°C 2, 4 and 6-week samples.

The diffraction peaks most often observed in the oxide layer can be indexed as Fe_3O_4 or FeCr_2O_4 . Although their structures are quite similar, the angular resolution of the microbeam synchrotron radiation diffraction enables us to differentiate between these two oxides [12]. The outer layer contains only Fe_3O_4 , which is consistent with the absence of chromium in that layer observed in the fluorescence data. On the other hand, the inner layer contains a mixture of Fe_3O_4 and FeCr_2O_4 and the diffusion layer contains a mixture of bcc iron, FeCr_2O_4 and Cr_2O_3 . In the diffusion layer the oxide precipitates form along the orientation of the metal grains, and appear to follow the lines of the white carbides. The diffusion layer also exhibits a thin (much thinner than for 9CrODS) Cr_2O_3 film at the diffusion layer-metal interface in certain regions. Additionally, base metal grains appear to be present all the way into the inner layer as suggested by the presence of peaks associated with iron bcc.

The alloy microstructure is revealed in the SEM image through white spots outlining the prior austenite metal grains and outlining laths inside these grains. These

white spots are likely to be carbides formed along metal grain boundaries and along lath boundaries between ferrite and martensite during the manufacturing of the alloy. These features in the metal were not observed in the SEM images of 9CrODS. This difference in the alloy morphology is likely due to different microstructures: 9CrODS is a purely martensitic alloy whereas HCM12A is a mixture of ferrite and martensite.

HCM12A 600°C 2-week sample:

Figure 32 shows the fluorescence data for the 600°C 2-week sample, in which we observe similar features to those observed in the 9CrODS samples: the outer oxide layer contains only iron, the inner oxide layer is enriched in chromium, and the diffusion layer is a transition region, between the inner oxide and the metal, where the chromium content decreases from its level in the inner oxide to that in the metal. In the same way, as observed some 9CrODS samples, the inner oxide layer is divided into two sub-layers. The elemental content in the sub-layer near the inner oxide-diffusion layer interface oscillates more than in the sub-layer near the outer oxide-inner oxide interface. At the interface between these two sub-layers, a small localized chromium enrichment is observed, suggesting the presence of chromium rich phases at that location. It is more difficult to distinguish the transition between the inner oxide layer and the diffusion layer in the fluorescence plot of HCM12A than in similar plots for the 9CrODS samples. This is due to the fact that the inner oxide layer is jagged, and it advances into the diffusion layer along small oxide dendrites (similar to what was observed for 9CrODS 600°C 6 weeks). Since the microbeam footprint on the surface is about 2 μm , the data collected averages all the features within this 2 μm range, causing the interface to be less distinct. Finally, a slight chromium enrichment is observed at the diffusion layer-metal interface. This enrichment is broad also because of the microbeam average over a 2 μm horizontal span, and the waviness of the diffusion layer.

Figure 32: Fluorescence data for the HCM12A 600°C 2-week sample.

Figure 33 shows the diffraction data for the HCM12A 600°C 2-week sample. The diffusion layer contains mainly FeCr_2O_4 and Cr_2O_3 . At the broad chromium enrichment located at the diffusion layer-metal interface, an increase in Cr_2O_3 content is inferred from the strong peaks at 30.5° indexed as (110) Cr_2O_3 . In the inner oxide layer, peaks associated with Fe_3O_4 become dominant but FeCr_2O_4 peaks remain present. This shift is observed by a gradual shift of the diffraction angle of the (311) peak from 29.94° (FeCr_2O_4) to 29.87° (Fe_3O_4). At the beginning of the inner oxide layer, strong peaks appear around a two-theta angle of 35.2° . These peaks are very similar to the ones observed in the inner layer of 9CrODS 600°C 4 weeks. It is not clear what phase these peaks are associated with, but the most probable phase associated with this peak is FeO , as seen in other studies [19]. This peak disappears in the 4- and 6-week samples, which suggests that this phase is an intermediate or transient phase in the oxidation process.

Figure 33: Diffraction data for the HCM12A 600°C 2-week sample.

HCM12A 600°C 4-week with and without yttrium surface coating:

Two samples were corroded under these conditions: one on which a yttrium surface coating was implanted before oxidation, and one without the yttrium surface coating. The sample containing the yttrium surface coating was the one studied using microbeam synchrotron X-ray diffraction and fluorescence. Nevertheless, the morphology of the oxide layer in both samples morphology was analyzed using the SEM. Figure 34 shows SEM images of both samples the one without the yttrium layer on the left and the one with the layer on the right.

Figure 34: SEM images of the HCM12A 600°C 4-week samples; without an yttrium layer (left) and with the layer (right).

The comparison between the thicknesses of the oxide layers formed on the sample with yttrium surface coating, with those formed on the sample without the yttrium surface coating, demonstrates that the yttrium surface coating has a significant influence on the evolution of the oxide structure and the corrosion resistance of the material. The yttrium coated sample presents overall thinner oxide layers than those of the non-coated sample, and is therefore more resistant to corrosion. Consequently, implanting a yttrium coating before oxidation will enhance the corrosion resistance of the sample.

The oxide layers formed on HCM12A 600°C 4 weeks with and without a yttrium surface coating appear similar in some respects, but with some key differences. In both cases the inner oxide layer is thick and somewhat porous, with the oxide-metal interface showing a “wavy” nature. It is clear from the SEM images that this waviness is related to the microstructure of the base metal, in particular the orientation of the former austenite grains, and the resulting lath orientation: when the laths are oriented in the oxide growth direction, growth occurs more easily. They also show clearly that the lath structure is maintained in the diffusion layer, indicating a growth process that is strongly dependent on the metal microstructure. In both cases, evidence of dendrite-like growth of the diffusion layer is observed along lath boundaries.

The notable differences are first the porosity of the outer oxide layer, which is much more marked in the sample without the yttrium surface coating. In the outer layer of the yttrium implanted sample, a thin white line is observed, which corresponds to the yttrium surface coating. The outer layer formed on the inward side of this line appears dense and adherent, while on the outward side, the oxide is more porous. Second, the diffusion layer is less continuous on the yttrium implanted sample, with some regions showing it to be completely absent.

EDS-mapping in the SEM was used to analyze the composition of this white line observed in the outer layer. Figure 35 shows the EDS-maps of iron, oxygen, molybdenum and yttrium. The EDS-maps shows that this white line is rich in yttrium and molybdenum, and depleted in iron and oxygen. This line corresponds to the yttrium surface coating that was implanted before oxidation, but it has moved from its original

position at the original solution-metal interface, which is thought to be the outer oxide-inner oxide layer interface. According to Tan et al., this displacement is due to the iron ions migrating outwards and interacting with the Y_2O_3 layer, thus forming $YFeO_3$ and moving the line inside the outer oxide layer[19]. To identify these phases in the white line and the overall phase layout in the oxide, diffraction and fluorescence data is used.

Figure 36 shows the fluorescence data for the 4-week sample with the yttrium coating. The fluorescence data present two main features: a localized chromium enrichment at the inner oxide layer-metal interface and an iron depletion at the location of the yttrium white line, as was observed using EDS-mapping. The data collected do not show evidence of a diffusion layer, in agreement with the SEM observation that, this layer was often not present in the yttrium coated sample. Apart from the chromium enrichment at the inner oxide layer-metal interface, no oscillation is observed in the fluorescence data for the inner oxide layer that would divide this layer into two sub-layers, as observed for 9CrODS. The chromium content decreases gradually from the chromium enrichment at the inner oxide layer-metal interface to its content at the outer oxide-inner oxide layer interface.

Figure 35: EDS-maps of iron, oxygen, molybdenum and yttrium.

Figure 36: Fluorescence data for the 4-week sample coated with an yttrium layer prior to oxidation.

Figure 37 shows the 3D Matlab plot of the diffraction data for the 4-week sample with the yttrium layer. As said previously, the oxide layers formed on this sample are composed of the same phases as usual. The inner oxide layer is a mixture of FeCr_2O_4 and Fe_3O_4 , and Cr_2O_3 is observed at the location where the chromium enrichment is observed at the inner oxide layer-metal interface. At this interface only peaks associated with FeCr_2O_4 and Cr_2O_3 are observed, therefore Fe_3O_4 appears after the chromium enrichment. The metal peak continues in the beginning of the inner oxide layer even though its intensity has decreased significantly at the inner oxide layer-metal interface. This is due to the fact that the metal grains are gradually oxidized in the inner oxide layer. At the location of the white line in the outer layer, small peaks appear which can be associated with Y_2O_3 and YFeO_3 .

Figure 37: 3D Matlab plot of the diffraction data for the 4-week sample with the yttrium layer.

HCM12A 600°C 6-week sample:

Figure 38 shows the fluorescence data for the HCM12A 600°C 6-week sample. The fluorescence data do not show a chromium enrichment either at the inner oxide-diffusion layer interface or at the diffusion layer-metal interface. Throughout the inner oxide layer, no variation of the chromium or iron content is observed, except near the inner oxide-diffusion layer interface where small variations occur. Consequently, the inner oxide layer can be divided in two regions: one in which the chromium content is flat and one in which it oscillates. The transition from the inner oxide layer to the diffusion layer is relatively sharp, which is due to the straight interface observed in the SEM image.

Figure 39 shows the diffraction data for the 6-week sample. In the inner oxide layer, Fe_3O_4 appears alongside FeCr_2O_4 , and both phases are observed until the outer oxide-inner oxide layer interface where only Fe_3O_4 remains. Overall, few sporadic peaks associated with the Cr_2O_3 phase are observed at the middle of the inner oxide layer. The peaks observed in the metal correspond to Cr_{23}C_6 and the iron bcc peaks, both of which continue partially in the inner oxide. This suggests that the chromium necessary for the formation of the chromium rich oxides in diffusion layer may come from the dissociation of the carbides.

Figure 38: Fluorescence data for the HCM12A 600°C 6-week sample.

Figure 39: 3D diffraction plot for the HCM12A 600°C 6-week sample.

2.2.2.2 Samples oxidized at 500°C

Figure 40 shows the SEM images of the oxide layers formed in HCM12A for the three exposure times at 500°C (2, 4 and 6 weeks). Only the 6-week sample was studied using microbeam synchrotron radiation fluorescence and diffraction. The oxide layers on the HCM12A 500°C samples are similar to those formed on the 9CrODS alloy at 500°C, with mainly 2 layers and a diffusion layer that appears to be essentially a solid solution of

oxygen ahead of the oxide. Porosity is observed at the inner-diffusion layer interface and the inner layer advances in the diffusion layer by small finger-like precipitates following the alloy microstructure.

Figure 40: SEM images of the HCM12A 500°C samples, respectively 2-week,4-week and 6-week samples from left to right.

Overall, the microstructure of these samples is quite simple with mainly Fe_3O_4 throughout both oxide layers. Almost no FeCr_2O_4 or Cr_2O_3 is observed as seen in the diffraction plot for the 6-week sample in Figure 41. The fluorescence data is shown in Figure 42 and is also feature less and mainly shows that the diffusion layer appears to contain a decreasing amount of chromium from its content in the inner layer to that in the metal. This suggests that the diffusion layer is likely only a solid solution of oxygen ahead of the oxide.

Figure 41: 3D Matlab diffraction plot for the HCM12A 500°C 6-week sample.

Figure 42: Fluorescence data for the HCM12A 500°C 6-week sample.

2.2.3 Influence of the alloy microstructure on the oxide advancement

The influence of the metal microstructure on the oxide growth is most visible in the diffusion layer where oxide precipitates are seen at the lath boundaries along the lines formed by the white spots in the SEM images. Figure 43 shows close-up SEM images of the diffusion layer of the 2-week and the 4-week with the yttrium coating. The dark streaks (arrowed) indicate the oxide formation at the lath boundaries. These boundaries correspond well to those seen in the base metal, which are outlined by particles that appear white in the SEM images.

Figure 43: SEM images of the diffusion layer of the 2-week (a) and 4-week (b) with yttrium coating samples showing the oxide precipitation along the metal lath boundaries.

The SEM images of Figure 43 clearly show that the base metal microstructure strongly influences the oxide advancement, not only in the diffusion layer but also at the

inner-diffusion layer interface. The inner layer advances into the diffusion layer preferentially along the lath boundaries, oxidizing preferentially the chromium rich particles as shown by TEM analysis.

A more detailed study of the diffusion layer of the 2-week sample was performed using TEM and especially energy filtered TEM using electron energy loss spectroscopy (EFTEM-EELS). Figure 44 shows a low magnification image and a close-up of the focused ion beam (FIB) TEM sample showing iron, chromium, and oxygen maps. The low magnification images show the lath boundary oxidation in the diffusion layer. The iron and oxygen/chromium maps are indeed complementary to each other indicating the oxides formed are depleted in iron, and rich in chromium and oxygen. The close-up analysis of the oxides shows that, in the lath boundary oxides, chromium and carbon are enriched in the form of lumps. This suggests that, along the lath boundaries, the chromium carbides present at the grain boundaries have been oxidized as chromium rich oxides.

A TEM sample of the base metal from the HCM12A 600°C 2-week sample was prepared using the FIB to identify the particles that formed at the lath boundaries. Figure 30 shows TEM bright field images of an area where three grain boundaries meet and a close-up of a grain boundary showing the particles formed. The TEM bright field images of Figure 45 demonstrate that small particles have formed all along the grain and lath boundaries. The mean particle size is about 200 nm long but can be smaller than 100 nm and larger than 400 nm. The EFTEM-EELS maps of Figure 45 confirm that the lath and grain boundary region is depleted in iron. The majority of the particles observed at these boundaries appear to be chromium rich. The lath and grain boundaries are also enriched in carbon but not all the chromium particles contain carbon. These results suggest that the oxide front initially advances into the metal by preferential oxidation of chromium carbides at the grain boundary, which allows the formation of the thermodynamically stable chromium oxides.

Figure 44: EFTEM-EELS energy filtered elemental maps of the inner and diffusion layer of HCM12A 600°C 2 weeks. The set of images on the right are close-up from the region outlined by the red square.

Figure 45: a): TEM bright field images of the base metal of HCM12A 600°C 2 weeks. Particles are observed along the grain and lath boundaries. b): EFTEM-EELS maps of the same sample for iron, chromium, and carbon of the particles observed at the lath boundaries.

2.3 Corrosion of NF616

2.3.1 Introduction

The analysis of the NF616 alloy can be compared with that for the 9CrODS alloy because both alloys contain about 9wt% of chromium, but the ODS alloy contains also the yttrium rich oxide nano-particles in its matrix. Consequently, the comparison of the two alloys highlights the influence of the ODS nano-particles on the corrosion behavior. Since chromium is the main element that determines the corrosion behavior of steel alloys, we would expect that both 9CrODS and NF616 would have similar corrosion behavior, but as we will see, this is not the case. 9CrODS has much better corrosion resistance than NF616.

The improved oxidation behavior of ODS steels relative to non-ODS alloys has been suggested to be due to the Reactive Element Effect (REE), caused by the presence of yttrium rich nano-particles in the matrix [21]. The presence of yttrium in the matrix has been proposed to improve corrosion behavior by its segregation to the grain boundaries, which slows down the diffusion processes [10, 21]. Additionally, the presence of a small amount of yttrium appears to diminish the minimum chromium content needed to form Cr_2O_3 which plays an active role in the corrosion resistance of a material [21]. The beneficial effect of yttrium can also be partially obtained by implanting an yttrium layer at the surface of the metal prior to oxidation. The NF616 sample exposed for 4 weeks was coated with such a layer prior to oxidation so we will be able to see how it affects the corrosion behavior.

Both alloys have been corroded in 600°C supercritical water for three exposure times (2, 4 and 6 weeks) at the University of Wisconsin. The main technique used to

characterize the oxide layers was microbeam synchrotron radiation diffraction and fluorescence, and was complemented by scanning electron microscopy (SEM).

2.3.2 Characterization of the oxide layer

Figure 46 shows SEM images and fluorescence plots illustrating the evolution with time of the oxide layers formed on NF616 exposed to 600°C supercritical water. The SEM images show a three-layer structure with the same main phases as in 9CrODS: Fe_3O_4 in the outer layer, a mixture of FeCr_2O_4 and Fe_3O_4 in the inner layer, and oxide precipitates within metal grains in the internal oxidation layer (diffusion layer). Although similar phases are present in both NF616 and the 9CrODS alloy, the oxide morphology is different. The outer and inner oxide layers of NF616 appear denser than those observed in the 9CrODS alloy, and the interface between the inner and diffusion layers is jagged as in the 9CrODS 6-week sample. As observed for HCM12A, the advancement of the internal oxidation layer appears to be influenced by the material microstructure [22]. In general the oxidation appears to follow the direction of the laths, likely by preferential oxidation of the lath boundaries, followed by oxidation of the rest. Finally, the thickness of the diffusion layer is approximately constant throughout the period studied, and no Cr_2O_3 film was observed at the internal oxidation layer-metal interface.

Figure 46: SEM images and fluorescence data for NF616 600°C 2, 4 and 6-week samples.

The fluorescence data of Figure 46 show chromium enrichment in the inner layer, but no localized chromium enrichment at interfaces, as in the 9CrODS alloy. Nevertheless, a slight localized chromium enrichment (circled) is observed in the NF616 4-week sample, but this sample was coated with an yttrium layer prior to oxidation. A

chromium enrichment localized at the interface between the inner and internal oxidation layers had also been observed for the HCM12A sample that had been coated with an yttrium coating prior to oxidation but not the other ones. Additionally, the internal oxidation layer is characterized by an exponential decrease in chromium content to reach that of the metal, rather than a relatively steady chromium content as in the 9CrODS alloy.

From the SEM images we can measure the oxide layer thicknesses for both alloys. Table 3 compares the outer and inner layer thicknesses of NF616 and the 9CrODS alloy. The thicknesses for the 9CrODS alloy are much smaller than that for NF616 even though both alloys have similar chromium content.

TABLE 3: Oxide layer thicknesses for NF616 and the 9CrODS alloy exposed to 600°C supercritical water.

Samples	NF616			9CrODS		
	2 weeks	4 weeks	6 weeks	2 weeks	4 weeks	6 weeks
Outer Layer (μm)	31	40	51	20	38	38
Inner Layer (μm)	23	31	42	10	23	24

Figure 47 shows the diffraction data for the NF616 600°C 2-week sample as a function of distance from the outer-inner layer interface and 2-theta. This data confirms the phase composition of the oxide layers: the outer layer contains only Fe_3O_4 , the inner layer contains a mixture of Fe_3O_4 and FeCr_2O_4 , and the diffusion layer contains mainly FeCr_2O_4 precipitates among metal grains. Very few small peaks associated with Cr_2O_3 are observed in the inner part of the inner layer. In the metal, peaks associated with Cr_{23}C_6 carbides are present, in agreement with SEM observations, in which small white particles are observed along the metal lath boundaries. Furthermore, in the metal, two peaks are observed near the location of the ferritic iron (110) peak. This suggests that two types of metal grains are present with slightly different unit cell parameters (2.8664 and 2.8794 Å), corresponding to the ferritic and martensitic lath structure of the base metal [23]. Overall, the main difference between the 9CrODS alloy and NF616 is the much smaller amount of Cr_2O_3 present in NF616, especially at interfaces.

Figure 48 shows the diffraction intensity versus diffraction angle 2-theta for the NF616 4-week sample as a function of distance from the outer-inner layer interface. The main oxide peaks are the same as in the 2-week sample, but additional peaks are observed. In the outer layer, in exact correspondence with the location of the yttrium layer, unidentified peaks are observed corresponding to neither Y_2O_3 nor YFeO_3 . In the same way as FeO was observed in the 9CrODS 4-week sample, that phase appears in the NF616 4-week sample. In the same location an additional peak is present but has not yet been indexed. Additionally, slightly more intense peaks associated with Cr_2O_3 are seen in both the inner and internal oxidation layers. Peaks associated with chromium carbide Cr_{23}C_6 are also seen in the metal. Finally, the ferritic and martensitic peaks are still observed but not in as uniform a manner as in the 2-week sample.

Figure 47: Diffraction data for the NF616 600°C 2-week sample as a function of distance from the outer-inner layer interface and 2-theta

Figure 48: Diffraction data for the NF616 4-week sample as a function of distance from the outer-inner layer interface and the diffraction angle 2-theta

2.3.3 Influence of the ODS particles on the corrosion behavior

The oxide layers formed on both NF616 and the 9CrODS alloys are similar since they have a three-layer structure consisting of an outer layer, an inner layer and an internal oxidation layer. In both cases the oxide phase compositions are the same, showing Fe_3O_4 in the outer layer, a mixture of Fe_3O_4 and FeCr_2O_4 in the inner layer, and a mixture of oxide precipitates (mainly FeCr_2O_4) and base metal grains in the internal oxidation layer. Only the presence of smaller phases, such as Cr_2O_3 , differentiates the oxide microstructure formed on the two alloys.

Figure 49 shows the inner oxide thicknesses for these two alloys as well as for HCM12A when exposed to supercritical water for the times indicated. The inner oxide was chosen because it corresponds to the most protective layer in the oxide. In general oxide protectiveness increases with increasing chromium content [24] (the oxide thickness of HCM12A (11Cr) is smaller than that of NF616 (9Cr)). However 9CrODS has a lower inner oxide thickness than HCM12A, even though its Cr content is lower. This suggests that the presence of the yttrium-rich ODS particles influences the corrosion behavior of the alloy.

Figure 49: Comparison of the total oxide layer thicknesses for 9CrODS alloy, HCM12A and NF616 exposed in 600°C supercritical water.

Various researchers have proposed that ODS particles have several corrosion benefits. It has been proposed that they reduce the amount of chromium needed to form Cr_2O_3 , thus making it easier to form Cr_2O_3 in alloys containing lower chromium contents than would be necessary to form Cr_2O_3 [21]. Furthermore, it has been proposed that the ODS particles can serve as nucleation sites for the oxide and thus help form Cr_2O_3 [25]. The formation of Cr_2O_3 is important for corrosion resistance since it slows down the diffusion of oxygen and iron [13, 14]. Second, yttrium has been shown to segregate at oxide grain boundaries thus inhibiting oxide grain growth and slowing down diffusion processes [10, 21, 25]. This was also observed for the 9CrODS alloy by Chen et al and was used to explain the enhanced corrosion resistance of that alloy [10].

The main difference between the 9CrODS alloy and NF616 is the lack of Cr_2O_3 in NF616, due to the absence of the ODS particles, which reduce the amount of chromium needed to form Cr_2O_3 to a value closer to 9 wt% (from 20 wt% to about 10-13 wt%) [21]. In the 9CrODS 2 and 4-week samples, Cr_2O_3 was present at the interface between the inner and internal oxidation layers, where a line of large pores was observed [26]. The

presence of Cr_2O_3 in this location inhibits the advancement of the oxide in the internal oxidation layer by slowing down the diffusion of oxygen. Additionally, pores form in this location because the iron needed to form the outer layer comes from the inner layer and Cr_2O_3 hinders the replenishment of the pores by inhibiting the outward diffusion of iron from the internal oxidation layer. The absence of Cr_2O_3 at the inner-internal oxidation layer interface may explain the jagged interface and the absence of a line of large pores in NF616. In the same way, the appearance of the Cr_2O_3 film in the 9CrODS alloy between the 2 and 4-week samples seems to have an important influence on the corrosion resistance of the alloy [26].

Additionally, it appears that the presence of yttrium helps segregate chromium at the interface between the inner and internal oxidation layers. The NF616 4-week sample, that was coated with an yttrium layer prior to oxidation, had a slight localized chromium enrichment at that interface, and such an effect of the yttrium coating had also been observed for HCM12A [22]. Consequently, the benefits observed due to the presence of ODS particles in the matrix can partially be obtained by implanting an yttrium layer on the alloy surface prior to oxidation. Nevertheless, the reactive element effect observed with such a technique is relatively small compared to that associated with ODS particles.

2.4 Corrosion of HT9

HT9 was normalized at 1040°C for one hour and then air cooled before being tempered at 740°C during 45 minutes before being air cooled again. HT9 is a 14 wt% Cr alloy containing 0.62 wt% of nickel. It was only oxidized at 500°C for 2 exposure times: 1 and 3 weeks.

2.4.1 HT9 500°C 1-week

Figure 50 shows an SEM image of the HT9 500°C 1-week sample. HT9 500°C 1 week shows a two-layer structure with an additional diffusion layer containing small finger-like oxide precipitates. The outer oxide layer is relatively dense, but shows some cracks at the grain boundaries of its large columnar grains. The inner oxide layer is also dense but pores are visible at the inner oxide-diffusion layer interface. Similarly to HCM12A, white spots and lines are observed in the inner oxide layer. It is possible that these may be metal grains trapped in the oxide layer.

Figure 51 shows the fluorescence data for the HT9 1-week sample. The fluorescence plot shows chromium enrichment in the inner oxide layer and a chromium depleted outer oxide layer, as was observed in all the other samples studied. No fluctuation is seen in the chromium or iron fluorescence in the inner oxide layer, near the inner oxide-diffusion layer interface. The chromium content decreases gradually in the diffusion layer from the inner layer content to its level in the metal. This is in agreement with the concentration profile of a solid solution of chromium in the metal which is

linked to the solid solution of oxygen in the metal ahead of the oxide. Nevertheless, some precipitates are observed in the diffusion layer, so the diffusion layer is a mixture of a solid solution of oxygen and oxide precipitates. The transition from the metal to the inner oxide layer occurs gradually through to the diffusion layer and therefore it is difficult to separate the end of the diffusion layer and the beginning of the inner layer. The only feature from the fluorescence data is a nickel enrichment peak at the inner oxide-diffusion layer interface, which was also observed in the other HT9 sample as well as in HCM12A. Both HT9 and HCM12A contain a significant amount of nickel, but HT9 has twice the nickel amount than HCM12A. 9CrODS does not contain nickel. Figure 52 shows the vanadium, nickel and copper fluorescence highlighting the nickel enrichment in the diffusion layer.

Figure 50: SEM image of the oxide layers formed on the HT9 500°C 1-week sample.

Figure 51: Iron and chromium fluorescence plot for HT9 500°C 1-week.

Figure 52: Vanadium, nickel and copper fluorescence plot for HT9 500°C 1-week.

Figure 53 shows the diffraction data for the HT9 500°C 1-week sample. This plot is quite simple with few small phases, and mainly just the Fe_3O_4 and FeCr_2O_4 peaks. Apart from the FeCr_2O_4 and Fe_3O_4 peaks, the other features present on the diffraction plot are peaks associated with the iron bcc peak and the carbide phases. The iron peak continues into the inner oxide layer even though its intensity decreases abruptly at the inner oxide-diffusion layer interface. The iron peak is also observed in the outer oxide layer, which is not coherent with the fact that the outer oxide layer grows by outward diffusion of iron ions to form Fe_3O_4 . Nevertheless, the intensity of this peak is low compared to the oxide peak and it is possible that the iron could be deposited in the outer layer during polishing.

Both in the diffusion and inner oxide layers, carbide peaks are observed. In the diffusion layer these peaks are associated with $\text{Cr}_{(23-x)}\text{Fe}_x\text{C}_6$ whose 100% intensity (511) peak is located at a two-theta angle of about 37.2° . This peak location varies with the proportion of iron present in the carbide. For example, the peak associated with Cr_{23}C_6 is located at 37.09° but that of the peak associated with $\text{Cr}_{15.58}\text{Fe}_{7.42}\text{C}_6$ is at 37.31° . Consequently, the more iron present in the carbide, the higher the diffraction angles observed. Once in the inner oxide layer, iron rich carbides, such as Fe_3C , appear. The 100% intensity peak for Fe_3C is the (102) plane at a diffraction angle of 36.78° . The shift from chromium rich carbides in the diffusion layer to iron rich carbides in the inner oxide layer is likely due to the fact that the majority of the chromium needed to form chromium rich oxides comes from the carbides. Consequently, the chromium rich carbides observed in the metal become depleted in chromium as the oxide is formed, and transform into iron rich carbides.

Figure 53: Diffraction data for HT9 500°C 1-week.

2.4.2 HT9 500°C 3-weeks

Figure 54 shows an SEM image of the oxide layers formed on the HT9 500°C 3-week sample. This sample exhibits a three layer structure with a distinct diffusion layer. The outer oxide layer is dense throughout, but the inner oxide layer is divided into two parts: a denser region near the outer oxide-inner oxide layer interface, and a porous region at the inner oxide-diffusion layer interface. In this respect, the inner layer is similar to the ones observed in the 9CrODS samples. The pores at the inner oxide-diffusion layer interface form two parallel lines. The line that is right at the interface is more porous than the one a little inside the inner oxide layer. Finally the diffusion layer is uniform throughout the sample and is similar to the diffusion layers found in the HCM12A 600°C samples, except that in the HT9 500°C 3 week sample no Cr_2O_3 precipitates are observed at the diffusion layer-metal interface. The diffusion layer consists of a solid solution of oxygen ahead of the oxide, and thin oxide dendrite precipitates following the microstructure of the metal. This is shown by the difference in contrast in the SEM image, between the diffusion layer and the metal.

Figure 55 shows the iron and chromium fluorescence plots for this sample. The plot is not as simple as the one for the HT9 500°C 1 week sample. There are some variations in the inner oxide layer near the inner oxide-diffusion layer interface, where the lines of pores are observed in the SEM image. The lines of pores are apparent in the fluorescence data by two small iron depletions near the inner oxide-diffusion layer interface, where no corresponding chromium enrichment is observed. There is a slight linear increase in chromium content in the inner oxide layer from the outer oxide layer to the inner oxide-diffusion layer interface. This is accompanied by a slight linear depletion

of iron through the inner oxide layer. The diffusion layer is characterized by a gradual decrease of chromium content to reach the content level of the metal. This is in agreement with a solid solution of oxygen ahead of the oxide. Nevertheless, a small chromium enrichment is visible at the diffusion layer-metal interface, which is characteristic of oxide precipitation such as the formation of Cr_2O_3 . Consequently, the diffusion layer contains both oxide precipitates and a solid solution of oxygen ahead of the oxide. Finally, the fluorescence data show nickel enrichment at the inner oxide-diffusion layer interface as in the HT9 500°C 1 week sample. Nevertheless, this enrichment is not associated with a particular phase.

Figure 54: SEM image of the HT9 500°C 3-week sample.

Figure 55: Iron and chromium fluorescence plot for the HT9 500°C 3-week sample.

Figure 56 shows the diffraction data as a function of the two-theta angle and the distance from the outer oxide-inner oxide interface for the HT9 500°C 3-week sample. These data show that the oxide layers are composed mainly of Fe_3O_4 . Very few traces of

FeCr_2O_4 are observed in this sample. Nevertheless, small $(\text{Fe,Cr})_2\text{O}_3/\text{Cr}_2\text{O}_3$ peaks are present at the inner oxide-diffusion layer interface and the beginning of the inner oxide layer. Therefore, this phase is likely to make the oxide layer protective. Since this phase cannot be seen in the diffraction plot of Figure 41, the presence of such a phase is highlighted by a more detailed analysis of the diffraction patterns using PeakFit. Figure 57 shows a diffraction pattern from the beginning of the inner oxide layer.

Figure 56: Diffraction data as a function of the two-theta angle and the distance from the outer oxide-inner oxide interface for the HT9 500°C 3-week sample.

Figure 57: Peak Fit of a diffraction pattern from the beginning of the inner oxide layer of HT9 500°C 3 weeks.

2.4.3 TEM investigation of the oxide structure of HT9 500°C 3-weeks

Figure 58 shows a TEM bright field image of all three sub-layers. Because this oxide layer is thinner overall, it is possible to make a cross-sectional TEM sample showing all the layers. The outer oxide layer shows large columnar grains up to 1 μm wide by 5 μm long, which is similar to those found in the oxide layer developed on 9CrODS. The outer oxide layer also exhibits small equiaxed grains (~ 500 nm in diameter) along the outer oxide/inner oxide interface. Similar to the oxide layer developed on 9CrODS, the inner oxide layer is composed of small equiaxed grains, no larger than 100 nm in diameter, as shown in Figure 59. Through TEM examination, and tilting, it was found that a large group of grains (with a diameter almost the size of the inner oxide layer) within the inner oxide layer is highly oriented. This group of grains is shown as the dark region enclosed by the arrows in Figure 59. The entire group of grains exhibited the same TEM diffraction pattern and the orientation is explained later in the TEM diffraction analysis corresponding to Figure 63.

Figure 58: TEM bright field image of all three oxide sub-layers on HT-9, after 3 weeks exposure to 500°C SCW. Artifacts are shown in boxes.

Figure 59: TEM bright field image of the inner oxide layer of HT-9 after 3 weeks exposure to 500°C SCW.

The majority of the grains in the inner oxide layer are equiaxed, with diameters of ~100 nm. Figure 60 shows a structure observed in the diffusion layer, near the interface with the inner oxide layer. This structure is composed of white platelets growing in two orthogonal directions, amidst a dark background. This region extends approximately 2 μm by 2 μm . The platelets grew parallel and perpendicular to the oxide growth direction.

Figure 60: TEM bright field image and magnification of highly ordered Fe-bcc and FeCr_2O_4 within the diffusion layer of HT-9, after 3 weeks exposure to 500°C SCW.

It appears that the dark region in Figure 60 corresponds to the iron spots in the diffraction pattern in Figure 64, while the light strips within this region correspond to the

FeCr₂O₄ spots from that same diffraction pattern. The dark field image of an Fe-bcc diffraction spot from the corresponding diffraction pattern in Figure 61 confirms this observation. The diffusion layer from this sample does not have a band of Cr₂O₃ at the oxide front nor does it have a finger-like structure of FeCr₂O₄, as found in the oxides developed on 9Cr ODS after 4 weeks and 2 weeks exposure to SCW, respectively.

Figure 61: TEM dark field analysis of Fe-bcc diffraction spot from diffusion layer of HT-9, after 3 weeks exposure to 500°C SCW. (Note: This diffraction pattern is indexed in Figure 64).

Diffraction analysis was performed to help determine which phases are present in each sub-layer.

Figure 62 shows a bright field image and corresponding diffraction pattern of an outer oxide grain. This diffraction pattern was indexed as Fe₃O₄ with a zone axis of [-111]. The remainder of the outer oxide layer provided diffraction patterns, which were indexed as Fe₃O₄.

Figure 62: TEM diffraction pattern and corresponding bright field image of Fe₃O₄, with a zone axis of [-111], from outer oxide layer of the HT-9 500°C 3-week sample.

The inner oxide layer shows a large region of grains that diffract together (that is, they respond to tilt in the same manner). This region takes up more than half of the viewable inner oxide layer of the TEM sample fabricated for this study. Figure 63 shows a diffraction pattern and bright field image showing highly oriented grains. The diffraction pattern was indexed as FeCr_2O_4 with two zone axes of $[111]$ and $[112]$, indicating two preferential orientations, and Fe-bcc with a zone axis of either $[112]$ or $[212]$. Simulated JEMS diffraction patterns were used to find the possible zone axes of $[112]$ and $[212]$ for Fe-bcc, which cannot be determined from the diffraction pattern because only a single row of diffraction spots can be seen in the diffraction pattern. The rest of the inner oxide layer provided diffraction patterns that were also indexed as FeCr_2O_4 .

Figure 63: TEM (a) bright field image of highly-oriented FeCr_2O_4 grains within the inner oxide of HT-9, after 3 weeks exposure to 500°C SCW, (b) corresponding diffraction pattern, and (c) JEMS indexing of the experimental diffraction pattern.

The diffusion layer also exhibits strong preferential grain orientation. Figure 64 shows a diffraction pattern from the highly oriented grains in the diffusion layer shown in Figure 60. The overall pattern is a composite of several sub-patterns: a dominant pattern of Fe-bcc with a zone axis of $[100]$ and two additional patterns of FeCr_2O_4 . The additional patterns of FeCr_2O_4 both have zone axes of $[011]$, and are perpendicular to each other as seen in the spot overlay of the experimental diffraction pattern in Figure 64.

Figure 64: TEM (a) bright field image of highly-ordered Fe-bcc and FeCr₂O₄ within the diffusion layer of HT-9, after 3 weeks exposure to 500°C SCW, (b) corresponding diffraction pattern with zone axis [001] for Fe-bcc and with zone axes of [011] and [101] for FeCr₂O₄, and (c) JEMS indexing of the experimental diffraction pattern.

Figure 65 shows a diffraction pattern taken from a different part of the diffusion layer than the diffraction pattern in Figure 68. This pattern is very similar (same orientation and same indexing) to the diffraction pattern in Figure 63, which was taken from the inner oxide layer. One possible explanation for these diffraction patterns being the same is that as the oxide grows into the diffusion layer, it transforms the Fe-bcc portions into FeCr₂O₄ following the orientation of the existing FeCr₂O₄ platelets.

Figure 65: TEM diffraction pattern and corresponding bright field image of highly-ordered FeCr_2O_4 , with zone axes $[111]$ and $[112]$, and Fe-bcc within the diffusion layer of HT-9, after 3 weeks exposure to 500°C SCW. This diffraction pattern is exactly the same as that shown in Figure 63.

Energy Dispersion Spectroscopy analysis, providing chemical information to be coupled with the preceding diffraction pattern analysis, was performed on each layer with the purpose of confirming the identification of phases within each layer. Just as EDS analysis showed no presence of chromium in the outer oxide layer for 9Cr ODS, no chromium was found in the outer oxide layer of HT-9. This information combined with TEM diffraction analysis indicates that the outer oxide layer consists of only Fe_3O_4 . In contrast, EDS analysis showed chromium to be present in the inner oxide layer, which is consistent with the presence of FeCr_2O_4 but does not tell us anything about the presence of Fe_3O_4 .

In the TEM image in Figure 58 it is difficult to see the interfaces on either side of the diffusion layer. However, TEM EDS spectra taken across the diffusion layer/inner oxide interface shows a sharp contrast in oxygen concentration between the diffusion layer to the inner oxide layer as seen in Figure 66. The dotted line in the figure shows the approximate location of the diffusion layer/inner oxide interface. Figure 66 shows the ratios of the amplitudes of the $K_{\alpha 1}$ peaks of Cr/Fe and O/Fe from a manual EDS line scan across the diffusion layer/inner oxide interface as indicated in Figure 67.

Figure 66: TEM EDS of the ratios of oxygen/iron and chromium/iron K α 1 spectral lines from diffusion layer to inner oxide of HT-9, after 3 weeks exposure to 500°C SCW.

Figure 67: Location of EDS line scan data presented in Figure 67.

3. Oxidation behavior analysis and comparison between the different alloys exposed to SCW

3.1 Oxidation rate

The corrosion rate is generally characterized by the inner oxide thickness (L) or the weight gain (W) being a power function of the exposure time (t), where k and k' are constants with the appropriate units, as shown in Equation (1).

$$L = (k \cdot t)^{1/n} \text{ or } W = (k' \cdot t)^{1/n} \quad (1)$$

If a diffusion process through a dense monophase layer determines the corrosion rate, the rate is parabolic and n is equal to 2. However, since the oxide layers formed in ferritic-martensitic steels are not mono-phasic and contain many pores, this theory cannot be applied, and thus it is likely that the corrosion rate does not follow a parabolic law.

The dependence on temperature is taken into account in the constant k in Equation (1). It is assumed that the temperature dependence can fit an Arrhenius law as described by Equation (2). In this equation, k_0 is a constant, Q is the activation energy, R the gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$) and T is the absolute temperature.

$$k = k_0.\exp(-Q/RT) \quad (2)$$

$$\text{so we have: } L = k_{\text{eff}}.\exp(-Q/nRT).t^{1/n} \text{ or } W = k'_{\text{eff}}.\exp(-Q/nRT).t^{1/n} \quad (3)$$

For the samples studied we have calculated the corrosion rate by plotting the oxide layer thickness that we measured from the SEM images as a function of exposure time. We calculated the corrosion rate using or the overall oxide thickness (outer + inner layers) or only the inner layer since it is the most protective one. Figure 68 and 69 show the corrosion rate curves of the overall oxide thickness and the inner oxide thickness, respectively, as a function of the exposure time for the 600°C samples. 9CrODS has the lowest corrosion rate in both cases with even thinner oxide thicknesses than HCM12A which has higher chromium content. It is not sure the corrosion rate exponent for 9CrODS has a real physical meaning since there was a drastic change in oxide microstructure between the 2-week and the 4-week sample by the formation of the Cr_2O_3 film at the diffusion layer-metal interface. Additional points for the 9CrODS sample would be necessary to obtain a more accurate corrosion rate exponent. Both HCM12A and NF616 on the other hand have a similar corrosion rate exponent around 0.5, which is characteristic of a parabolic corrosion rate. Therefore it appears that ferritic and martensitic alloys follow a parabolic corrosion rate at 600°C. Additionally, it seems that both measurements using the overall or just the inner oxide thickness give similar values for the corrosion rate, which confirms that the inner oxide corresponds to the protective layer.

Figure 68: Corrosion rate of the overall oxide thickness at 600°C as a function of exposure time

Figure 69: Corrosion rate of the inner oxide thickness at 600°C as a function of exposure time.

Figure 70 and 71 show the same corrosion rate curves for the same alloys using or the overall oxide thickness or only the inner oxide thickness as a function of time at 500°C. Once again, 9CrODS has the lowest corrosion rate compared to both HCM12A and NF616 and both calculations using the overall or just the inner oxide thickness give similar values for the corrosion rate. Nevertheless, at 500°C, the corrosion rate exponents are closer to a cubic rate (HCM12A), or in between a parabolic and cubic rate (NF616). 9CrODS stands out again with a corrosion rate exponent around 0.25.

Figure 70: Corrosion rate of the overall oxide thickness of 9CrODS, HCM12A and NF616 at 500°C as a function of exposure time.

Figure 71: Corrosion rate of the inner oxide thickness of 9CrODS, HCM12A and NF616 at 500°C as a function of exposure time.

The corrosion rate calculations show that there are kinetic differences between 500°C and 600°C. The exponent is quite different at the two temperatures, which suggests differences in the oxidation mechanism, which in turn is coherent with the differences in oxide microstructure observed at the two temperatures. This difference in rate exponent and mechanism makes it impossible to calculate the activation energy for which a common exponent at both temperatures is necessary.

3.2 Calculations of the outward flow of iron to form the outer layer

Analysis of the results:

The oxide formed on ferritic and martensitic alloys exhibits a three-layer structure with Fe_3O_4 in the outer layer, with a mixture of Fe_3O_4 and FeCr_2O_4 in the inner layer, and with a diffusion layer containing a mixture of Cr rich oxide grains and metal grains. Nevertheless each alloy presents different oxidation kinetics depending on the Cr content or the presence of ODS particles. Table 4 summarizes the oxide layer thicknesses for the alloys studied.

Table 4: Summary of the oxide layer thicknesses for the alloys studied.

Alloy			Outer layer	Inner layer	diffusion layer	Porosity IL (%)
9CrODS	500°C	2 weeks	4.8	3.5	N/A	13
		4 weeks	6.5	4	N/A	11.5
		6 weeks	7	4.3	5.5	17
	600°C	2 weeks	22	10	32	21
		4 weeks	38	23	22	15
		6 weeks	38	24	20	19
HCM12A	500°C	2 weeks	7.5	5.5	N/A	8.5
		4 weeks	7	5.5	2.2	8
		6 weeks	10.5	8	N/A	12
	600°C	2 weeks	25	18	0-14	15
		4 weeks	30	23.5	7.50	14
		4 weeks Y	25	21	0-22	21.5
		6 weeks	42	32	10	8
HT9	500°C	1 week	4.2	3.5	1.2	9.5
		3 weeks	7	5	3.5	21
NF616	500°C	4 weeks	11	8	N/A	10
		8 weeks	15	10.5	N/A	9
		18 weeks	20	15	N/A	9.5
	600°C	2 weeks	31	23	8	19.5
		4 weeks Y	40	31	7	16.5
		6 weeks	51	42	7	10
T91	500°C 18weeks	AR	20.5	16	4.5	15.5
		ECAP	18	12.8	6	24
		SP	17.5	13	6	

When the Cr content is higher in the alloy, the oxide layer thicknesses are smaller; except concerning the 9CrODS alloy, which has thinner oxide layer thicknesses than the rest of the alloys. As Table 2 will show, it appears that overall the ratio of the inner over the outer layer thickness is about 0.75. Only the 9CrODS sample exhibits smaller ratios compared to the other alloys. The average of this ratio for all alloys except 9CrODS is 0.75.

→ IL/OL thickness ratio = 3/4

Additionally, we calculated the amount of porosity present in the inner layer by using ImageJ. Figure 72 shows the SEM image of the inner layer of HCM12A 600°C 2 weeks and the analysis of the porosity obtained with ImageJ. From the black and white image showing the porosity ImageJ gives us an area fraction of the pores. Thus we are able to calculate the percentage of porosity in the inner layer.

Figure 72: SEM image of the inner layer of HCM12A 600°C 2 weeks and analysis of the porosity using ImageJ

Finally, using the fluorescence data obtained at the synchrotron, we calculated various composition ratios to see if there were any trends. Table 5 shows these ratios as well as the ratio of inner over outer layer thickness.

The main conclusions concerning these ratios are:

- Fe IL/ Fe OL: in between 2/3 and 3/4, average = 0.69. Ratio slightly higher for 9CrODS than other alloys. Cr content may have an influence since it seems lower Cr content is associated with higher values of this ratio.
- Cr IL/ Fe IL: Ratio depends on Cr content and temperature. For 11-12% Cr it is around 0.3 whereas it is around 0.25 for 9% Cr. Additionally this ratio appears slightly lower at lower temperature. Nevertheless it does not seem to depend on the exposure time.
- Cr IL/ Cr metal: The Cr content in the inner layer is about 75% higher than in the metal. A Cr depletion is observed in the metal for 9CrODS 600°C 4 and 6 weeks, associated with the formation of the Cr₂O₃ film at the diffusion layer – metal interface, and which explains the high values for these samples.
- Cr metal/ Fe metal: This ratio was measured to compare it with the same ratio using the alloy composition. Overall, the values obtained are similar to the composition ratio. A Cr depletion is observed near the Cr₂O₃ film in the 9CrODS samples.

The fact that the Fe IL/Fe OL and the Cr IL/ Fe IL ratios do not depend on exposure time suggests that there is an equilibrium that is reached quickly.

Table 5: Calculations of concentration ratios using the synchrotron fluorescence data.

Alloy			Thicknesses		Fluorescence analysis				Cr metal/ Fe metal composition
			IL/OL	IL/OL average	Fe IL/Fe OL	Cr IL/ Fe IL	Cr IL/ Cr metal	Cr metal/ Fe metal	
9CrODS	500°C	2 weeks	0.73	0.65					9.78
		4 weeks	0.62		0.73	0.22	1.58	11.16	
		6 weeks	0.61		0.74	0.23	1.73	10.38	
	600°C	2 weeks	0.45	0.56	0.72	0.23	1.91	9.80	
		4 weeks	0.61		0.70	0.26	2.49	7.71	
		6 weeks	0.63		0.70	0.25	2.32	8.14	
HCM12A	500°C	2 weeks	0.73	0.76					12.86
		4 weeks	0.79						
		6 weeks	0.76		0.67	0.28	1.58	13.68	
	600°C	2 weeks	0.72	0.78 0.75 without Y	0.62	0.33	1.76	13.37	
		4 weeks	0.77						
		4 weeks Y	0.88		0.63	0.31	1.82	13.42	
		6 weeks	0.76		0.66	0.30	1.73	13.27	
HT9	500°C	1 week	0.83	0.77	0.69	0.28	1.56	14.09	14.15
		3 weeks	0.71		0.66	0.30	1.59	14.43	
NF616	500°C	4 weeks	0.73	0.73	0.71	0.22	1.63	10.47	10.05
		8 weeks	0.70						
		18 weeks	0.75						
	600°C	2 weeks	0.74	0.78	0.65	0.25	1.96	10.64	
		4 weeks Y	0.77		0.68	0.25	1.71	10.61	
		6 weeks	0.82		0.70	0.25	1.76	10.37	
T91	500°C 3000h	AR	0.78	0.74		0.24	1.85	11.10	9.39
		ECAP	0.71		0.73	0.24	1.77	10.99	
		SP	0.74		0.79	0.21	1.87	9.69	
Average			0.72		0.69	0.26	1.81		

Calculation of the outward flux of iron to form the outer layer:

Figure 73 shows a schematic of the oxidation mechanism of the ferritic and martensitic steels in SCW. The outer layer is formed by outward migration of iron ions and the inner layer is formed by inward migration of oxygen. This mechanism had been confirmed by the marker experiments. The outward migration of chromium across the oxide layer because its diffusion coefficient is negligible compared to that of iron. Moreover the outer layer does not contain any chromium, which also suggests that the diffusion of chromium is too slow to be taken into consideration.

Figure 73: Schematic of the oxidation mechanism of ferritic and martensitic alloys in SCW

The oxidation reactions take place at both the outer oxide-water interface for the growth of the outer layer, and at the inner oxide-metal interface for the inner layer growth. These reactions are given below:

From the experimental data several assumptions can be made concerning the oxidation mechanism.

Assumptions:

1. The iron fluorescence data, which can be associated with the concentration of iron in the oxide layer, show an increase in iron concentration from the inner oxide-metal interface to the outer layer. This goes against an outward diffusion of iron controlled by differences in concentration because then the iron flux should be inwards. Consequently, this suggests that the outward migration of iron may follow an *inverse Kirkendall effect* mechanism, where it is an inward flux of iron vacancies, which creates the outward flux of iron. Another, experimental

observation that correlates with the inverse Kirkendall effect is the segregation of chromium to the inner oxide-metal interface, where sinks for the iron vacancies are present, because $D_{Fe} > D_{Cr}$. $J_V = J_{Fe} + J_{Cr} = J_{Fe}$.

2. The oxidation process reaches **steady state** and some form of equilibrium relatively quickly because the concentration **ratios do not evolve with exposure time**.
3. There is no ionic dissolution of the oxide in the water because SCW has lower ionic solvency than water since it is less polar.
4. The electroneutrality in ionic crystals such as Fe_3O_4 gives a relationship between the iron and oxygen flux:

$$\frac{J_{Fe}}{3} = \frac{J_O}{4}$$

This relationship may be linked to the fact that the ratio of the inner over the outer layer thickness is in average about 0.75.

Local electroneutrality gives: $n_h = 2n_{v_1} + 3n_{v_2}$,

5. Chromium may be segregating at the IL-metal interface because of a decrease in oxygen concentration right at this interface (due to the diffusion profile) thus a decrease in oxygen potential, which favors the formation of chromium rich oxides compared to iron rich oxides. The presence of yttrium in ODS particles or the presence of an yttrium coating (to a lesser extent) accentuate this phenomenon.

Outward flow of iron:

In this section we calculate the amount of iron that has left the inner layer and see if this quantity is enough to form the outer layer. For this we use the ratio of concentrations measured from the synchrotron fluorescence data and given in Table 5.

$$\begin{aligned} c_{Fe_{OL}} &= \frac{n_{Fe_{OL}}}{n_{Fe_{OL}} + n_{O_{OL}}} & c_{O_{OL}} &= \frac{n_{O_{OL}}}{n_{Fe_{OL}} + n_{O_{OL}}} \\ c_{Fe_{IL}} &= \frac{n_{Fe_{IL}}}{n_{Fe_{IL}} + n_{Cr_{IL}} + n_{O_{IL}}} & c_{Cr_{IL}} &= \frac{n_{Cr_{IL}}}{n_{Fe_{IL}} + n_{Cr_{IL}} + n_{O_{IL}}} \\ c_{Fe_{metal}} &= \frac{n_{Fe_{metal}}}{n_{Fe_{metal}} + n_{Cr_{metal}}} & c_{Cr_{metal}} &= \frac{n_{Cr_{metal}}}{n_{Fe_{metal}} + n_{Cr_{metal}}} \end{aligned}$$

$$\Delta c_{Fe_{IL}} = \frac{n_{Fe_{metal}}}{n_{Fe_{metal}} + n_{Cr_{metal}}} - \frac{n_{Fe_{IL}}}{n_{Fe_{IL}} + n_{Cr_{IL}} + n_{O_{IL}}} = \frac{1}{1 + \frac{c_{Cr_{metal}}}{c_{Fe_{metal}}}} - \frac{1}{1 + \frac{4}{3-x} + \frac{c_{Cr_{IL}}}{c_{Fe_{IL}}}}$$

$$n_{O_{IL}} = \frac{4}{3-x} n_{Fe_{IL}}$$

In the inner layer, we have in average a composition of $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$, therefore we have the relationship between n_{O} and n_{Fe} in the inner layer. We are able to calculate x from the concentration ratios:

$$\frac{c_{\text{Cr}_{IL}}}{c_{\text{Fe}_{IL}}} = \frac{x}{3-x}$$

The difference in iron concentration of the inner layer gives us the fraction of iron that has left the inner layer, which multiplied by the inner layer thickness, gives us the equivalent length of pure iron that has left the inner layer. In order to obtain the outer layer thickness we have to multiply this equivalent length by the Pillings-Bedworth ratio for Fe_3O_4 ($\text{PBR} = 2.086$). In order to take the porosity of the inner layer into consideration, we have to add to that value the product of the porosity fraction γ by the inner layer thickness. Consequently the equation for the outer layer thickness is as follows:

$$h_{OL} = \Delta c_{\text{Fe}_{IL}} h_{IL} \times \text{PBR} + \gamma h_{IL}$$

The results for this calculation are shown below in Table 6:

Table 6: Calculation of the outer layer thickness by outward flow of iron from the inner layer.

Alloy			Outer layer	Inner layer	porosity IL (%)	Cr metal/ Fe metal composition	Cr IL/ Fe IL	x	h OL
9CrODS	500°C	2 weeks	4.8	3.5	13	9.78			4.54
		4 weeks	6.5	4	11.5		0.22	0.54	5.13
		6 weeks	7	4.3	17		0.23	0.56	5.78
	600°C	2 weeks	22	10	21		0.23	0.56	13.83
		4 weeks	38	23	15		0.26	0.62	30.83
		6 weeks	38	24	19		0.25	0.60	33.00
HCM12A	500°C	2 weeks	7.5	5.5	8.5	12.86			6.79
		4 weeks	7	5.5	8				6.76
		6 weeks	10.5	8	12		0.28	0.66	10.16
	600°C	2 weeks	25	18	15		0.33	0.74	23.87
		4 weeks	30	23.5	14				30.69
		4 weeks Y	25	21	21.5		0.31	0.71	29.00
		6 weeks	42	32	8		0.30	0.69	39.70
HT9	500°C	1 week	4.2	3.5	9.5	14.15	0.28	0.66	4.28
		3 weeks	7	5	21		0.30	0.69	6.75
NF616	500°C	4 weeks	11	8	10	10.05	0.22	0.54	10.10
		8 weeks	15	10.5	9				13.15
		18 weeks	20	15	9.5				18.87
	600°C	2 weeks	31	23	19.5		0.25	0.60	31.63
		4 weeks Y	40	31	16.5		0.25	0.60	41.70
		6 weeks	51	42	10		0.25	0.60	53.77
T91	500°C 3000h	AR	20.5	16	15.5	9.39	0.24	0.58	21.46
		ECAP	18	12.8	24		0.24	0.58	18.25
		SP	17.5	13			0.21	0.52	15.19

Overall, the calculated values of the outer oxide layer thickness agree with the measured values with most differences below 10% and the maximum difference being 30%. For the 9CrODS alloy the calculated values are quite smaller than the measured ones. If we add the iron that has migrated from the diffusion layer we reach slightly better agreement but the calculated values remain lower than the measured values.

3.3 Qualitative oxidation behavior for the 9CrODS alloy

From the preliminary study of the oxide microstructure formed on ferritic-martensitic alloys, but especially 9CrODS, the description of a qualitative oxidation behavior was undertaken. For this several assumptions are made. First the outer-inner layer interface corresponds to the original water-metal interface. Moreover, since the inner layer is enriched in chromium and no chromium is observed in the outer layer, we assume that the outer layer is formed by outward diffusion of iron but that chromium

stays in place or only diffuses on shorter distances. We also assume that the two interfaces of oxide growth are the water-outer layer interface and the inner layer-metal interface. Consequently, the inner layer is formed by inward diffusion of oxygen and the outer layer by outward diffusion of iron.

Chromium enrichment accompanied by the presence of Cr_2O_3 was observed at the inner-diffusion layer interface for the 9CrODS 600°C 2-week sample and at the diffusion layer-metal interface for the 9CrODS 600°C 4-week and 6-week samples. Cr_2O_3 was still observed at the inner-diffusion layer interface in the 9CrODS 600°C 4-week sample, but not in the 6-week sample. The Cr_2O_3 present at the inner-diffusion layer interface is part of a mixture of FeCr_2O_4 and Cr_2O_3 , but a Cr_2O_3 ribbon forms at the diffusion layer-metal interface in the 9CrODS 600°C 4 and 6-week samples. Over a thickness of a few microns in this ribbon, Cr_2O_3 is the only oxide phase present and appears to stop oxygen diffusion.

Thermodynamics show that Cr_2O_3 is the most stable oxide and is formed at the lowest partial pressure of oxygen, followed by FeCr_2O_4 at slightly higher oxygen partial pressures and finally Fe_3O_4 at much higher partial pressures of oxygen [10, 27]. Consequently, Cr_2O_3 and FeCr_2O_4 form at low oxygen concentrations while Fe_3O_4 forms at higher oxygen concentrations. The Cr_2O_3 at the inner-diffusion layer interface and the diffusion layer-metal interface serves as a kinetic and thermodynamic barrier. The presence of Cr_2O_3 decreases the diffusion coefficients of iron and oxygen, and also decreases the oxygen potential at the inner interface of Cr_2O_3 precipitates [28]. It is assumed that the Cr_2O_3 ribbon stops the diffusion of oxygen beyond the ribbon and also the outward diffusion of iron from the metal towards the oxide. In the same way, FeCr_2O_4 slows down the diffusion of both oxygen and iron because of its high chromium concentration but does not stop the diffusion. Additionally, we will assume that chromium diffuses short distances at 600°C but not at 500°C [29, 30]. Figure 74 shows a schematic of a possible oxidation mechanism for 9CrODS.

Figure 74: Schematic of the oxidation mechanism for 9CrODS.

As an example, this qualitative oxidation behavior will be developed for the evolution with time of the oxidation behavior of 9CrODS exposed to 600°C supercritical water. Figure 75 shows the mechanism applied to 9CrODS 600°C 2 weeks taking into consideration the observations made in the characterization of the oxide layer.

Figure 75: Schematic of the oxidation behavior of 9CrODS 600°C 2 weeks.

In the 9CrODS 600°C 2-week sample, the diffusion layer ends in a distinct line, which is thought to correspond to the location of the solubility limit of oxygen in iron. Cr₂O₃ was observed at the inner-diffusion layer interface along with a local chromium enrichment in the fluorescence data. The presence of Cr₂O₃ at this interface likely explains the formation of such a large diffusion layer by hindering the advancement of the inner layer, but since Cr₂O₃ is mixed with other phases, oxygen still diffuses through in smaller amount. Additionally, the Cr₂O₃ hinders the outward diffusion of iron ions from the diffusion layer. Consequently, not enough iron diffuses outward to compensate the iron that has migrated from the inner layer, engendering an agglomeration of pores at the interface.

Figure 76 shows the schematic of the mechanism for 9CrODS 600°C 4 weeks. In this sample, the Cr₂O₃ ribbon has formed, which stops further diffusion of oxygen beyond the ribbon. Consequently, the inner to diffusion layer ratio has increased. Nevertheless, Cr₂O₃ is still present at the inner-diffusion layer interface, which once again explains the presence of pores at that interface. In the SEM image we can also observe a region of that interface containing no pores, where the inner layer advances more in the diffusion layer than the rest of the inner layer. This suggests that the Cr₂O₃ in that location has dissolved which makes the diffusion of oxygen easier, thus explaining the advancement of the inner layer, but also makes the diffusion of iron easier, thus explaining the replenishment of the pores by outward diffusion of iron ions coming from the oxidation of the diffusion layer. This phenomenon is the beginning of what is observed throughout the interface of the 9CrODS 600°C 6-week sample. Figure 77 shows the schematic of the oxidation behavior for 9CrODS 600°C 6-weeks.

Figure 76: Schematic of the oxidation behavior for 9CrODS 600°C 4 weeks.

Figure 77: Schematic of the oxidation behavior for 9CrODS 600°C 4 weeks.

In the 9CrODS 600°C 6-week sample, the Cr_2O_3 at the inner-diffusion layer interface has disappeared enabling the inner layer to advance in the diffusion layer as suggested by the non-linearity of that interface. Once the Cr_2O_3 has disappeared, the diffusion processes are facilitated thus enhancing oxidation. Additionally, this disappearance leads to an increase in the oxygen potential in the diffusion layer, which explains the presence of Fe_3O_4 or $\text{Fe}_{1+x}\text{Cr}_{2-x}\text{O}_4$, which are iron rich oxides compared to

the chromium rich oxides previously observed in the diffusion layer. In the same way, if the oxygen potential increases too much at the location of the Cr_2O_3 ribbon, this ribbon might dissolve leading to a situation similar to that observed in the 2-week sample, leading to a certain periodicity in the oxidation process.

To conclude, the oxidation behavior appears to be closely linked to the presence and location of Cr_2O_3 in the oxide layers. The formation of the Cr_2O_3 ribbon may be an effective way of hindering the corrosion of these alloys.

4. Alloys exposed to the Lead-Bismuth Eutectic (LBE)

4.1 Introduction

A summary of the corrosion conditions and examination performed for the alloys exposed to the lead-bismuth eutectic is given in Table 7. Each of the five samples will be discussed individually.

Table7: Comparison of corrosion and examination conditions for alloys discussed

Sample Name	Metal Alloy	Corrosion Loop	Corrosion Temp. (°C)	Corrosion Time (hours)	Microbeam Step Size (μm)	Microbeam 2θ Angular Range
HT-9 DELTA	HT-9	DELTA	500	666	0.2 μm	24°-39°
HT-9 DELTA Annealed	HT-9	DELTA	500	666	0.2 μm	24°-39°
HT-9 IPPE	HT-9	IPPE	550	3000	0.2 μm	24°-39°
T91	T91	DELTA	500	666	0.2 μm	24°-39°
Alloy 3	Model	DELTA	500	666	0.25 μm	23°-39°

4.2 HT9 DELTA 500°C 666h

4.2.1 Microbeam synchrotron radiation diffraction and fluorescence analysis

This sample was corroded in the Los Alamos National Laboratory (LANL) DELTA loop at 500°C for 666 hours. It was examined using the following techniques, the results of which will be discussed in this section: SEM, EDS, μ -XRF, TEM, and μ -XRD.

Figure 78 is a scanning electron micrograph showing an overall cross-sectional view of the oxide layers formed on HT-9 DELTA. It can be seen in the figure that the alloy exhibits a continuous duplex oxide layer approximately 10.1 μm thick in total. The sub-layers in this oxide are referred to as the inner oxide layer and the outer oxide layer.

Figure 78: SEM image of HT9 DELTA 500°C 666h.

The inner layer exhibits a wavy interface with the metal. This phenomenon has been observed both in SEM and TEM studies to be due to preferential oxidation dictated

by the structure of the underlying metal's grain morphology. The oxidation proceeds more quickly along the metal lath within the former austenite grains, causing oxidized material to reach deeper in some parts of the metal, and leaving packets of uncorroded metal behind in the inner oxide layer.

The inner oxide layer also exhibits slight porosity, as indicated by the arrows in Figure 78. Since it is believed that the outer layer is formed by the outward diffusion of iron from the inner layer, these pores may be due to the resulting depletion of iron left in the inner oxide layer.

Unlike the inner oxide layer, the formation of outer oxide layer is not affected by the metal's microstructure. This layer is mostly dense with occasional cracks or a missing grain (likely pulled out during the polishing process). It consists of two sublayers, which can be seen in Figure 78: the first is filled with bright "spots" which are absent in the second. These lighter-colored spots in the first sublayer are believed to arise from the presence of lead and/or bismuth incorporated into the oxide layer from the coolant and will be discussed in more detail later. Previous studies have also shown that this layer contains medium-sized equiaxed grains closer to the inner layer interface, which become larger and more columnar towards the outer surface.

Figure 79 shows EDS maps of oxygen, iron, chromium, lead, and bismuth from HT-9 DELTA's oxide layers obtained using the SEM. The concentration of oxygen throughout the oxide layers appears to be constant, disappearing only in the metal. Iron shows stronger concentrations in the outer oxide and the metal with a depletion in the inner oxide. Chromium appears to only be present in the inner oxide and metal, whereas lead and bismuth are strongest in the first half of the outer oxide, corresponding to the bright spots observed in the SEM. These data are in broad agreement with the SEM image outlined in the previous section.

The metal is an alloy consisting mainly of iron and chromium in which the iron is preferentially pulled from the inner oxide to form the outer oxide. The resulting depletion of iron in the inner oxide can be seen in the iron $K\alpha$ map given in Figure 79. The bismuth and lead $L\alpha$ maps in the figure show presence of lead and bismuth incorporated from the coolant in the outer oxide. More detailed data regarding the elemental composition of oxide structure is available in the next section.

Figure 79: EDS-maps for the HT9 DELTA 500°C 666h sample.

Figure 80 shows the fluorescence data obtained using microbeam synchrotron radiation for the major alloying elements, iron and chromium, from the oxide layers shown in Figure 78. In the metal the fluorescence signal for both elements remains relatively constant; however, in the inner oxide the iron content decreases and chromium content increases – just as expected. Interestingly, just before the inner oxide/outer oxide interface, there is a distinct section of chromium enrichment and iron depletion. Here it is expected that higher levels of chromium phases will be detected. The outer oxide contains almost no chromium and especially high levels of iron, as would be predicted by models based on corrosion of similar materials in other environments.

Figure 80: Iron and chromium microbeam x-ray fluorescence data from oxide layers

X-Ray fluorescence data from minor contaminants and alloying elements (lead and nickel, respectively) are shown in Figure 81. The fluorescence signal for nickel is much weaker than those from chromium and iron due to the very low nickel content in the alloy (less than 1 atomic percent). The fluorescence signal for lead is weak and somewhat noisy, however it does show a noticeable increase in the first half of the outer oxide. This corresponds to the bright spots observed in the scanning electron micrograph which were previously identified in Figure 79 as lead and/or bismuth.

The nickel in this alloy remains constant throughout the metal, then shows an enrichment right at the metal-inner oxide interface, and a second enrichment in the outer oxide. Nickel has been observed by Zhang et al. to be enriched at the metal/inner oxide interface during corrosion of similar alloys under similar conditions. These researches came to the preliminary conclusion that this was due to nickel diffusion away from the inner oxide towards the metal during oxide formation. If this were the case it would be expected that nickel concentrations in the inner and outer oxide would then be very low; however, because of the fine resolution granted by microbeam x-ray diffraction, it can be seen in Figure 81 that this is not the case. Instead, nickel fluorescence intensity remains constant after the inner oxide enrichment, and then shows a second enrichment in the first

half of the outer oxide. This means that the mechanism proposed by Zhang et al. does not entirely explain what is going on with nickel in this alloy. Later in this thesis, when Alloy #3 is examined, it will be shown that the nickel enrichment in the outer oxide is probably due to coolant deposition in that region. The nickel enrichment at the metal-inner oxide interface, on the other hand, could be due to either ingress or egress of nickel.

Figure 81: Ni and Pb fluorescence data for the HT9 DELTA 500°C 666h sample.

As the μ -XRF data is collected, μ -XRD data is collected simultaneously at each step along the sample's oxide layer. Since it is not practical to show the peak fit for every diffraction pattern taken, a 3-D contour plot is generated to visually illustrate the peaks present. While the majority of peaks are visible this way, some peaks with very low intensity or some peaks that overlap with other peaks may be less visible. These, as well as the visible peaks, will be shown using fitted data and diffraction patterns later on in this section. Figure 82 shows the 3-D contour plot from HT-9 DELTA of the diffracted intensities from phases as a function of 2-theta angle and location taken in 0.2 μ m steps across the sample's oxide layer. The identification of each of these peaks is discussed in the following sections for each region of the oxide, as well as the metal.

Figure 82: Contour plot showing the diffraction data alongside the iron and chromium fluorescence data for HT9 DELTA 500°C

In the metal region several major peaks are visible, most prominently the two indexed as bcc iron (Ferrite), and Cr_{23}C_6 (chromium carbide) located at 37.42° , and 37.14° respectively. Both the bcc Fe (1 1 0) and Cr_{23}C_6 (5 1 1) peaks continue through the metal region, and are also observed in the inner oxide layer of the sample. This indicates the presence of uncorroded metal in the oxide layer, consistent with the TEM findings.

Figure 82 also indicates that all four peaks of a phase labeled as $(\text{Fe,Cr})_3\text{O}_4$ appear in the metal. This phase actually consists of Fe_3O_4 , FeCr_2O_4 , or a combination of the two, however in the contour map in Figure 82 the peaks from the separate phases are too close together to distinguish. During the peak fitting process, however, these two phases can be distinguished clearly. Peak fits on integrated intensity versus 2-theta plots further on in

this section will show more clearly which of these phases is present the oxide layers. Seeing the $(\text{Fe,Cr})_3\text{O}_4$ phase, an oxide, in the metal region may seem strange, however their presence there is quite common. This is due to the earlier discussed preferential oxidation along lath boundaries in the metal ahead of the oxide front. These oxide phases can go quite deep into the metal, and give the metal-inner oxide interface its wavy appearance, as seen in the SEM image in Figure 78. These oxide phases slowly appear in the metal layer and grow stronger as they traverse the metal towards the inner oxide.

Figure 83 shows a diffraction pattern taken from the metal, as well as the corresponding peak fit from that diffraction pattern. Note that this diffraction pattern is somewhat noisier than patterns taken in the oxide layers due to low intensity of the peaks. 5 peaks are present: three corresponding to the strongest diffracting orientations of Fe_3O_4 , one from the Cr_{23}C_6 , and one from the bcc Fe. It should be noted that the oxide peaks in the metal region are composed entirely of Fe_3O_4 magnetite, with no evidence of the FeCr_2O_4 spinel phase in the μ -XRD data until well into the inner oxide layer.

It can be seen in part (a) of Figure 83 that the diffracted intensities from bcc Fe (1 1 0) and Cr_{23}C_6 (5 1 1) are restricted to only one portion of the diffraction pattern, while the Fe_3O_4 phase tends to make “rings” (only one of which will be easily visible in the figure). This means that the bcc Fe and Cr_{23}C_6 phases are diffracting from either large-sized grains or highly-oriented smaller grains in this region. Fe_3O_4 , on the other hand, is diffracting from smaller, more random, less textured grains than the bcc Fe and Cr_{23}C_6 grains. This makes sense with the proposal that the as-fabricated and annealed metal contained the bcc Fe and Cr_{23}C_6 grains, while the oxide formed later via preferential grain boundary oxidation.

Figure 83: Diffraction pattern in the metal region and its PeakFit analysis.

The inner oxide layer of the HT-9 DELTA sample exhibits diffraction peaks consistent with a mixture of Fe_3O_4 , FeCr_2O_4 , Cr_2O_3 , bcc iron, and Cr_{23}C_6 phases. Figure 84 shows a diffraction pattern taken from the inner oxide. It should be noted that the bcc iron (1 1 0) and Cr_{23}C_6 (5 1 1) peaks observed in the metal region and in Figure 83 (a) are both still present in the diffraction pattern and in nearly the same positions, but with lower intensities compared to those seen in the metal.

Figure 84: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from the inner layer of HT-9 DELTA 500°C 666h.

The four observed peaks of the Fe_3O_4 phase increase in intensity in the inner oxide by approximately an order of magnitude relative to their intensities in the metal region. Also, some smaller FeCr_2O_4 spinel peaks are become visible and are shown in Figure 84 (b) with the purple dotted lines. The FeCr_2O_4 spinel peaks are more intense closer to the inner-outer oxide interface, consistent with the fluorescence findings, which showed an enrichment of chromium in that region.

Two Cr_2O_3 peaks, (1 1 0) and (1 1 3), are identified in Figure 84 (b), and a third, (1 0 4), can be seen further on in the inner oxide. All peaks from the Cr_2O_3 phase identified have very low intensity, and represent only three of the five possible Cr_2O_3 peaks at this angular range. Fluorescence data in Figure 80 show that further on in the inner oxide layer the chromium content increases even further, giving rise to more intense FeCr_2O_4 and Cr_2O_3 peaks. It is believed that, since chromium oxide phases tend to be protective against oxygen and iron transport, this increase in chromium oxide phases could be responsible for slowing the corrosion of the metal.

The outer oxide is likely formed by outward migration of iron from the inner oxide and, according to fluorescence data, does not contain chromium. As a result, no chromium containing phases are expected in the outer oxide layer. In agreement with this, it can be seen in Figure 82 that both the carbide and bcc iron phases decrease in intensity dramatically meaning that no metal or carbides are present in the outer oxide structure. This also is consistent with the theory that the outer oxide is formed by outward diffusion of iron from the metal, and therefore would not contain any retained metal structures.

As mentioned previously, the outer oxide is composed of 2 sublayers. Figure 85 shows a diffraction pattern and a peak fit from the first half of the outer layer (near the inner layer). The fit in Figure 85 (b) shows that the FeCr_2O_4 and Cr_2O_3 peaks have entirely disappeared, whereas the Fe_3O_4 peaks are more intense. The Fe_3O_4 peaks continue through the entire outer oxide with intensities, which sometimes vary from their powder diffraction expected relative intensities. This is likely due to the large size of the grains in the outer oxide. Since the footprint of our beam is on the order of the grain size,

diffraction patterns may represent only a few grains in the outer oxide region, and as a result would represent contain only a few crystallographic reflections.

Figure 85: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 13.4 μm into HT-9 DELTA in the outer oxide layer after 666 hours of exposure to 500°C lead-bismuth eutectic.

Two new peaks are also identified in Figure 85, and these are associated with an fcc Pb-Bi phase. As shown earlier, the first half of the outer layer contains bright spots, and using EDS these were associated with the presence of lead and bismuth, likely from the coolant. Identifying the exact phase formed by the lead and bismuth, however, was not possible due to the numerous possibilities with very similar d-spacings. All of the likely candidates are fcc phases comprised of either lead or both lead and bismuth, and all show the same two peaks in this angular range. For the purposes of this study, we will identify this phase as the fcc (Pb, Bi) phase.

Table 8 gives a summary of the observations made for the HT9 DELTA 500°C 666h sample.

Table 8: summary of the observations made for the HT9 DELTA 500°C 666h sample.

	Metal Region	Inner Oxide (4.6 μm)		Outer Oxide (5.5 μm)	
		Main layer (3.8 μm)	Cr Enrichment (0.8 μm)	Pb-Bi layer (2.4 μm)	Outermost layer (3.1 μm)
Observations	Dense, uneven interface with inner oxide	Porous, small grains with retained metal lath	Porous, small grains	Dense, large equiaxed grains with bright spots	Dense, large columnar grains
Chemical Composition	Fe: 0% Cr: 0% Ni: 0% Pb: 0%	Fe: -8% Cr: 46% Ni: 5% Pb: 2%	Fe: -24% Cr: 53% Ni: -3% Pb: 3%	Fe: -12% Cr: -53% Ni: 12% Pb: 12%	Fe: 3% Cr: -80% Ni: -9% Pb: 5%
Crystal Structure	bcc Fe Cr_{23}C_6 Fe_3O_4	bcc Fe Cr_{23}C_6 Fe_3O_4	bcc Fe Cr_{23}C_6 Fe_3O_4	Fe_3O_4	Fe_3O_4

4.2.2. TEM analysis of HT9 DELTA 500°C 666h

The full TEM sample is shown in the bright field image in Figure 86. This sample underwent damage during milling, which can be seen by the FIB artifacts.

Figure 86: TEM bright field image of entire HT-9, after 4 weeks exposure to 500°C LBE and sketch of FeCr_2O_4 grains (region "A") within the inner oxide layer with pores and small grains in between the grains depicted as dashed lines.

The outer oxide consists of long thin grains (up to 2 μm long by 400 nm wide) and smaller equiaxed grains (~300-400 nm in diameter). An equiaxed grain (800 nm long by 400 nm wide) was found within the outer oxide layer at the inner oxide/outer oxide interface. This grain appeared dark, during bright field imaging, at all angles of rotation of the sample. The inner oxide/outer oxide interface is clearly distinguishable in the TEM

image and is shown by the white dotted line at the right in Figure 86. The inner oxide exhibits bright field contrast from a group of narrow elongated grains, approximately 2 μm long by 300-400 nm wide (arrowed), as sketched schematically in Figure 86. These grains are also visible in the metal region (arrowed), and are likely a inter lath grain boundary phase, either retained austenite or ferrite. In the inner oxide these grains are associated with fine porosity (shown in more detail in Figure 87(b)), possibly resulting from the oxidation process. There are also equiaxed oxide grains within the inner oxide layer up to 250 nm in diameter. The metal layer has a large metal grain of approximately 2 μm wide by 3 μm long at the metal/inner oxide interface.

Figure 87: TEM diffraction patterns and corresponding bright field images from HT-9, after 4 weeks exposure to 500°C LBE, of (a) a Fe_3O_4 grain within the outer oxide layer, with a zone axis of $[-112]$ and (b) a FeCr_2O_4 grain within the inner oxide, with a zone axis of $[-111]$ showing a highly-structured region within the inner oxide layer.

After initial SEM and TEM bright field analysis, TEM diffraction patterns were

taken to help determine which phases are present in each sub-layer.

A diffraction pattern was taken from a grain within the outer oxide layer (Figure 87(a)) and indexed as Fe_3O_4 with a zone axis of $[-112]$. Another diffraction pattern was taken from a grain within the inner oxide layer (Figure 87(b)) and indexed as FeCr_2O_4 with a zone axis of $[-111]$. The highly oriented area of the inner oxide layer, from which the diffraction pattern was taken for the inner oxide grain, exhibits the exact same diffraction pattern. There are small areas within this region that do not diffract to the same conditions, as seen by the contrast of lighter areas as opposed to the generally dark region. These lighter areas mostly consist of pores but also of very fine grains.

Energy Dispersion Spectroscopy analysis, providing chemical information to be coupled with the preceding diffraction pattern analysis, was performed on each layer with the purpose of confirming the identification of phases within each layer. EDS analysis shows no chromium to be present in the outer oxide layer, therefore, combined with the TEM diffraction analysis this indicates that the outer oxide layer consists of only Fe_3O_4 . In contrast, EDS analysis shows chromium to be present in the inner oxide layer, therefore it can be said that FeCr_2O_4 is definitely present but nothing can be said of the presence of Fe_3O_4 in the inner oxide layer.

The diffraction pattern from the region of highly structured grains within the inner oxide layer was indexed as FeCr_2O_4 and EDS analysis shows chromium to be present throughout the area, which indicates the entire sub-structure to consist of FeCr_2O_4 .

It is interesting to note that a large equiaxed lead grain (400 nm wide by 600 nm long) was found within the outer oxide along the outer oxide/inner oxide interface. The lead grain was discovered through EDS and its presence is verified by the spectrum in Figure 88, which shows strong lead peaks.

Figure 88: EDS spectrum of lead grain in outer oxide of HT-9, after 4 weeks exposure to 500°C LBE.

The metal grain at the inner oxide/metal interface is about the same size and shape of the highly structured group of grains within the inner oxide along the metal/inner oxide interface. This indicates that the oxide grains within the inner oxide layer are developed from the iron grains in the metal, although, unlike the inner oxide layer for the HT-9 SCW sample the TEM diffraction analysis from the inner oxide layer for this sample did not have Fe-bcc diffraction spots.

4.3 HT9 DELTA Annealed 500°C 666h

This sample of HT-9 was corroded under the same conditions as the HT-9 sample discussed in the previous section, but it was heat treated before being corroded. HT-9 DELTA Annealed was heat treated at 1060 °C for 1 hour, then air cooled; and then annealed at 730 °C for 2 hours, and air-cooled again. This process would temper out much of the retained austenite structures, leaving behind larger and more highly oriented ferrite and martensite grains as well as carbides. After heat treatment, the sample was corroded in the LANL DELTA loop at 500°C for 666 hours.

Figure 89 shows an overall view of the oxide layers formed on the HT-9 annealed sample. The alloy exhibits a continuous oxide layer approximately 7.2 micro-meters thick containing an inner and outer oxide. Just as in the HT-9 DELTA sample, the inner layer is slightly porous and exhibits dendrites, which reach into the bulk metal preceding it. This layer's interface with the metal is wavy and appears to be dictated by the original structure of the metal just as in the case of the HT-9 DELTA sample. The outer oxide layer in Figure 89 also contains structures resembling those in HT-9 DELTA. It consists of two sublayers: the first is filled with bright "spots" which are absent in the 2nd. The outer oxide layer is dense with occasional cracks or missing pieces (like the one seen at the top of the SEM image).

Figure 90 shows the fluorescence data for major alloying elements, iron and chromium, obtained during the scan of the oxide layers at APS. In the metal, the iron and chromium concentrations remain relatively constant until the near the inner oxide. In the inner oxide, the iron content is decreased and chromium content increases, which would be expected in the case of outward diffusion of iron and inward diffusion of oxygen. Unlike the HT-9 DELTA sample, there is no additional enriched peak of chromium in this sample's fluorescence data – only a fairly flat plateau in the inner oxide. The outer oxide contains almost no chromium and very high levels of iron. In this layer, we would expect to see phases containing chromium to disappear.

Figure 89: SEM image of the HT9 DELTA Annealed 500°C 666h sample.

Figure 90: Iron and chromium fluorescence data for HT9 DELTA Annealed

Fluorescence data from minor alloying and contaminating elements lead and nickel is given in Figure 91. The fluorescence signals from these elements were weaker than those emitted by iron and chromium due to their extremely low content in the alloy. The lead fluorescence signal is fairly weak and noisy, but it does have a distinct peak in the first half of the outer oxide corresponding to the bright spots seen there in the SEM image. Just as in HT-9 DELTA, this indicates the presence of a lead-containing phase in the first half of the outer oxide.

The nickel fluorescence signal starts off constant in the in the metal, then shows and enrichment at the metal-inner oxide interface just as seen in HT-9 DELTA previously. It also has a second, smaller enrichment in the outer oxide as well. This is again probably due to nickel diffusion outward from the bulk metal into the coolant because of nickel's high solubility in lead-bismuth eutectic.

Figure 91: Nickel and lead fluorescence data for HT9 DELTA Annealed.

Figure 92 gives the contour plot of the diffracted intensities from phases as a function of 2-theta angle and location taken in 0.2μm steps across HT-9 DELTA Annealed's oxide layers. The following sections will discuss these diffraction results in detail for each layer of the sample.

In the metal region, several peaks are visible, and others are notably absent. Three of the four $(\text{Fe,Cr})_3\text{O}_4$ peaks are present with relative intensities very close to those expected. These peaks are seen in the metal due to the preferential oxidation along the metal lath ahead of the oxide front. They consist solely of the Fe_3O_4 phase, and they increase dramatically in intensity, as they get closer to the inner oxide region. Strangely, there are no diffraction peaks from ferrite or carbides observed in the metal region. The likely explanation for this comes from the fact that this metal was annealed,

reducing stresses at grain boundaries and giving it a more oriented structure. Since only the (1 1 0) bcc Fe peak is visible in this angular range, if the metal was oriented in a different hkl direction then we might not see this specific orientation's peak. Similarly, the carbides in this region may have adopted different orientations than the 3 observable ones in this angular range. TEM studies or further XRD data over a wider angular range would be needed to confirm or refute this.

Figure 92: Summary of data obtained using microbeam synchrotron radiation on oxide layers formed on HT-9 DELTA Annealed after 666 hours of exposure to 500°C lead-bismuth eutectic. (a) Iron and chromium microbeam x-ray fluorescence data, (b) contour plot showing diffracted intensity vs. two-theta angle vs. distance into sample. Indexed peaks are indicated as well as approximate distance between oxide layers. The asterisks denote locations of individual diffraction patterns discussed further on in this section.

The very beginning of the inner oxide of the sample contains both magnetite (Fe_3O_4) and spinel (FeCr_2O_4) peaks, however the spinel peaks are once again about an order of magnitude smaller than the magnetite peaks. They are all close to their relative expected intensities, with the exception of the Fe_3O_4 (4 0 0) and the FeCr_2O_4 (4 0 0) peaks. Both of these peaks diffracted slightly stronger than expected. Also, only the (1 1 0) Cr_2O_3 peak appears in this sample, and its appearance is very brief near the inner-outer oxide interface.

Two carbide peaks are present, but only in the inner oxide region of this sample. Carbides in the previously discussed HT-9 DELTA sample were highly oriented, so in the case of HT-9 DELTA Annealed, the annealing process may have increased this effect. The presence of carbides in the inner oxide might indicate that there is uncorroded metal present there as well, however without either TEM studies or XRD information taken over a larger angular range, we cannot know for sure. The (5 1 1) carbide peak appears in the beginning of the inner oxide, and continues just into the outer oxide region of the sample. The (4 2 0) peak appears only at the inner oxide/outer oxide interface where the signal from the (5 1 1) peak is strongest.

Figure 93 shows a full peakfit from the inner oxide near the inner oxide-outer oxide interface. The strongest Cr_2O_3 and FeCr_2O_4 signals come from this section of the sample, however they are still much smaller than those observed in the HT-9 DELTA sample. It is worthwhile to note that the diffraction pattern in Figure 93 shows two Cr_{23}C_6 peaks, while the integrated data only shows one. This is due to the shape of the region of interest used to sum intensities not being located over the diffracted Cr_{23}C_6 (4 2 0) peak in this case. Generally, the shape of the ROI should not strongly effect which peaks are seen, but in the case of highly oriented phases like the carbides, these inconsistencies sometimes arise.

A new peak not observed in HT-9 DELTA is also present in this diffraction pattern. This peak belongs to the (1 0 4) orientation of hematite, Fe_2O_3 . While we typically develop magnetite during the corrosion process, it appears that the heat treatment caused a restructuring of the underlying metal to also allow the formation of hematite.

Figure 93: Diffraction pattern and peakfit of a scan in the inner layer of the HT9 DELTA Annealed 500°C 666h sample.

Similar to HT-9 DELTA, the first half of the outer oxide of HT-9 DELTA Annealed contains strong Fe_3O_4 peaks as well as both of the fcc Pb-Bi phase's peaks. Unlike HT-9 DELTA, however, the HT-9 DELTA Annealed sample also contains the Fe_2O_3 phase which continues into this region, growing stronger in the first half of the layer, then weaker in the second.

As expected from the location of the bright spots in the SEM, as well as the presence of lead in the micro-x-ray fluorescence data, the fcc Pb-Bi (2 0 0) and (1 1 1) peaks are seen in the outer oxide and are strongest for the first half of the oxide. A diffraction pattern and fitted peaks from the first half of the outer oxide 6.0 μm into the sample is given in Figure 94. While difficult to see due to its low intensity, the fcc Pb-Bi peak (1 1 1) does form a ring, and the (2 0 0) peak is a very light broken ring, indicating that these peaks may be diffracting from smaller grains without much texture. It can also be seen that the Fe_2O_3 (1 0 4) peak remains a series of spots, almost virtually in the same positions as those seen in Figure 93 from the inner oxide of the sample.

Because of its very large grain sizes in the outer oxide, diffracted peaks from Fe_3O_4 vary dramatically in intensity. This was explained previously to be due to the fact that the footprint of the synchrotron beam is on the order of the grain size, resulting in diffraction patterns representing only a few grains in the outer oxide.

Figure 94: Diffraction pattern and peakfit of a scan in the outer layer of the HT9 DELTA Annealed 500°C 666h sample.

Table 9 shows a summary of the observations made for the HT9 DELTA Annealed sample. While very similar to the HT-9 DELTA sample, the HT-9 DELTA annealed sample did show some key differences. Firstly, it did not have an extra chromium enrichment in the inner oxide near the inner-outer oxide interface. As a result, it also did not show a noticeable increase in chromium-containing phases near this region. In fact, in general this sample exhibited a lower presence of FeCr_2O_4 and even more notably, Cr_2O_3 peaks than the HT-9 DELTA sample.

Another difference from the HT-9 DELTA sample was that the HT-9 DELTA Annealed sample did not diffract a (1 1 0) bcc Fe peak, probably due to highly oriented metal grains as a result of the annealing process. The final difference between the two

samples was the presence of a new phase in HT-9 DELTA Annealed: Fe_2O_3 or hematite. For further comparison, the next section will look at the final HT-9 sample studied in this thesis: an unannealed sample corroded at a higher temperature for a longer period than the previous two.

Table 9: Summary of the observations made for HT9 DELTA Annealed.

Metal Region	Inner Oxide (3.0 μm)	Outer Oxide (4.2 μm)	
		Sublayers	
Dense	Porous	Dense, Bright Spots, larger grains	Dense, larger grains
Average Fe, Cr, Ni	High Cr & Ni, Depleted Fe	High Ni & Pb, Average Fe, No Cr	High Fe, No other
Cr_{23}C_6 , steadily increasing Fe_3O_4	Fe_3O_4 , FeCr_2O_4 , Fe_2O_3 , some Cr_{23}C_6 & Cr_2O_3	Fe_3O_4 , Fe_2O_3 , fcc Pb-Bi phase	Fe_3O_4 only

4.4 HT9 IPPE 550°C 3000h

The last sample of HT-9 studied in this thesis comes from the same stock as the HT-9 DELTA sample, however it was corroded at a higher temperature for a longer period in the IPPE loop. The sample was corroded in flowing LBE for 3000 hours at 550°C, so it is expected that its oxide layers will be further developed than those corroded in the DELTA loop.

Figure 95 shows an overall view of the oxide layers formed on the HT-9 IPPE sample. The alloy exhibits a continuous oxide layer approximately 19.2 micro-meters thick, the thickest seen thus far, and contains an inner and outer oxide. Similar to the two previous HT-9 samples, the inner layer is slightly porous and exhibits a wavy interface with bulk metal preceding it. This layer's interface with the metal appears to be dictated by both the grain structure of the metal as well as the lath of the grain boundaries. The outer oxide layer in Figure 95, however, is quite different than that of the other HT-9 samples. While it is fairly solid with occasional cracks or missing grains, it does not contain the two sublayers seen in the previous samples. Instead, it is a single layer of highly columnar grains. It also appears to have a lower concentration of the bright spots signifying the lead and bismuth phases.

Finally, the layer's interface with the lead bismuth coolant is very uneven and shows signs of major dissolution. During corrosion, this sample exhibited weight gain for the first 2000 hours, then weight loss in between 2000 and 3000 hours. This loss was attributed to dissolution of the outer oxide layer, and the SEM image in Figure 95 shows this has resulted in an uneven outer oxide-coolant interface.

Figure 95: SEM image of the oxide layers formed on HT9 IPPE 550°C 3000h.

Figure 96 shows the fluorescence data for iron and chromium obtained during the scan at APS. Iron and chromium levels are fairly constant in the metal until the inner oxide-metal interface where there is a large enrichment of chromium and depletion of iron. In the inner oxide, the iron content remains decreased and chromium content higher than that in the bulk metal. The outer oxide contains almost no chromium and very high levels of iron.

Figure 96: Iron and chromium fluorescence for HT9 IPPE 550°C 3000h.

Figure 97 gives fluorescence data for lead and nickel. It can be seen that the lead fluorescence signal for this sample is basically noise, meaning that the area scanned was either lower in lead content than the previous two samples, or did not contain lead at all. Nickel, however, shows an enrichment in the metal just preceding the inner oxide layer, followed by a depletion in the actual oxide. There is also a small nickel enrichment about midway through the inner layer.

Figure 97: Nickel and lead fluorescence data for HT9 IPPE 550°C 3000h.

Figure 98 shows the contour plot of the diffracted intensities from phases as a function of 2-theta angle and location taken in 0.2 μm steps across HT-9 IPPE oxide layer. In the metal layer, there are several major peaks, the most notable of which is a very strongly diffracting Ferrite (1 1 0) peak. This peak continues on into the inner oxide layer as well indicating that, just as in the other HT-9 samples, there is some uncorroded metal within the inner oxide. Also similar to the previous two samples, the metal layer contains all four Fe_3O_4 peaks, which steadily increase in intensity as they get closer to the inner oxide. There are also carbide peaks present in this sample; however they are located at 35.79 and 37.09 degrees, meaning that instead of the Cr_{23}C_6 carbides seen in the two previous HT-9 samples, they are Cr_7C_3 carbides.

Only the most intense diffraction orientation for Cr_7C_3 , (1 5 1), is seen in the metal layer. The second most intense, (1 1 2) is seen later on in the inner oxide, and (1 5 0) and (0 6 0) peaks are never observed. Since these are smaller magnitude peaks, they may be lost in the noise, or the carbide may be highly oriented causing the other peaks

not to appear. The (1 5 1) Cr_7C_3 peak is somewhat overshadowed in the contour plot by the very intense Ferrite (1 1 0) peak, however this peak can be seen in the peakfits, like the one shown in Figure 99 from 2.6 μm into the sample.

Figure 98: Summary of data obtained using microbeam synchrotron radiation on oxide layers formed on HT-9 IPPE after 3000 hours of exposure to 550°C lead-bismuth eutectic. (a) Iron and chromium microbeam x-ray fluorescence data, (b) contour plot showing diffracted intensity vs. two-theta angle vs. distance into sample. Indexed peaks are indicated as well as approximate distance between oxide layers.

Figure 99: Diffraction pattern and peakfit of a scan in the metal region of the HT9 IPPE 550°C 3000h sample.

Following the metal is the inner oxide region. The very beginning of the inner oxide has the highest chromium concentrations, and, not surprisingly also contains the largest magnitudes of the chromium-containing phases Cr_2O_3 and FeCr_2O_4 . There are also two peaks from the Cr_7C_3 carbide phase visible in this region. A diffraction pattern and peaks identified from this section is given in Figure 100. It should be noted that the Cr_2O_3 peaks diffract in ring patterns with some spots in them, rather than spot patterns. Their peaks in the peakfits are also fairly broad, with wide FWHM, both of which indicate that the Cr_2O_3 phase has smaller grains with no strong preferential orientations. All of the Cr_2O_3 peaks get weaker as they move further away from the metal-inner oxide interface until about 10 μm into the sample where they disappear, with the exception of the (1 1 0) peak, which briefly reappears about 13 μm into the oxide layer.

Similarly, the carbide peaks continue into the inner oxide for only a very short distance, and by 9 μm in they are gone. The FeCr_2O_4 spinel phase, however, continues with about the same intensity through the remainder of the inner oxide, stopping at the outer oxide at the same time as the chromium fluorescence intensity drops off.

Besides the chromium-containing phases, the inner oxide also displays all the bcc Fe peak, as well as all 4 of the Fe_3O_4 peaks. The bcc iron peak grows weaker further into the sample until about 14 μm where it disappears. The Fe_3O_4 peaks, however, continue throughout the entire inner oxide, increasing in intensity as they near the Fe-enriched outer oxide. They stay fairly close to their expected relative intensities, and continually diffract in ring patterns meaning that in the inner oxide, the Fe_3O_4 phase does not have particularly large grains and is not highly textured.

Figure 100: Diffraction pattern and peakfit of a scan in the inner layer of the HT9 IPPE 550°C 3000h sample.

The outer oxide of the HT-9 IPPE sample consists of only one layer, unlike HT-9 DELTA or HT-9 DELTA Annealed which each had two sublayers in the outer oxide. Also unlike the two previous HT-9 samples, the HT-9 IPPE sample does not show diffraction peaks from the fcc Pb-Bi phase. Electron dispersive spectroscopy was used to confirm that there is in fact lead and bismuth in the outer oxide of this sample, and maps of this can be viewed in Figure 101. The light blue arrows in the figure indicate areas of enriched lead and bismuth, which appear as bright spots in the SEM image.

While EDS does confirm presence of lead and bismuth, there are several reasons the fcc Pb-Bi phase might not show up in diffraction images. In the SEM image of this oxide seen in Figure 95 the concentrations of bright dots representing the presence of lead and bismuth are much lower than in the previous two samples. It is possible that the area scanned at APS may have missed these Pb-Bi areas entirely, or that their concentrations were so low that they didn't diffract strongly enough to be seen in the diffraction patterns. It is also possible that the lead and bismuth formed a phase other than the fcc Pb-Bi phase, and that this phase did not diffract in the angular range over which data was taken.

With no fcc Pb-Bi phase, the outer oxide then consists solely of Fe_3O_4 magnetite, as well as one "noise peak." This peak is located at approximately 34.14° and is believed to come from the setup used at the synchrotron source rather than the sample itself. It is believed by the synchrotron operators that the peak diffracts from the pinhole through which the incident beam passes. A small piece of lead tape is used to block this from happening most of the time, but this measure is occasionally unsuccessful. Fortunately the noise peak is easily identified since it always diffracts as a perfect ring (something uncharacteristic of the samples studied) within a very tight 2-theta range of 34.12° to 34.15° . Figure 102 shows a diffraction pattern and peak fit from the outer oxide of the sample. It can be seen that the noise peak exhibits both of its defining characteristics: a perfect diffraction ring at a 2-theta angle of 34.13° .

Just as in the two previously discussed HT-9 samples, the Fe_3O_4 peaks in HT-9 IPPE vary dramatically in intensity throughout the outer oxide layer. These peaks also have very narrow full-width half maxes – both of which indicate that they are diffracting from larger or highly oriented grains (large columnar grains in the outer oxide).

Figure 101: EDS-maps of iron, oxygen, chromium, lead and bismuth of the outer layer of the HT9 IPPE 550°C 3000h sample.

Figure 102: Diffraction pattern and peakfit of a scan in the outer layer of the HT9 IPPE 550°C 3000h sample.

Table 10 gives a summary of the observations made for the HT9 IPPE 550°C 3000h sample. Compared with the two HT-9 DELTA samples, HT-9 IPPE exhibits several differences. Firstly, HT-9 IPPE has a much thicker oxide layer than the previous two samples. This was expected since HT-9 IPPE was corroded for a longer time at a higher temperature than the other HT-9 samples. Another difference was the relative thickness of these oxide layers. In the two HT-9 DELTA samples, the outer oxide layer was thicker than the inner oxide layer, however for HT-9 IPPE, the inner oxide layer was much thicker. This may have been due to the high dissolution (and resulting weight loss) seen by HT-9 IPPE during its corrosion process. Another difference with HT-9 IPPE's outer oxide layer was that it contained no sublayers. It also did not exhibit as high of concentrations of lead and bismuth as the other HT-9 samples, and it did not diffract a lead-bismuth phase.

Also unlike the previous HT-9 samples, HT-9 IPPE had an area of especially high chromium and chromium-containing phases at its metal-inner oxide interface. HT-9 DELTA has a similar enrichment at its inner oxide-outer oxide layer, and HT-9 DELTA Annealed did not exhibit an especially high chromium enrichment at all. Finally, HT-9 IPPE's carbide phase identified was Cr_7C_3 instead of Cr_{23}C_6 seen in previous samples. The next sample studied was a T91 sample corroded in the DELTA loop in the same manner as the other two HT-9 DELTA samples.

Table 10: Summary of the observations made for the HT9 IPPE 550°C 3000h sample.

Metal Region	Inner Oxide (12.5 μm)		Outer Oxide (6.7 μm)
	Sublayers		
Dense	Porous, smaller grains	Porous, smaller grains	Dense, Bright Spots, large columnar grains
Average Fe, Cr, Enriched Ni	Very High Cr, Depleted Fe	High Cr, Small Ni enrichment, Depleted Fe	High Fe, No/Low Other
bcc Fe, Cr ₇ C ₃ , steadily increasing Fe ₃ O ₄	Fe ₃ O ₄ , FeCr ₂ O ₄ , Cr ₂ O ₃ , some uncorroded bcc Fe and Cr ₇ C ₃	Fe ₃ O ₄ , FeCr ₂ O ₄	Fe ₃ O ₄ only

4.5 T91 500°C 666h

The T91 sample studied in this thesis was corroded in the LANL DELTA loop at 500°C for 666 hours. Previous researchers including Barbier and Rusanov found that T91 exposed to flowing LBE at 470°C developed the expected 2-layer oxide, the outer layer of which was porous whereas the inner layer was compact. They found that this outer layer was primarily Fe_3O_4 whereas the inner layer was composed of the metal's alloying elements in their initial weight concentrations with the exception of a small increase in chromium. They concluded from electron microprobe analysis and XRD that this inner layer was composed of a combination of Fe_3O_4 and $(\text{Fe,Cr})_3\text{O}_4$ [27]. Our results will confirm and extend those of Barbier and Rusanov.

T91 exhibits a continuous oxide layer, which is approximately 8.5 micro-meters thick and contains an inner and outer oxide. Figure 103 shows a scanning electron microscope image taken using backscattered electrons is shown with labels denoting each of the oxide layer locations. It can be seen that the outer oxide is extremely porous, whereas the inner oxide is denser. The inner oxide does also exhibit some porosity, but its pores are much smaller than those seen in the outer oxide. The interface between the outer oxide and the coolant is mostly straight, but does show some signs of liquid metal dissolution. The interface representing the initial metal's pre-corrosion surface in between the outer and inner oxide is straight as would be expected. The interface between inner oxide and metal is wavy similar to the interfaces seen in the previous HT-9 samples. It is unknown if these dendrites extends along the lath of the grain boundaries like in HT-9, or if the uneven corrosion is due to a different factor such as grain orientation.

The outer oxide of T91 exhibits 2 sub-layers just as in HT-9 DELTA and HT-9 DELTA Annealed. In the SEM image, it can be seen that the first half of the layer contains the bright spots seen in the previous HT-9 samples attributed to the presence of lead and bismuth. Unlike previous samples, which had dense outer oxides, however, T91's outer oxide layer is highly porous.

Figure 103: SEM image of the oxide layers formed on the T91 500°C 666h sample.

Figure 104 shows the fluorescence data for iron and chromium gathered at the synchrotron source. Similar to HT-9 DELTA, the inner oxide exhibits a drop in iron content and an increase in chromium content, with an especially high peak of chromium just before the inner-outer oxide interface. The outer oxide shows a drop in chromium

and an increase in iron content of the sample. In the first half of the outer oxide layer, the iron fluorescence intensity dips down slightly, then rises again. This may be due to the porosity of the first half of the outer oxide layer, or due to the presence of other elements in this area.

Figure 104: Iron and chromium fluorescence for the T91 500°C 666h sample.

Figure 105 shows the lead and nickel fluorescence data from the T91 sample. Not surprisingly, the lead signal shows an enrichment in the first half of the outer oxide, corresponding to the bright spots seen in the SEM image. There is also a small enrichment in lead on the outside of the outer oxide layer, likely from coolant left behind on the surface of the outer oxide. Just as in all of the previous samples, the nickel fluorescence signal shows a small enrichment right at the inner oxide-metal interface. Unlike previous samples, however, T91 shows an unusually large nickel enrichment in the outer oxide – nearly double the signal seen in the metal. This is interesting considering the nickel content of T91 is lower than that of the HT-9 samples: about 0.13 weight percent.

Figure 105: Nickel and lead fluorescence for the T91 500°C 666h sample.

Figure 106 gives the contour plot of the diffracted intensities from phases as a function of 2-theta angle and location taken in 0.2 μm steps across HT-9 IPPE's oxide layer. Starting in the metal layer the most intense peak diffracts from ferrite (1 1 0), which, as usual, drops off in intensity as it continues into the inner oxide. This indicates that there are packets of uncorroded metal remaining in the inner oxide layer just as in the HT-9 samples. All four of the Fe_3O_4 magnetite peaks are also present, again, due to the uneven nature of the inner oxide-metal interface. These four peaks increase in intensity as they get closer to the inner oxide layer.

No carbide peaks are seen in the metal layer, however they do appear in the inner oxide. Since carbides in previous samples have been highly oriented, it is possible that peaks from them would appear inconsistently to in the sample. Also, T91 has only 8.26wt% chromium whereas HT-9 has 11.95%, so fewer, lower intensity chromium phases are expected in T91.

Figure 107: Diffraction data as a function of 2-theta and the distance into the sample for T91 500°C 666h. Image (a) corresponds to the iron and chromium fluorescence data.

The inner oxide of the T91 sample does contain two of the three carbide peaks – the (5 1 1) peak and the (4 2 0) peak. These do not appear in the expected relative intensities, but if they come from a highly oriented phase as expected, this would be of little surprise. It can be seen in Figure 104 that both peaks seem to continue into the outer oxide layer, but as will be explained in more detail later, both peaks deviate substantially from their initial positions in opposite directions indicating the presence of completely different phases in the outer oxide.

Besides chromium carbides and ferrite, the inner oxide layer also contains large magnetite peaks, and spinel peaks about an order of magnitude smaller. These spinel peaks grow weaker as they get closer to the inner-outer oxide interface. Simultaneously, several low-intensity Cr₂O₃ peaks appear and grow stronger closer to this interface. The Cr₂O₃ peaks are strongest at the inner-outer oxide interface where fluorescence data

showed largest enrichment of chromium. This also is where the two visible carbide peaks are strongest, although this does not necessarily indicate the location of the strongest enrichment of carbides if we expect that they are highly oriented.

A diffraction pattern and peakfit from the chromium enriched area is shown in Figure 108. In this figure, the Cr_2O_3 (1 0 4) and (1 1 0) peaks are fairly low intensity and difficult to detect. The carbide phases, however, are intense, and diffract as spots rather than rings providing further backing for the theory that they are a highly oriented phase. Generally speaking, other identified peaks in the inner oxide diffracted near their expected intensities, meaning that they were probably not as highly oriented as the carbides.

Figure 108: Diffraction pattern and peakfit of a scan in the inner layer of the T91 500°C 666h sample.

Entering the outer oxide, there is a sharp iron enrichment and chromium depletion, as well as the corresponding disappearance of phases containing chromium, as well as increased Fe_3O_4 magnetite peaks. Just as seen in the HT-9 DELTA and HT-9 DELTA annealed samples, the fcc Pb-Bi (2 0 0) and (1 1 1) peaks appear and endure for approximately the first half of the outer oxide. Unlike these samples, however, there are two new peaks in positions very close to those of the previously observed carbide peaks. It is not believed that these peaks represent the carbides, however, because a) there is not chromium in the fluorescence data for this layer, and b) these peaks are both shifted from the position of the carbide peaks, but in opposite directions. Shifts in the angular position of peaks is not unusual, however there shifts should occur all in the same direction for a given phase, not opposite ones as we see in this case. Figure 109 clearly the relationship of the carbide peaks to the ones seen in the outer oxide using an end-on view. The combination of the peak shifts and the lack of chromium in the outer oxide points strongly towards the conclusion that these peaks in the outer oxide do not in fact represent the carbide phase.

Since the outer oxide contains very large pores, it is not unexpected that materials used in the polishing process might become lodged in some of those pores. The polishing process involved silicon carbide paper, 1 μm diamond paste and 0.05 μm colloidal silica. As a result, the peak seen at ~37.1 degrees could be identified as synthetic diamond from

the diamond paste used in the polishing process. The peak at 32.0 degrees, however, remains unindexed.

Figure 109: End-on view of carbide peaks as they traverse from the metal layer into the inner oxide layer, followed by similar but shifted peaks in the outer oxide layer of T91 500°C 666h.

In addition to the peaks at 32.0 and 37.1 degrees, another pair of new peaks can be seen in the outer oxide at ~24.3 and 24.6 degrees. Again, these peaks have no positive identification, but are also believed to also belong to a foreign object caught in one of the large pores in the outer oxide layer. A diffraction pattern from this area in the outer oxide is given in Figure 110. It can be seen that both of the fcc Pb-Bi phases form light, spotted rings similar to in previous samples. The diamond peak is a very strong single spot, presumably diffracting from a large or well-oriented piece of diamond lodged in the pores of the outer oxide. The other unindexed peaks are also all formed from spots rather than rings indicating that they are either from highly oriented phases, or from very big grains.

The outermost part of the outer oxide is mainly composed of strongly diffracting Fe_3O_3 magnetite peaks, as well as the continued unindexed peak at 32.0°. Just as those in previous samples, these Fe_3O_3 peaks vary dramatically in relative intensity, and as a result are believed to be diffracting from very large grains.

To conclude, T91's oxide layers and main diffraction peaks were very similar to those found in HT-9 DELTA, however there were a few key differences. The phases containing chromium in T91 were much lower intensity than those in the HT-9 samples, and did not continue through much of the inner oxide layer. This is little surprise since the T91 alloy has lower chromium content than HT-9. Also, T91 also had a much more porous outer oxide than any of the HT-9 samples, and exhibited several unknown peaks in this region probably due to polishing materials or impurities getting stuck in the pores. Table 11 gives a summary of the observations made for the T91 500°C 666h sample.

Figure 110: Diffraction pattern and peakfit of a scan in the outer layer of the T91 500°C 666h sample.

Table 11: Summary of the observations made for T91 500°C 666h.

Metal Region	Inner Oxide (3.8 μm)		Outer Oxide (4.6 μm)	
	Sublayers		Sublayers	
Dense	Small pores, small grains	Small pores, small grains	Large pores, bright spots, large grains	Dense, large grains
Average Fe, Cr, Ni	High Cr, Elevated Ni, Depleted Fe	Very High Cr, Average Ni, Depleted Fe	Very High Ni & Pb, Average Fe	High Fe
bcc Fe, steadily increasing Fe_3O_4	Fe_3O_4 , FeCr_2O_4 , some bcc Fe and Cr_{23}C_6	Fe_3O_4 , FeCr_2O_4 , Cr_2O_3 , Cr_{23}C_6 , some bcc Fe	Fe_3O_4 , fcc Pb-Bi, syn. diamond, several unindexed	Fe_3O_4 , unindexed 32.0° peak

4.6 Alloy 3 500°C 666h

4.6.1. Microbeam synchrotron radiation diffraction and fluorescence analysis

Alloy 3 is a purely austenitic model alloy created solely from 91 wt% iron and 9 wt% chromium. While its chromium content is similar to that found in T91, it lacks all of the other alloying elements used to stabilize other phases such as martensite or ferrite, as well as add strength. The sample was corroded in the same manner as T91, HT-9 DELTA, and HT-9 DELTA Annealed: in flowing LBE in the DELTA loop for 666 hours at 500°C. The alloy was scanned at APS in June 2006 using a step size of 0.25 μm , over a slightly different angular range than the other alloys.

Figure 111 shows an overall view of the oxide layers formed on Alloy 3 during corrosion. Unlike previous alloys studied, Alloy 3's oxide layer has disconnected from the metal structure at the metal-inner oxide boundary in almost all places on the sample. In other sections of this alloy, this oxide layer was missing completely. It is not clear if the oxide layer delaminated during corrosion, cooling, or sample preparation, however presence of lead and bismuth found in the open gap by this work suggests that this happened while the sample was still in contact with the liquid LBE. In the area scanned at APS, this gap was approximately 1.7 μm thick, just as shown in the SEM image. The alloy exhibits an inner and an outer oxide layer measuring about 6.3 micro-meters thick in total. The inner oxide/outer oxide interface exhibits some porosity, which was also seen in the TEM studies.

Figure 111: SEM image of the oxide layers formed on Alloy3.

The Alloy 3 sample was scanned at APS using a step size of 0.25 μm . Figure 112 shows the fluorescence data for iron and chromium (the only alloying elements in the sample) gathered at the synchrotron source. In the metal the iron and chromium contents remain steady, then both drop off as the beam falls into the gap. After the gap the inner oxide shows a chromium enrichment and iron depletion. In the outer oxide, the chromium

tails off while the iron content raises some, although not to levels above those seen in the metal as with previous samples.

Figure 112: Iron and chromium fluorescence for the Alloy3 sample.

Figure 113 shows the fluorescence data for lead and nickel in Alloy 3's oxide layers. These two elements both start out at noise levels in the metal, then in the gap lead increases dramatically indicating the presence of coolant in this region. The outer oxide is also enriched in lead, and on the outer surface of the outer oxide a large lead peak is seen as well – likely a result of coolant adhered to the outer surface of the outer oxide.

What is surprising about the fluorescence data in Figure 113 is that there is any nickel content at all. Nickel is not an alloying element in Alloy 3, so its presence in the outer oxide is unexpected. There are several explanations for this. First, it could be noise or an error in the data acquisition system. This seems unlikely since data collected from empty sample holders did not contain any false nickel peaks. Second, it could have been deposited during sample preparation or polishing. Again, this seems unlikely since there is not nickel or nickel-containing substances used in these processes. The third, and most likely, explanation is that the coolant deposited the nickel there. It is known that the lead-bismuth coolant tends to leach nickel out of alloys during the corrosion process, and lead-bismuth eutectic is typically contaminated by nickel removed from the materials inside of the corrosion loops. Since lead and bismuth are regularly deposited from the coolant into

the outer oxide layers of the samples studied, it is likely that nickel contaminating that coolant would also deposit. In light of this, nickel enrichments in the outer oxides of previous samples may also be a result of deposition from the coolant, rather than nickel leaching out of the metal structure as previously suspected.

Previous samples did also exhibit nickel enrichments at the metal-inner oxide interface. Since Alloy 3 did not show a similar enrichment in this region, it seems likely that nickel enrichments closer to the metal region do come from nickel being leached out of the bulk metal during the corrosion process.

Figure 113: Nickel and lead fluorescence for the Alloy3 sample.

Figure 114 gives the contour plot of the diffracted intensities from phases as a function of 2-theta angle and location taken in 0.25 μm steps across Alloy 3's oxide layers. The metal region begins with an extremely strong bcc Fe (1 1 0) peak. Strangely, this peak continues throughout all of the oxide layers, and even out into the epoxy. This may be due to actual presence of ferrite out this far, or, the more likely explanation is that it is an artifact. This is backed up by TEM study, which did not observe the bcc ferrite phase anywhere outside of the metal layer. Since the bcc Fe (1 1 0) peak is the most intense peak encountered in any of the samples, it is possible that it saturated the CCD, causing it to seem as though it were present when it really wasn't.

Magnetite (Fe_3O_4) peaks are also present in the metal region, indicating that there is some oxidation going on deeper into the metal than SEM and TEM results had previously indicated. There are no carbide peaks present, which is little surprise since carbon was not an alloying element used in Alloy 3. There are, however, 2 Cr_2O_3 peaks in the metal, again indicating oxidation in the metal grains. Also, there is a new peak present in the metal region— one belonging to a rhombohedral bismuth phase. The TEM study identified a grain of this exact same bismuth phase in this sample as well, however the grain was observed in the gap in between the metal and inner oxide. In the case of the synchrotron data, however, peaks from this phase are seen close to the gap as well as in the outer oxide. This difference in location is most likely due to the fact that both the TEM and the synchrotron sample only very small areas, and the bismuth phase appears to be distributed throughout multiple regions of the sample.

Figure 114: Diffraction data as a function of 2-theta and the distance into the sample for Alloy 3. Image (a) corresponds to the iron and chromium fluorescence data.

In the gap between the metal and inner oxide most of the same peaks seen in the metal are present, as well as the fcc Pb-Bi (2 0 0) peak. At the same time as the fcc Pb-Bi (2 0 0) peak, the $\sim 30.5^\circ$ peak appears. This peak had previously been indexed as either Cr_2O_3 (1 1 0) or fcc Pb-Bi (1 1 1) depending on its location with respect to chromium and lead in the sample. While previously the location of chromium and lead/bismuth were mutually exclusive, this sample has the both located in the same region. Since there are no other Cr_2O_3 peaks in this region, and the other fcc Pb-Bi peak appears at the same time, it is logical to conclude that the peak at 30.5° is diffracting from fcc Pb-Bi (1 1 1) in this region.

The phases observed in the inner oxide are quite similar to those seen in the gap. There is a continuation of the bcc Fe peak, all 4 magnetite peaks, and both fcc Pb-Bi peaks. A diffraction pattern and peakfit from $6.0\ \mu\text{m}$ this region is given in Figure 115. It can be seen that the magnetite is diffracting in spotted rings as opposed to previous inner oxide regions where it tended to diffract as more of a solid ring. This is likely because while the grains in the inner oxide are smaller than those in the outer oxide, TEM studies revealed them to be larger than those seen in the inner oxide of HT-9 DELTA.

None of the previously examined samples exhibited peaks from the fcc Pb-Bi phase in the inner oxide, so seeing them here is something of a surprise. Unfortunately, it is unclear how or when this may have occurred. Because it is unknown when the delamination of the oxide layers occurred, it is also unknown whether or not the inner oxide was ever in contact with liquid lead-bismuth eutectic. Contact with the porous inner oxide might have allowed coolant to seep into these pores and solidify there, however without further studies it is not possible to say if this is the case.

Further on in the inner oxide, from about 6.75 to $8.0\ \mu\text{m}$, there is also the rise of some spinel phase. The spinel peaks, just as in all of the previous samples, are about an order of magnitude smaller than the magnetite peaks. As the chromium content of the sample decreases heading into the outer oxide, so does the presence of the spinel peaks, disappearing entirely in the outer oxide.

Figure 115: Diffraction pattern and peakfit of a scan in the inner layer of Alloy 3.

The outer oxide of the sample contains magnetite peaks as well as the two observed rhombohedral bismuth peaks. The lowest intensity Bi peak, (0 1 5) at just 5% relative intensity, is never observed probably because it was lost in the noise. It can be seen in the fluorescence that the outer oxide does not end abruptly, but instead fades out slowly. All of the magnetite peaks behave similarly, fading slowly as the outer oxide is traversed. TEM studies showed these outer oxide grains to be large and box-like, about 2 μm in length and up to 400 nm wide. It is little surprise then that the Fe_3O_4 peaks vary from their relative expected intensities as the beam, with a footprint of 0.2 μm x 2 μm , travels across the outer oxide.

To conclude, Alloy 3 is quite different from the other samples studied for a number of reasons. Firstly, it was the only alloy studied that experienced complete delamination of both oxide layers. Its oxide layers were messy, and diffracted phases in new and sometimes seemingly sporadic places when compared to previous samples. In TEM studies, it did not show preferential oxidation along grain boundaries or lath, nor did it exhibit leftover metal in the inner oxide layer. In the synchrotron, however, a high-intensity bcc Fe (1 1 0) peak appeared to be diffracting from the entire inner and outer oxide layers. While it is believed that this is due to an error in data collection, it was not possible to verify if this was the case. Alloy 3 also differed from other alloys in that it exhibited the fcc Pb-Bi phase all throughout the inner oxide as well as in the outer oxide. It also exhibited a new bismuth phase not seen in any previous sample.

Another major difference between Alloy 3 and other alloys is that it did not contain any carbon to form carbides with. It also had the lowest occurrence of chromium-containing phases, and when they did appear, they had the lowest intensity of any of the samples studied, including T91, which had a similar amount of chromium in it. The fluorescence data from Alloy 3 did not indicate that chromium was at all depleted in the metal, so the likely explanation is that the chromium-containing phases formed in other alloys simply formed with less intensity in Alloy 3. This could indicate that the presence of alloying elements besides chromium in the other samples helped to form and stabilize FeCr_2O_4 and Cr_2O_3 phases. Table 12 gives a summary of the observations made for Alloy3.

Table 12: Summary of the observations made for Alloy3.

Metal Region	Gap Region (1.7 μm)	Inner Oxide (2.5 μm)	Outer Oxide (3.8 μm)
Dense, large grains	Open with assorted debris	Small pores, small-medium grains	Dense, large equiaxed, then columnar grains
Average Fe, Cr	Low Fe & Cr, high Pb	High Cr, Depleted Fe & Pb	Very High Ni, high Pb, some Fe
bcc Fe, Cr_2O_3 , Bi, increasing Fe_3O_4	bcc Fe, fcc Pb-Bi, Fe_3O_4	Fe_3O_4 , FeCr_2O_4 , bcc Fe, fcc Pb-Bi	Fe_3O_4 , Bi, bcc Fe (noise?)

4.6.2. TEM analysis of Alloy 3 500°C 666h

The oxide layer formed on Alloy #3 after corrosion exhibits two distinct sub-layers: an outer oxide and an inner oxide layer. No diffusion layer was found using TEM. The SEM image in Figure 116 shows the interface between the inner oxide/metal to be porous. The location chosen for the TEM specimen appeared on the surface to have the least porosity, but the porosity beneath the surface between the inner oxide/metal layers caused the specimen to split along the interface during preparation in the FIB, as shown in Figure 116. The image shows the outer and inner oxide layers to be approximately 3.75 μm and 2.5 μm , respectively.

Figure 115: (a) SEM backscatter electron image of Alloy #3 showing the oxide layers and (b) FIB image of porous inner oxide/metal interface during sample preparation.

Figure 116 shows a TEM bright field image, which reveals the entire oxide sub-layer structure. Starting from the top of the image, the regions shown are: the epoxy, the outer oxide, the porous region within the inner oxide along the inner oxide/outer oxide interface, the inner oxide, the remaining porous region along the metal/inner oxide interface, and the metal.

The surface of the outer oxide layer varies up to one micron from minimum to maximum distance from the outer oxide/inner oxide interface as seen in Figure 116. The outer oxide layer exhibits mostly columnar grains, which are either perpendicular or are slightly angled from the normal to the outer oxide/inner oxide interface. The outer oxide grains are up to 2 μm in length and up to 400 nm wide. There are equiaxed grains of up to 400 nm in diameter as seen in the outer oxide layer at the outer oxide/inner oxide interface in the TEM bright field image in Figure 117. The porosity along the outer oxide/inner oxide interface is less than the porosity along the inner oxide/metal interface so that the specimen has remained intact along that interface.

Figure 116: TEM bright field image of entire Alloy #3 specimen.

Figure 117: TEM bright field image of large equiaxed grains along outer oxide/inner oxide interface of Alloy #3. (Note: The beam stop is present in this image)

The inner oxide layer shown in Figure 118 has short semi-columnar grains as well as equiaxed grains, which are up to one micron in length and 400 nm wide. The inner oxide grains show no preferred orientation.

Figure 118: TEM bright field image of the inner oxide grain structure of Alloy 3.

After initial SEM and TEM bright field analysis, TEM diffraction patterns were taken to help determine which phases are present in each sub-layer.

The TEM diffraction pattern in Figure 119(a) was taken from the outer oxide layer and indexed as Fe_3O_4 with a zone axis of $[-112]$. All diffraction patterns from the outer oxide layer were indexed as Fe_3O_4 .

Diffraction patterns within the inner oxide along the outer oxide/inner oxide interface that included the semi-porous region showed spotty to full rings, as shown in Figure 119(b), as opposed to the crystalline spot pattern that would be expected considering the outer oxide and inner oxide have crystalline spot diffraction patterns. The diffraction patterns characteristic of this region are clearly distinct from the other regions but could not be indexed. The bright field images show smaller grains along the outer oxide/inner oxide interface in contrast to the larger grains found in each respective layer.

A TEM diffraction pattern from the inner oxide layer is shown in Figure 119(c) and indexed as FeCr_2O_4 with a zone axis of $[011]$. All diffraction patterns from the inner oxide were indexed as FeCr_2O_4 .

An oval grain approximately 300 nm wide by 400 nm long was found (Figure 120) still attached to the metal and has a spot pattern much smaller (approximately a factor of 3) than the metal, indicating a larger lattice parameter. The diffraction pattern was indexed with a zone axis of $[101]$ and found to have d-spacings of 3.96, 3.75, and 3.30 Å corresponding to values tabulated in the Powder Diffraction File for bismuth (44-1246) of 3.954, 3.737, and 3.28 Å, respectively.

Figure 119: TEM diffraction patterns and corresponding bright field images of (a) a Fe_3O_4 grain with zone axis $[-112]$ within the outer oxide layer, (b) an unindexed pattern from a region at the outer oxide/inner oxide interface, and (c) a FeCr_2O_4 grain with zone axis $[011]$ within inner oxide layer of Alloy #3.

Figure 120: TEM bright field image and corresponding diffraction pattern of bismuth grain with zone axis [101].

Energy Dispersion Spectroscopy analysis, providing chemical information to be coupled with the preceding diffraction pattern analysis, was performed on each layer for the purpose of confirming the identification of phases within each layer.

EDS analysis shows no chromium to be present in the outer oxide. This information combined with TEM diffraction analysis indicates that the outer oxide consists of only Fe_3O_4 . EDS analysis shows chromium to be present within the inner oxide which indicates FeCr_2O_4 to be present, but does not confirm or deny the presence of Fe_3O_4 .

EDS analysis shows minute traces of lead and bismuth within the inner oxide, but shows larger amounts of lead throughout the outer oxide. Figure 121 shows plots of the ratios of the amplitudes of the $L_{\alpha 1}$ spectral lines for Bi/Fe and Pb/Fe. It can be seen from these plots that there is a significant enrichment of bismuth at the metal/inner oxide interface while lead is enriched throughout the outer oxide. The presence of lead in the outer layer is not unexpected, since the sample was corroded in lead bismuth eutectic and it is generally agreed that the outer oxide/inner oxide interface corresponds to the original metal surface before oxidation. Therefore, the penetration of lead is more likely in the outer oxide layer as opposed to the inner oxide layer.

Figure 121: TEM EDS of bismuth and lead $L_{\alpha 1}$ spectral emission lines throughout Alloy #3 from metal/diffusion layer interface with emphasis on (a) Bi/Fe ratio and (b) Pb/Fe ratio.

The outer surface of the outer oxide layer shows a box-like grain structure. EDS spectra taken from those grains and shown in Figure 122 exhibit, surprisingly, slightly less lead and bismuth than the rest of the outer oxide. EDS analysis confirms that the box-like structures are extensions of the grains within the outer oxide or, possibly, re-deposition of particulates from the solution, as opposed to particles of LBE adhering to the surface.

Figure 122: EDS (a) locations and (b) spectra overlay of box-like surface structures and a reference point within the outer oxide layer for Alloy #3.

It is interesting to note that large amounts of lead and bismuth were found by EDS analysis along the inner oxide/metal interface. EDS analysis was performed on two grains at the inner oxide/metal interface and on a reference inner oxide grain for comparison as shown in Figure 123. The spectra (Figure 124) for the grains at locations 2 & 20 have four well-defined bismuth peaks as well as reduced iron, chromium, and oxygen peaks. This confirms the TEM diffraction information, which indicated the grains to be bismuth.

Figure 123: EDS locations of reference inner oxide (3) and bismuth grains (2 & 20).

Figure 124: EDS spectra of bismuth grains (black & green) and reference inner oxide spectrum (red).

5. Conclusions

In this study, oxide layers formed on ferritic-martensitic alloys, exposed to both supercritical water and lead-bismuth eutectic, were analyzed using synchrotron radiation diffraction and fluorescence, and electron microscopy (both SEM and TEM). The oxide microstructure was characterized to understand the oxidation behavior of the alloys. The main conclusions are as follows:

1. The oxide formed on ferritic-martensitic steels often has a three-layer structure with an outer layer of Fe_3O_4 , an inner layer of FeCr_2O_4 - Fe_3O_4 , and a diffusion layer that often contains oxide precipitates. In the samples corroded at 500°C, the diffusion layer is essentially a solid solution of oxygen ahead of the oxide and contains few precipitates. In the 600°C samples, the diffusion layer consists of a mixture of oxide precipitates and metal grains. The TEM study shows that the outer oxide is made of large columnar grains while the inner oxide is formed of small equiaxed grains. The outer oxide columnar grains of the LBE samples tended to be smaller than those of the SCW samples, while the equiaxed inner oxide grains of the LBE samples were larger than those of the SCW samples.
2. In the 9CrODS samples corroded at 600°C, a Cr_2O_3 film formed at the diffusion layer-metal interface between the 2- and 4-week samples. This continuous layer of Cr_2O_3 appeared to stop or dramatically slow down the diffusion of oxygen beyond the ribbon and thus served as a barrier for further oxidation.
3. For the supercritical water samples, chromium enrichment associated with the presence of Cr_2O_3 was also observed at the inner oxide-diffusion layer interface for the 9CrODS 600°C 2-week sample, and at the diffusion layer-metal interface for the 600°C 4 and 6-week samples. Similar enrichment was observed for HCM12A and NF616 samples where an yttrium layer was deposited on the surface prior to oxidation. These phenomena are linked to the rare earth element effect (REE), which suggests that yttrium facilitates localized enrichment and segregation of chromium at grain boundaries.
4. The study of the diffusion layer of HCM12A showed that oxide advancement occurs by preferential oxidation of the chromium rich particles, likely carbides, present at the lath boundaries of the base metal. Therefore, the alloy microstructure has a strong influence on the corrosion behavior of the alloy.
5. Concerning the oxidation behavior in supercritical water, two different processes form the outer oxide layer and the inner oxide layer. The outer layer is formed by the outward diffusion of Fe^{2+} , created by the oxidation of the metal. These iron ions then react with the supercritical water to form Fe_3O_4 . The inner oxide layer is formed by the inward diffusion of O^{2-} , created by the reduction of water. These oxygen anions then react with the iron or chromium cations to form the oxide. Consequently, the outer oxide-inner oxide layer interface corresponds to the original metal-solution interface. If the oxidation of the metal is too slow, the

amount of Fe^{2+} ions created is too low to compensate for the outward migration of these cations from the inner layer, thus creating pores at the inner-diffusion layer interface.

6. In supercritical water, the oxide dispersion strengthened steel forms the most protective oxide (as measured by the inner oxide layer thickness) even though it has the least chromium alloying content since it has the smallest oxide thickness. This might be due to the yttrium-rich oxide nano-particles that catalyze the nucleation of stable and protective oxide. This is in agreement with the fact that the implantation of a yttrium surface coating before oxidation has a positive effect on the corrosion resistance.
7. Evidence was found for ingress of the lead-bismuth coolant into the oxide layer. An EDS analysis at the outer oxide/inner oxide interface of HT-9 found a lead grain, and two bismuth grains were found at the inner oxide/metal interface of Alloy #3. SEM images show light features in the outer oxide layers of the LBE corroded samples, which can be correlated to LBE contamination. Since lead and bismuth were found individually within the oxide layer, this suggests that the lead and bismuth may separate during cool-down, or possibly upon ingress into the layer at high temperature.

6. Publications

Three students principally worked on the project as part of their graduate work. Here is a list of these theses:

1. Andrew Siwy, "Transmission Electron Microscopy of Oxides formed on Generation IV Candidate Steel Alloys", M.Sc. thesis in Nuclear Engineering, Penn State, May 2008.
2. Jeremy Bischoff, "Evolution of the Oxide Structure of Ferritic-Martensitic Steels Exposed to Supercritical Water", M.Sc. thesis in Nuclear Engineering, Penn State, May 2008.
3. Jamie Kunkle, "Study of Candidate Steel Alloys for Lead-bismuth eutectic Cooled Reactor Applications" M.Sc. thesis in Nuclear Engineering, Penn State, December 2009.
4. Jeremy Bischoff, "Corrosion of Ferritic-Martensitic Alloys in Supercritical Water", Ph.D. thesis in Nuclear Engineering, Penn State, expected December 2010.

Refereed Publications

1. Jeremy Bischoff, Arthur T. Motta, Robert J. Comstock, "Evolution of the Oxide Structure of 9CrODS Exposed to Supercritical Water," Journal of Nuclear Materials, vol. 392, p.272.
2. A. D. Siwy, T. E. Clark, and A. T. Motta, "Transmission Electron Microscopy of oxide development on 9CrODS in Supercritical water", Journal of Nuclear Materials, vol. 392, p.280.

The research was presented at several conferences and articles were written for the proceedings of these conferences:

1. A.T. Motta, J. Bischoff, A. Siwy, M.J. Gomes da Silva, R.J. Comstock, Z.Cai and B.Lai, "Characterization of Oxide Layers Formed During Corrosion in Supercritical Water," Proceedings of the 17th NACE International Corrosion Congress, Las Vegas, October 2008, paper #4868.
2. J. Bischoff, A.T. Motta, Y. Chen, T. R. Allen, "Oxidation of 9CrODS Exposed to Supercritical Water," Proceedings of the NACE 2009 Corrosion Conference, Atlanta, Ga, paper # 09248.
3. J. Kunkle, A. T. Motta, R. J. Comstock, and P. Hosemann, "Characterization of HT-9 Ferritic-Martensitic Steels Oxidized in Lead Bismuth Eutectic", Transactions of the American Nuclear Society, v 98, Embedded Topical Meetings: Nuclear Fuels and Structural Materials for the Next Generation Nuclear Reactors, NFSM, 2008, p 1115-1116

4. Jeremy Bischoff, Arthur T. Motta, Lizhen Tan and Todd R. Allen, "Influence of Alloy Microstructure on Oxide Growth in HCM12A in Supercritical Water", Materials Research Society (MRS) Proceedings Symposium R: Materials for Future Fusion and Fission Technologies, 2008, paper ID R # 519941
5. Arthur T. Motta, Andrew D. Siwy, Jamie M. Kunkle, Jeremy B. Bischoff, Robert J. Comstock, Yun Chen, Todd R. Allen, "Microbeam Synchrotron radiation Diffraction and Fluorescence Study of Oxide Layers formed on 9CrODS steel in Supercritical Water," Proceedings of the 13th International Conference on Environmental Degradation of Materials in Nuclear Systems-Water Reactors. Whistler, Canada, (2007), TMS.
6. J. Bischoff, A.T. Motta, X. Ren and T.R. Allen, "Comparison of the Oxide structure formed on 9Cr ODS steel and NF616 in supercritical water," Proceedings of the 14th Environmental Degradation of materials Conference, Va. Beach, USA, (2009), TMS.

Presentations

- Three posters were presented at the ANS Embedded Topical Meeting: Nuclear Fuels and Structural Materials for the Next Generation Nuclear Reactors, June 8-12, 2008, Anaheim CA entitled:
 "Characterization of HT-9 Ferritic-Martensitic Steels Oxidized in Lead Bismuth Eutectic", J. Kunkle, A. T. Motta, and R. J. Comstock.
 "TEM Investigation of Oxide Development on 9Cr ODS in SCW", A. D. Siwy, T. E. Clark, and A. T. Motta
 "Evolution of Oxide Structure in Ferritic-martensitic Alloys in Supercritical Water," J. Bischoff, A. T. Motta and R.J. Comstock
- The poster by Andrew Siwy was chosen as the best poster for the meeting. As a consequence Andrew Siwy made a presentation entitled "TEM Investigation of Oxide Development on 9Cr ODS in SCW" at Idaho National Laboratory in July 2008.
- "Characterization of Oxide Layers Formed During Corrosion in Supercritical Water", A.T.Motta, J.Bischoff, A. Siwy, M.J. Gomes da Silva, R.J. Comstock, Zhonghou Cai and Barry Lai, Invited presentation by A. Motta at the 17th NACE International Corrosion Congress, Las Vegas, October 2008.
- "Comparison of the Oxide structure formed on 9Cr ODS steel and NF616 in supercritical water", J. Bischoff, A.T. Motta, X. Ren and T.R. Allen. Presentation at the 14th Environmental Degradation of materials Conference in Va. Beach, August 2009.

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References

- [1] A. Yilmazbayhan, A. T. Motta, R. J. Comstock, G. P. Sabol, B. Lai, and Z. Cai, *Journal of Nuclear Materials*, 324, (2004), 6-22.
- [2] K. Sridharan, S. P. Harrington, A. K. Johnson, J. R. Licht, M. H. Anderson, and T. R. Allen, *Materials & Design*, 28, (2007), 1177-1185.
- [3] K. Sridharan, A. Zillmer, J. R. Licht, T. R. Allen, M. H. Anderson, and L. Tan, "Corrosion Behavior of Candidate Alloys for Supercritical Water Reactors," *Proceedings of Proceedings of ICAPP 04*, Pittsburgh, PA, (2004).
- [4] V. Tcharnotskaia, C. Ammerman, T. Darling, J. King, N. Li, D. Shaw, L. Snodgrass, and K. Woloshun, http://www.physics.princeton.edu/mumu/target/pb-bi/pb_bi_loop_tcharnotskaia_01.pdf, Accessed March 27, 2008.
- [5] A. Yilmazbayhan, "Microstructural Basis of Uniform Corrosion in Zr Alloys," in *Nuclear Engineering*: Penn State University, 2004.
- [6] M. Silva, "Influence of Oxide Microstructure on Corrosion Behavior of Zirconium Based Model Alloys," in *Nuclear Engineering*: Penn State, 207.
- [7] "PeakFit," 4.0 for Windows ed: SPSS Chicago, IL, USA, . 1997.
- [8] S. Ohtuska, S. Ukai, M. Fujiwara, T. Kaito, and T. Narita, *Materials Transactions*, 46, (2005), 1.
- [9] S. Ukai, S. Mizuta, T. Yoshitake, T. Okuda, M. Fujiwara, S. Hagi, and T. Kobayashi, *Journal of Nuclear Materials*, 283-287, (2000), 702.
- [10] Y. Chen, K. Sridharan, T. R. Allen, and S. Ukai, *Journal of Nuclear Materials*, 359, (2006), 50.
- [11] Y. Chen, K. Sridharan, S. Ukai, and T. R. Allen, *Journal of Nuclear Materials*, 371, (2007), 118-128.
- [12] A. T. Motta, A. D. Siwy, J. M. Kunkle, J. B. Bischoff, R. J. Comstock, Y. Chen, and T. R. Allen, "Microbeam Synchrotron Radiation Diffraction and Fluorescence Study of Oxide Layers formed on 9CrODS Steel in Supercritical Water," *Proceedings of 13th Environmental Degradation of Materials in Nuclear Power Plants*, (2007).
- [13] Y. Ishikawa, T. Yoshimura, and M. Arai, *Vacuum*, 47, (1996), 701-704.
- [14] A. C. S. Sabioni, A. M. Huntz, F. Silva, and F. Jomard, *Materials Science and Engineering A*, 392, (2005), 254-261.
- [15] L. Tan, Y. Yang, and T. R. Allen, *Corrosion Science*, 48, (2006), 3123-3138.
- [16] A. D. Siwy, T. E. Clark, and A. T. Motta, *Journal of Nuclear Materials*, submitted, (2008).
- [17] J. Cermák, J. Ruzicková, and A. Pokorná, *Scripta Materialia*, 35, (1996), 411-416.
- [18] Z. Tkei, K. Hennesen, H. Viehhaus, and H. J. Grabke, *Materials Science and Technology*, 16, (2000), 1129-1138.
- [19] L. Tan, M. T. Machut, K. Sridharan, and T. R. Allen, *Journal of Nuclear Materials*, 371, (2007), 161-170.

- [20] L. Tan, Y. Yang, and T. R. Allen, *Corrosion Science*, 48, (2006), 4234-4242.
- [21] J. Stringer, *Materials Science and Engineering, A*, 120, (1989), 129.
- [22] J. Bischoff, A. T. Motta, L. Tan, and T. R. Allen, *Proceedings of MRS Fall 2008 Conference, Symposium R: Materials for Future Fusion and Fission Technologies*, Boston, MA, Paper # 519941, (2008).
- [23] M. Jung, S.-J. Lee, and Y.-K. Lee, *Metallurgical and Materials Transactions A*, 40, (2009), 551-559.
- [24] P. Ampornrat and G. S. Was, *Journal of Nuclear Materials*, 371, (2007), 1-17.
- [25] J. Stringer, *Oxidation of metals*, 5, (1972), 11-47.
- [26] J. Bischoff, A. T. Motta, Y. Chen, and T. R. Allen, *Proceedings of NACE Corrosion 2009, Corrosion in Supercritical Systems*, Atlanta, GA, Paper # 09248, (2009).
- [27] F. Barbier and A. Rusanov, *Journal of Nuclear Materials*, 296, (2001), 231-236.