STRUCTURE OF OXIDE LAYERS FORMED ON CANDIDATE STEEL ALLOYS EXPOSED TO FLOWING LEAD-BISMUTH EUTECTIC FOR GENERATION IV REACTOR APPLICATIONS

A Thesis in
Nuclear Engineering

by

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ABSTRACT

Ferritic-martensitic steels of interest for use in Generation IV lead cooled fast reactors were corroded in a flowing lead-bismuth eutectic environment and the microstructures of the oxide layers they formed were characterized using microbeam synchrotron radiation. Five samples were studied, four of which (HT-9, HT-9 Annealed, T91, and a model alloy) were corroded at 500°C for 666 hours and one of which (HT-9) was corroded at 550°C for 3000 hours in flowing lead bismuth eutectic environments. Studies performed on oxide layers using microbeam synchrotron radiation yielded a detailed view of fluorescence and diffraction data from each of the oxide layers and sublayers formed.

Each alloy exhibited a duplex oxide structure consisting of an inner and outer oxide layer. The interface of these two layers corresponded to the original pre-corrosion metal surface. In general, the oxide layers appeared to have been formed in a manner similar to those formed in other gaseous and liquid environments i.e. via the simultaneous ingress of oxygen ($O^{2-}$) and egress of iron ($Fe^{2+}$) across the inner oxide – outer oxide interface. The outer oxide layers observed were formed entirely of $Fe_3O_4$ magnetite, contained contaminants (Pb, Bi) from the coolant, and showed evidence of liquid metal dissolution. Inner oxide layers were formed primarily from $Fe_3O_4$, but also contained retained ferrite from the bulk metal, carbides, and chromium oxides. Chromium oxides, specifically $Cr_2O_3$, are known to act as barriers against the diffusion of oxygen and iron in these materials, slowing oxidation in these materials. The retained bcc iron, or ferrite, in the inner oxide combined with preferential oxidation along lath boundaries suggest that
the oxide front advancement proceeded into the metal via preferential oxidation along lath boundaries, followed by selective oxidation of the laths.
# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... viii

LIST OF TABLES ............................................................................................................. xiii

ACKNOWLEDGEMENTS ............................................................................................... xv

Chapter 1 Introduction and Background......................................................................... 1

1.1 Generation IV Nuclear Reactors ........................................................................... 1

1.2 The Lead Cooled Fast Reactor ............................................................................ 2

1.2.1 Cooling the Lead Cooled Fast Reactor ......................................................... 4

1.2.2 Materials selection for the Lead Cooled Fast Reactor ................................ 5

1.3 Ferritic-Martensitic Steels ............................................................................... 5

1.3.1 Ferritic-Martensitic Steels under Irradiation .............................................. 6

1.3.2 Corrosion of Ferritic-Martensitic Steels in Lead-Bismuth Eutectic .... 6

1.3.2.1 Effect of Scale Removal on Corrosion in Lead Bismuth Eutectic ................. 8

1.3.3 Long-Term Corrosion Behavior of Ferritic-Martensitic Steels ............... 9

Chapter 2 Experimental Procedures ........................................................................ 11

2.1 Ferritic-Martensitic Materials Studied ................................................................ 11

2.1.1 Alloy History .............................................................................................. 11

2.1.2 Alloy Composition ....................................................................................... 12

2.1.3 Metallurgy .................................................................................................. 12

2.2 Corrosion Conditions ......................................................................................... 17

2.3 Sample Preparation ............................................................................................ 18

2.4 Sample Examination ......................................................................................... 21

2.4.1 SEM Examination ....................................................................................... 21

2.4.2 Microbeam Synchrotron Analysis ............................................................... 22

2.4.2.1 μ-X-Ray Fluorescence Data ................................................................. 25

2.4.2.2 μ-X-Ray Diffraction Data .................................................................. 28

2.4.2.2.1 Diffraction Peak Analysis .............................................................. 31

2.4.2.2.2 Diffraction Peak Information ......................................................... 33

Chapter 3 Experimental Results ............................................................................... 35

3.1 Examination of Oxide Layers Formed on HT-9 DELTA after 666 hours of exposure to 500°C Lead-Bismuth Eutectic ......................................................... 36

3.1.1 Scanning Electron Microscope Examination of HT-9 DELTA .................... 36

3.1.2 Energy Dispersive Spectroscopy Mapping of HT-9 DELTA ....................... 38

3.1.3 Microbeam X-Ray Fluorescence Examination of HT-9 DELTA ............. 40

3.1.4 Microbeam X-Ray Diffraction Examination of HT-9 DELTA ............... 43
3.1.4.1 Metal Region ................................................................. 46
3.1.4.2 Inner Oxide Layer ..................................................... 51
3.1.4.3 Outer Oxide Layer ..................................................... 56
3.1.5 HT-9 DELTA Summary .................................................. 58

3.2 Examination of Oxide Layers Formed on HT-9 DELTA Annealed after 666 hours of exposure to 500°C Lead-Bismuth Eutectic ........................................... 60
3.2.1 Scanning Electron Microscope Examination of HT-9 DELTA Annealed .......................................................... 61
3.2.2 Microbeam X-ray Fluorescence Examination of HT-9 DELTA Annealed .......................................................... 62
3.2.3 Microbeam X-Ray Diffraction Examination of HT-9 DELTA Annealed .......................................................... 65
   3.2.3.1 Metal Region .......................................................... 67
   3.2.3.2 Inner Oxide Region .................................................. 67
   3.2.3.3 Outer Oxide Region .................................................. 71
3.2.4 HT-9 DELTA Annealed Summary of Findings .................. 72

3.3 Examination of Oxide Layers Formed on HT-9 IPPE after 3000 hours of exposure to 550°C Lead-Bismuth Eutectic .................................................. 74
3.3.1 Scanning Electron Microscope Examination of HT-9 IPPE .......................................................... 74
3.3.2 Microbeam X-ray Fluorescence Examination of HT-9 IPPE .......................................................... 76
3.3.3 Microbeam X-Ray Diffraction Examination of HT-9 IPPE .......................................................... 78
   3.3.3.1 Metal Layer .......................................................... 80
   3.3.3.2 Inner Oxide Region .................................................. 81
   3.3.3.3 Outer Oxide Region .................................................. 83
3.3.4 HT-9 IPPE Summary of Findings ..................................... 86

3.4 Examination of Oxide Layers Formed on T91 after 666 hours of exposure to 500°C Lead-Bismuth Eutectic .................................................. 87
3.4.1 Scanning Electron Microscope Examination of T91 .......................................................... 88
3.4.2 Microbeam X-ray Fluorescence Examination of T91 .......................................................... 90
3.4.3 Microbeam X-Ray Diffraction Examination of T91 .......................................................... 93
   3.4.3.1 Metal Region .......................................................... 95
   3.4.3.2 Inner Oxide Region .................................................. 95
   3.4.3.3 Outer Oxide Region .................................................. 97
3.4.4 T91 Summary of Findings ................................................ 100

3.5 Examination of Oxide Layers Formed on Alloy 3 after 666 hours of exposure to 500°C Lead-Bismuth Eutectic .................................................. 102
3.5.1 Scanning Electron Microscope Examination of Alloy 3 .......................................................... 102
3.5.2 Microbeam X-Ray Diffraction Examination of Alloy 3 .......................................................... 105
3.5.3 Microbeam X-Ray Diffraction Examination of Alloy 3 .......................................................... 108
   3.5.3.1 Metal Region .......................................................... 110
   3.5.3.2 Gap between Metal Region and Inner Oxide Region .......................................................... 111
   3.5.3.3 Inner Oxide Region .................................................. 111
   3.5.3.4 Outer Oxide Region .................................................. 113
3.5.4 Alloy 3 Summary of Findings ........................................ 113
LIST OF FIGURES

Figure 1-1: Design of the Lead-Cooled Fast Reactor [1] .........................................................3
Figure 1-2: Phase diagram for lead and bismuth [2].................................................................4
Figure 1-3: Comparison between oxide layers developed in gaseous environments versus those developed in LBE [16].................................................................................................9
Figure 2-1: Schaeffler-Schneider diagram for HT-9, T91, and Alloy 3 [19]. .................14
Figure 2-2: Optical Micrograph of Alloy 3 after etching. ....................................................15
Figure 2-3: Optical Micrographs of etched a) HT-9 and b) HT-9 Annealed samples. Ferrite grains are circled in yellow. .................................................................................................17
Figure 2-4: Schematic representation of sample preparation process .........................19
Figure 2-5: Optical Micrograph of a final polished cross sectional sample ready for examination ..........................................................................................................................20
Figure 2-6: Setup of $\mu$-XRF and $\mu$-XRD collection technique .................................24
Figure 2-7: Schematic of beam being stepped along cross sectioned oxide layer.......25
Figure 2-8: K-lines and ROI’s (shown in yellow) for vanadium, chromium, manganese, iron, and cobalt....................................................................................................................27
Figure 2-9: Schematic representation of the tiff images being processed into intensity versus two theta data.................................................................29
Figure 2-10: Comparison of tiff image processing program outputs.............................30
Figure 2-11: Sample fitting of peaks using PeakFit..............................................................32
Figure 2-12: Creation of a 3-D contour plot from sets of peak fitted diffraction data.............................................................................................................................33
Figure 3-1: Scanning electron micrograph of oxide layers formed on HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic.................................37
Figure 3-2: Energy dispersive spectroscopy maps from oxide layers formed on HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic............40
Figure 3-3: Iron and chromium microbeam x-ray fluorescence data from oxide layers formed on HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic. .................................................................41

Figure 3-4: Lead and nickel microbeam x-ray fluorescence data from oxide layers formed on HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic................................................................................................................................................43

Figure 3-5: Summary of data obtained using microbeam synchrotron radiation on oxide layers formed on HT-9 DELTA 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 versus 2-theta angle versus distance into the sample. Indexed peaks are indicated as well as approximate distance between layers. The asterisks denote locations of individual diffraction patterns discussed later in this section. ...............................................45

Figure 3-6: TEM bright field image from oxide layers formed on HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic with schematic of inner oxide region (region A) containing dashed lines representing retained metal grains in the inner oxide [25]........................................................................48

Figure 3-7: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 3.2 µm into the HT-9 DELTA metal region after 666 hours of exposure to 500°C lead-bismuth eutectic.................................................................51

Figure 3-8: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 9.2 µm into HT-9 DELTA in the inner oxide after 666 hours of exposure to 500°C lead-bismuth eutectic.................................................................52

Figure 3-9: TEM bright field image (a) and corresponding diffraction pattern (b) from a (Fe,Cr)₃O₄ grain within the inner oxide with a zone axis of [-111] from HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic. Arrows indicate retained metal grains. [25].........................................................53

Figure 3-10: Diffraction pattern taken from 11.2 µm into HT-9 DELTA in the inner oxide after 666 hours of exposure to 500°C lead-bismuth eutectic.................54

Figure 3-11: (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.................................57

Figure 3-12: Fluorescence data from iron and chromium shown with regions of interest (in yellow) over which chemical composition for each element was averaged. ..................................................................................................................60
Figure 3-13: Scanning electron micrograph of oxide layers formed on HT-9 DELTA Annealed after 666 hours of exposure to 500°C lead-bismuth eutectic

Figure 3-14: Iron and chromium microbeam x-ray fluorescence data from oxide layers formed on HT-9 DELTA Annealed after 666 hours of exposure to 500°C lead-bismuth eutectic

Figure 3-15: Lead and nickel microbeam x-ray fluorescence data from oxide layers formed on HT-9 DELTA Annealed after 666 hours of exposure to 500°C lead-bismuth eutectic

Figure 3-16: 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 the 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.

Figure 3-17: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 4.6 μm into HT-9 DELTA Annealed’s inner oxide layer after 666 hours of exposure to 500°C lead-bismuth eutectic

Figure 3-18: Diffraction patterns from an unindexed phase from multiple locations in metal and inner and outer oxide layers.

Figure 3-19: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 6.0 μm into HT-9 DELTA Annealed’s inner oxide layer after 666 hours of exposure to 500°C lead-bismuth eutectic

Figure 3-20: Scanning electron micrograph of oxide layers formed on HT-9 IPPE after 3000 hours of exposure to 550°C lead-bismuth eutectic

Figure 3-21: Iron and chromium microbeam x-ray fluorescence data from oxide layers formed on HT-9 IPPE after 3000 hours of exposure to 550°C lead-bismuth eutectic

Figure 3-22: Lead and nickel microbeam x-ray fluorescence data from oxide layers formed on HT-9 IPPE after 3000 hours of exposure to 550°C lead-bismuth eutectic

Figure 3-23: 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 the 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. ........................................ 79

Figure 3-24: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 2.6 µm into HT-9 IPPE’s metal region after 3000 hours of exposure to 550°C lead-bismuth eutectic.............................................. 81

Figure 3-25: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 8.2 µm into HT-9 IPPE’s inner oxide region after 3000 hours of exposure to 550°C lead-bismuth eutectic. .............................................. 82

Figure 3-26: Energy dispersive spectroscopy maps from outermost oxide layer formed on HT-9 IPPE after 3000 hours of exposure to 550°C lead-bismuth eutectic. Arrows indicate areas of enriched lead and bismuth......................... 84

Figure 3-27: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 22.6 µm into HT-9 IPPE’s outer oxide region after 3000 hours of exposure to 550°C lead-bismuth eutectic.............................................. 85

Figure 3-28: Scanning electron micrograph of oxide layers formed on T91 after 666 hours of exposure to 500°C lead-bismuth eutectic.................................................. 89

Figure 3-29: Iron and chromium microbeam x-ray fluorescence data from oxide layers formed on T91 after 666 hours of exposure to 500°C lead-bismuth eutectic.................................................................................................................. 91

Figure 3-30: Lead and nickel microbeam x-ray fluorescence data from oxide layers formed on T91 after 666 hours of exposure to 500°C lead-bismuth eutectic.................................................................................................................. 92

Figure 3-31: Summary of data obtained using microbeam synchrotron radiation on oxide layers formed on T91 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 the 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. .............................................. 94

Figure 3-32: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 5.0 µm into T91’s inner oxide region after 666 hours of exposure to 500°C lead-bismuth eutectic.............................................. 97

Figure 3-33: 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 after 666 hours of exposure to 500°C lead-bismuth eutectic.................................................................................................................. 98

Figure 3-34: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 7.8 µm into T91’s outer oxide region after 666 hours of exposure to 500°C lead-bismuth eutectic.......................................................... 100

Figure 3-35: Scanning electron micrograph of oxide layers formed on T91 after 666 hours of exposure to 500°C lead-bismuth eutectic.................................................. 103

Figure 3-36: Bright field transmission electron microscope images of oxide layers formed on T91 after 666 hours of exposure to 500°C lead-bismuth eutectic [25]........................................................................................................................ 104

Figure 3-37: Iron and chromium microbeam x-ray fluorescence data from oxide layers formed on Alloy 3 after 666 hours of exposure to 500°C lead-bismuth eutectic.................................................................................................................. 106

Figure 3-38: Lead and nickel microbeam x-ray fluorescence data from oxide layers formed on Alloy 3 after 666 hours of exposure to 500°C lead-bismuth eutectic.................................................................................................................. 107

Figure 3-39: Summary of data obtained using microbeam synchrotron radiation on oxide layers formed on Alloy 3 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 the sample. Indexed peaks are indicated as well as approximate distance between oxide layers. The asterisk denotes the location of the diffraction pattern discussed further on in this section........................................... 109

Figure 3-40: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 6.0 µm into Alloy 3’s inner oxide region after 666 hours of exposure to 500°C lead-bismuth eutectic.................................................. 112
**LIST OF TABLES**

Table 2-1: Chemical compositions of HT-9, T91, and Alloy 3 in weight percent. .....12  
Table 2-2: Nickel and chromium equivalents for HT-9, T91, and Alloy 3. ..............14  
Table 2-3: Heat treatment parameters for HT-9, T91, and Alloy 3 .............................16  
Table 2-4: Comparison of corrosion parameters in the DELTA and IPPE loops........18  
Table 2-5: Fluorescence line energies and their regions of interest.........................26  
Table 2-6: 2θ Angular ranges of diffraction data taken for each sample...............28  
Table 3-1: Comparison of corrosion and examination conditions for alloys discussed.............................................................................................................35  
Table 3-2: Expected peaks for bcc Fe (Ferrite) and bcc Cr structure in the studied angular range (PDF: 00-006-0696).................................................................46  
Table 3-3: Expected peaks for fcc Cr23C6 (chromium carbide) in the studied angular range (PDF: 04-007-5437).................................................................46  
Table 3-4: Expected peaks for Fe3O4 (magnetite) and FeCr2O4 (spinel) in the studied angular range (PDFs: 04-008-8147, 04-006-2807).................................49  
Table 3-5: Expected peaks for Cr2O3 (chromium oxide) in the studied angular range (PDF: 04-009-2109).................................................................55  
Table 3-6: Fcc Pb-Bi phases corresponding to peak locations in the studied angular range (PDFs: 04-005-9303, 04-003-0604, and 04-004-6681).................58  
Table 3-7: Summary of findings for oxide layers formed on HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic........................................59  
Table 3-8: Fe2O3 Hematite peak locations (PDF: 04-008-7625).................................71  
Table 3-9: Summary of findings for oxide layers formed on HT-9 DELTA Annealed after 666 hours of exposure to 500°C lead-bismuth eutectic..............73  
Table 3-10: Cr7C3 Carbide peak locations (PDF: 00-036-1482).................................80  
Table 3-11: Summary of findings for oxide layers formed on HT-9 IPPE after 3000 hours of exposure to 550°C lead-bismuth eutectic.................................86  
Table 3-12: Diamond (C) peak locations (PDF: 01-075-0410).................................99
Table 3-13: Summary of findings for oxide layers formed on T91 after 666 hours of exposure to 500°C lead-bismuth eutectic

Table 3-14: Rhombohedral bismuth (Bi) peak locations (PDF: 00-044-1246 )

Table 3-15: Summary of findings for oxide layers formed on Alloy 3 after 666 hours of exposure to 500°C lead-bismuth eutectic

Table 4-1: Corrosion conditions and examination methods for samples studied

Table 4-2: Summary of Findings for Alloys studied
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Chapter 1

Introduction and Background

1.1 Generation IV Nuclear Reactors

As the world’s population increases and its overall standard of living rises, so do its energy needs. As the evidence for global warming caused by CO$_2$ emissions increases and concern about sustainability and dependence on foreign sources of fossil fuels grows, it has become increasingly necessary to review and change our energy policies. While no energy source is without political and environmental difficulties, nuclear power can provide a safe, clean, reliable, and long-term alternative to fossil fuel based energy production methods.

In order to address these continuing concerns, ten countries including the United States have joined together in the Generation IV International Forum (GIF) to research and develop new and innovative power plant designs for the future of nuclear power production. It is hoped that these plants will be implemented by the year 2030. The reactor design concepts were designed to meet the following goals set out by the GIF [1]:

* Sustainability: Provide sustainable energy generation which meets clean air objectives while minimizing and managing nuclear waste.

* Economics: Energy generation with lower life-cycle cost and lower level of financial risk than other generation methods.
Safety and reliability: Plants which excel in safety and reliability with very low likelihood of reactor core damage, eliminating the need for offsite emergency response.

Proliferation resistance: Plants which are unattractive targets for theft of weapons-grade material or terrorist attack.

To meet these goals, six innovative designs were chosen by the Generation IV International Forum for more in-depth study and development. In alphabetical order, these are:

a) The Gas-Cooled Fast Reactor (GFR)
b) The Lead-Cooled Fast Reactor (LFR)
c) The Molten Salt Reactor (MSR)
d) The Sodium-Cooled Fast Reactor (SFR)
e) The Supercritical-Water-Cooled Reactor (SCWR)
f) and The Very-High-Temperature Reactor (VHTR) [1]

Each of these designs has its unique advantages and disadvantages, and merit further study. This thesis will focus on the Lead-Cooled Fast Reactor System.

1.2 The Lead Cooled Fast Reactor

The Lead-Cooled Fast Reactor (LFR), shown in Figure 1-1, is a closed cycle fast spectrum reactor which is cooled by the natural convection of either liquid lead or lead-bismuth eutectic. LFR’s have been envisioned to produce anywhere from 50 to 1200 MWe with a core outlet temperature of approximately 550°C. The LFR features a turnkey
style core with a very long refueling interval of approximately 15-20 years leading to very high total neutron flux seen by core materials. It is also relatively inexpensive and small-sized due to the natural radiation shielding of its coolant as well as lack of complicated pumping systems in the primary loop. Also, the LFR can quickly change power output to adjust to demand. These advantages make it an attractive option for electricity production on small grids, as well as in developing countries lacking their own fuel cycle infrastructure.

Figure 1-1: Design of the Lead-Cooled Fast Reactor [1]
1.2.1 Cooling the Lead Cooled Fast Reactor

As mentioned previously, the lead cooled fast reactor can be built using either lead or lead-bismuth eutectic (LBE) as its coolant. Figure 1-2 shows the main advantage of using LBE over lead – LBE’s melting point (123.5°C) is substantially lower than that of pure lead (327°C) [2]. Since LBE has a melting point 203.5°C lower than lead, the chances of coolant solidification within the core would be drastically reduced, leading to safer and more reliable operation of the reactor. LBE also has the advantages of excellent heat transfer characteristics, good neutron yield, and low vapor pressure. The major disadvantage of using LBE over lead as a coolant, however, is that neutrons in the core can transmute bismuth into $^{210}\text{Po}$, a short-lived, hazardous alpha emitter and neutron poison. In spite of this, LBE is still an excellent candidate coolant for the lead cooled fast reactor, and it is the coolant material that will be used in this study [2].

Figure 1-2: Phase diagram for lead and bismuth [2]
1.2.2 Materials selection for the Lead Cooled Fast Reactor

Unfortunately, both lead and LBE as coolants at the temperatures required by the reactor present a very challenging environment for the reactor core materials, especially the cladding. On top of this, the long burnup times in the reactor present radiation problems for the internal materials as well. Because the cladding will spend up to 20 years at temperatures between 350-600°C in molten metal and experience up to 200 displacements per atom, it must have exceptional resistance to oxidation and dissolution as well as excellent tolerance to damage. This means that one of the critical areas of research for this Generation IV design will be in its materials selections, especially for the cladding for lead cooled fast reactors [1]. Many materials are under review for this selection, one promising candidate being Ferritic-Martensitic Steels.

1.3 Ferritic-Martensitic Steels

Originally developed for applications in fast breeder reactors, Ferritic-Martensitic steels (F-M steels) have excellent thermal conductivity, low expansion coefficients, and very good resistance to radiation effects [3]. In addition to this, these materials have especially high strength at elevated temperatures, and contain large additions of chromium for added oxidation and corrosion resistance [4]. For these reasons, Ferritic-Martensitic steels are of great interest for study in Lead-Cooled Fast Reactors.
1.3.1 Ferritic-Martensitic Steels under Irradiation

Many experiments have been undertaken to determine radiation effects on different Ferritic-Martensitic (F-M) Steel alloys. It has been found that in general these steels have low activation relative to other carbon steels [3], experience relatively low swelling (an order of magnitude lower than commercial austenitic steels) [5,6], slight increase in strength [7], and have fairly low creep even at high neutron fluence (about half that of austenitic steels) [8]. The F-M steels studied in this thesis have large amounts of radiation experience and have been found to display the above characteristics even to very high displacements per atom [3]. The data has shown that these steels, at elevated temperatures (above about 400°C), approach very similar yield stress and elongation behaviors to those of unirradiated (thermally aged) steels [9,10]. These steels were chosen for this thesis due to their favorable radiation characteristics at elevated temperatures and high doses.

1.3.2 Corrosion of Ferritic-Martensitic Steels in Lead-Bismuth Eutectic

Depending on the oxygen concentration dissolved in the lead-bismuth eutectic, corrosion of the reactor components may happen by either dissolution or oxidation [11]. To avoid either runaway dissolution or oxidation of materials, it is important to carefully control oxygen concentrations in the LFR environment. The dissolved oxygen content at a given temperature must be above the concentration required to form magnetite (Fe₃O₄), but below that which would cause precipitation of lead oxide (PbO) [12,13]. Under these
carefully calibrated oxygen concentrations, the ideal material quickly forms a stable, protective oxide layer thereby preventing major dissolution of the material.

Most corrosion studies performed on Ferritic-Martensitic steels in LBE have been done in static rather than flowing coolant which is believed to yield somewhat different results. In flowing LBE, the dissolution rate is affected by the flow rate of the coolant. In static LBE, however, the dissolution rate is instead affected by the volume of the LBE and the concentration of other dissolved metals in it [14]. Since the reactor core will be flowing, the samples studied in this thesis were all corroded under flowing conditions. This means that, while higher dissolution and scale removal of the materials tested is seen, the conditions used better reflect those that will be seen by the materials in the eventual reactor.

Due to dissolution and scale removal in the flowing LBE loops, samples studied in this thesis experienced both weight gain and weight loss over the course of the experiment. It is generally accepted that the Ferritic-Martensitic steels initially lose some of their material to the coolant, in conditions above about 400°C (the temperatures of interest for this reactor), and then quickly begin forming an oxide layer which is much less susceptible to dissolution than the base metal [14]. The oxide formation of F-M steels in LBE is similar to that seen on the same steels in other flowing metal, water, or gaseous environments [15]. This layer grows in 2 directions by the inward diffusion of oxygen and the outward diffusion of iron. This forms a duplex oxide structure – one which has an inner layer and an outer layer, at the interface of which sits at initial metal’s surface. The inner layer has been found by previous researches to be composed of a Fe-Cr spinel (Fe$_{3-x}$Cr$_{x}$O$_4$) structure, whereas the outer layer is mostly magnetite (Fe$_3$O$_4$).
While the oxide continues to grow, the LBE coolant simultaneously removes the outer scale [14]. Because of this, it is expected that the oxide thickness may reach a plateau for long term operations in LBE where the oxidation rate at the substrate is equal to the dissolution rate at the oxide/LBE interface. While the oxide growth rate alone approximates the parabolic law, several things affect the rate at which the scale is removed including temperature, flow rate, and oxygen concentration. For shorter term operation, it is possible that the dissolution would have little effect on the oxide layer thickness. For longer term-operation, however, with good control of oxygen concentration and flow rate in the LBE, it has been seen in previous experiments that at 550°C, the oxidation process dominates until it reaches a turning point at around 2000 h. After this, scale removal rate dominates and weight loss is seen [14]. This issue of dissolution and scale removal is considered to be one of the major differences in the corrosion of materials in the LFR environment compared to those in different environments [16].

1.3.2.1 Effect of Scale Removal on Corrosion in Lead Bismuth Eutectic

A qualitative comparison of oxide layers developed in a gaseous environment (no scale removal) versus those developed in a flowing LBE environment is shown in Figure 1-3 [16]. Part (a) shows the expected oxide development for a situation in which the liquid metal enhances the oxidation rate in LBE, $k_{p,c}$, over that of the rate in a gaseous environment, $k_p$. This results in an initially thicker inner and outer oxide than those formed in the gaseous environment, but in the long term, the outer oxide in the LBE
becomes thinner due to scale removal, whereas the inner oxide becomes thicker due to continued inward diffusion of oxygen from the surface. Figure 1-3 (b) shows a situation in which the two rates are equal, so that the inner oxide layer thickness is the same as that developed in the gaseous environment, but the outer oxide is thinner due to scale removal. Finally, Figure 1-3 (c) shows a regime in which the LBE limits the rate of oxide growth compared to the gaseous environment. Here, both the inner and outer layers are thinner than those developed in gas, and liquid metal scale removal of the layers might eventually remove the outer layer completely in the long term [16].

Figure 1-3: Comparison between oxide layers developed in gaseous environments versus those developed in LBE [16].

1.3.3 Long-Term Corrosion Behavior of Ferritic-Martensitic Steels

According to models proposed by several researchers, long term effects of oxidation and dissolution on Ferritic-Martensitic Steels may take a variety of routes.
Most desirably, the oxide would reach a steady-state in which both dissolution and oxidation of the material are minimal enough that little to no material is lost into the coolant over the reactor’s operation life. Since the outer-oxide scale removal at the flow rates and temperatures proposed for this design have already been shown to be too high for the pure magnetite outer layer, it is hoped that the inner layer spinel structures or other structures within this layer will be sufficiently protective. While it is known that chromium rich-structures are protective again runaway oxidation [3], researchers have also found that chromium-rich oxides resist dissolution as well. Recent findings suggest that it is believed that a minimum of 18% Cr is needed to form Cr$_2$O$_3$ structures which would be sufficiently protective against the effects of dissolution & scale removal [17]. At present, there is insufficient study of the composition of oxide layers to determine their protective capabilities.

The studies performed on the corrosion of Ferritic-Martensitic steels so far have not been able to obtain sufficiently detailed phase or elemental information from the individual sub-layers or the interfaces between these layers. Because of this, they are unable to predict the longer term behavior of the oxide or the long-term effects of oxide-coolant interaction. This information can be obtained using microbeam synchrotron radiation diffraction and fluorescence to collect data from the individual oxide sub-layers and interfaces. The description of this process is given in Section 2.4.2. Using this information, we hope to better understand the corrosion mechanisms and thus predict long-term corrosion behavior. This information can be used to improve upon existing materials, or design new materials with improved corrosion resistance.
Chapter 2
Experimental Procedures

2.1 Ferritic- Martensitic Materials Studied

In this thesis, the oxides formed on alloys during exposure to flowing lead-bismuth eutectic in the Los Alamos National Laboratory DELTA loop are studied. These include the commercial steels HT-9 and T91, an annealed version of HT-9, and a model alloy created at Los Alamos National Laboratories designated as Alloy 3. Also studied are the oxide layers formed on another sample of HT-9 steel corroded at the Institute of Physics and Power Engineering flowing LBE loop. The material compositions, metallographic information, and corrosion conditions of the alloys are discussed in detail in the following sections.

2.1.1 Alloy History

Ferritic-Martensitic alloys have long been of interest in nuclear applications, especially those involving fast breeder reactors. Before Ferritic-Martensitic alloys, austenitic steels were commonly used, however it was observed that austenitic alloys encountered difficulties with irradiation induced void swelling. Ferritic-Martensitic steels, on the other hand, were not susceptible to irradiation induced void swelling, and had numerous other favorable properties including high thermal conductivity, high strength
(even at elevated temperatures) and low expansion coefficients, making them excellent candidates for use in fast reactors [3].

2.1.2 Alloy Composition

Typically, high-chromium steels such as these are considered desirable for their increased corrosion resistance [3]. The chemical composition of each of the three alloys is given in Table 2-1. Of the three alloys, HT-9, has the highest chromium concentration, as well as very high concentrations of other alloying elements. T91 and Alloy 3 have approximately the same chromium concentrations, however T91 also has many additional additives for hardness, radiation resistance and strength. Effects of these alloying elements on the properties of these steels are discussed in the next section.

Table 2-1: Chemical compositions of HT-9, T91, and Alloy 3 in weight percent.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>C</th>
<th>Ni</th>
<th>Si</th>
<th>Mn</th>
<th>Mo</th>
<th>W</th>
<th>V</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-9</td>
<td>84.45</td>
<td>11.95</td>
<td>0.2</td>
<td>0.57</td>
<td>0.4</td>
<td>0.6</td>
<td>1</td>
<td>0.5</td>
<td>0.33</td>
<td>-</td>
</tr>
<tr>
<td>T91</td>
<td>89.47</td>
<td>8.26</td>
<td>0.105</td>
<td>0.13</td>
<td>0.43</td>
<td>0.38</td>
<td>0.95</td>
<td>-</td>
<td>0.2</td>
<td>0.075</td>
</tr>
<tr>
<td>Alloy 3</td>
<td>91</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

2.1.3 Metallurgy

Both HT-9 and T91 are low-carbon, high-chromium Ferritic-Martensitic (F-M) steels. Alloy 3, on the other hand, is a simpler model alloy containing only iron and chromium. All three alloys are made by first melting the constituent metals using the standard method of vacuum-induction-melting. They are then formed and held at
austenitizing temperatures ranging from 850°C to 1200°C, causing the alloys to become either pure austenite or a combination of austenite and $\delta$-ferrite depending on stoichiometry. Alloys are then quenched to room temperature, transforming some or all of the austenite into ferrite or martensite. Different quench rates can be used to adjust the structure of the alloys, however a first-order prediction of their crystal structures post-quench may made based on their stoichiometry alone [3].

Some alloying elements such as chromium, silicon, molybdenum, and tantalum act as ferrite stabilizers helping austenite to transform into ferrite during quenching or heat-treatment processes. Other elements such as Nickel and Manganese, however, work against the stabilization of ferrite, transforming it into martensite or causing the retention of austenite during the quench process. Alloy compositions pre-tempering are predicted using the Schaeffler-Schneider diagram [3]. In order to do this, the nickel and chromium equivalents of the alloying elements are calculated using Eq. 2.1 and Eq. 2.2 [18].

$$\text{Ni equivalent (wt%) } = (\%\text{Ni}) + (\%\text{Co}) + 0.5(\%\text{Mn}) + 0.3(\%\text{Cu}) + 30(\%\text{C}) + 25(\%\text{N})$$

Eq. 2.1

$$\text{Cr equivalent (wt%) } = (\%\text{Cr}) + 2(\%\text{Si}) + 1.5(\%\text{Mo}) + 5(\%\text{V}) + 1.75(\%\text{Nb}) + 0.75(\%\text{W}) + 1.5(\%\text{Ti}) + 5.5(\%\text{Al}) + 1.2(\%\text{Ta}) + 1.2(\%\text{Hf}) + 1.0(\%\text{Ce}) + 0.8(\%\text{Zr}) + 1.2(\%\text{Ge})$$

Eq. 2.2

The calculated nickel and chromium equivalents for the three alloys of interest are shown in Table 2-2.
These calculated values for Ni and Cr equivalents can then be placed into the Schaeffler-Schneider diagram shown in Figure 2-1. In this figure it can be seen that both T91 and Alloy 3 should be purely martensitic, whereas HT-9 would contain a mixture of austenite, martensite, and ferrite.

Table 2-2: Nickel and chromium equivalents for HT-9, T91, and Alloy 3.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni equivalent (wt%)</th>
<th>Cr equivalent (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-9</td>
<td>6.87</td>
<td>16.28</td>
</tr>
<tr>
<td>T91</td>
<td>3.47</td>
<td>11.68</td>
</tr>
<tr>
<td>Alloy 3</td>
<td>0</td>
<td>9</td>
</tr>
</tbody>
</table>

In order to verify this, samples are etched using a solution of hydrochloric acid, nitric acid, and water, then examined using optical microscopy. While HT-9 and T91 exhibit their predicted structures, Alloy 3 does not contain the lath structures.
characteristic of martensite due to a lack of other martensite stabilizing elements besides chromium. Instead, Alloy 3 exhibits a structure more similar to that of ferrite as shown in Figure 2-2.

![Optical Micrograph of Alloy 3 after etching.](image)

Figure 2-2: Optical Micrograph of Alloy 3 after etching.

After the quenching process, alloys are tempered for various times at various temperatures in order to obtain their final structure as well as the desired combination of strength, ductility, and toughness. The heat treatment parameters for each of the alloys studied are given in Table 2-3. Samples received from the Timken Company of HT-9 were austenitized at 1060°C for 1 hour, and then air-cooled. Two heats of HT-9 were made from these samples: one left un-annealed, and the other annealed at 730°C for 2 hours then air cooled. T-91 and Alloy 3 were both heat treated in accordance with ASTM standard A213. They were austenitized at 1050°C for 1 hour, then tempered at 750°C for 2 hours [20].
Tempering of steels can allow changes in their microstructures that reduce stresses and are more thermodynamically favorable. In the case of high chromium steels, the formation of ferrite or ferrite + $M_23C_6$ carbides is favored, and tempering will generally result in the creation of these structures [3]. For HT-9 Annealed, this tempering process would cause the alloy to favor ferrite over martensite, as well as exhibit a more oriented structure. Figure 2-3 gives optical micrographs of the etched microstructures of HT-9 and HT-9 Annealed. The majority of the structures seen in the micrographs are martensitic lath and retained austenite. There are also ferritic structures present, circled in green, which are clearly favored in the Annealed HT-9 sample, especially along its grain boundaries.

Table 2-3: Heat treatment parameters for HT-9, T91, and Alloy 3

<table>
<thead>
<tr>
<th></th>
<th>HT-9</th>
<th>HT-9 Annealed</th>
<th>T91</th>
<th>Alloy 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Austenitizing</strong></td>
<td>1060°C for 1 hour</td>
<td>1060°C for 1 hour</td>
<td>1050°C for 1 hour</td>
<td>1050°C for 1 hour</td>
</tr>
<tr>
<td></td>
<td>Air Cooled</td>
<td>Air Cooled</td>
<td>Oil-Quenched</td>
<td>Oil-Quenched</td>
</tr>
<tr>
<td><strong>Tempering</strong></td>
<td>None</td>
<td>730°C for 2 hours</td>
<td>750°C for 2 hours</td>
<td>750°C for 2 hours</td>
</tr>
<tr>
<td></td>
<td>Air Cooled</td>
<td>Air Cooled</td>
<td>Air-Cooled</td>
<td>Air-Cooled</td>
</tr>
</tbody>
</table>
Upon completion of their heat treatments, these alloys were ready for corrosion and examination as described in the following sections.

### 2.2 Corrosion Conditions

Corrosion experiments are performed in two different flowing Lead-Bismuth Eutectic (LBE) loops: the DELTA loop located at Los Alamos National Laboratories (LANL), and a Russian loop located at the Institute of Physics and Power Engineering (IPPE). A comparison of the parameters used in the two loops is shown in Table 2-4. 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

Figure 2-3: Optical Micrographs of etched a) HT-9 and b) HT-9 Annealed samples. Ferrite grains are circled in yellow.
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.

Table 2-4: Comparison of corrosion parameters in the DELTA and IPPE loops

<table>
<thead>
<tr>
<th></th>
<th>DELTA</th>
<th>IPPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Velocity</td>
<td>2 m/s</td>
<td>2 m/s</td>
</tr>
<tr>
<td>Dissolved Oxygen Concentration</td>
<td>$10^{-6}$ wt% in LBE</td>
<td>$10^{-6}$ wt% in LBE</td>
</tr>
<tr>
<td>Temperature</td>
<td>500°C</td>
<td>550°C</td>
</tr>
<tr>
<td>Oxidation Time</td>
<td>666 hours</td>
<td>3000 hours</td>
</tr>
</tbody>
</table>

All of the alloys discussed in Section 2.1 were corroded in the DELTA loop. For comparison, one sample of the unannealed HT-9 was corroded in the IPPE loop. While it started in the same state as the other unannealed HT-9 sample corroded in the DELTA loop, for the sake of clarity this sample has been named and will be referred to as HT-9 IPPE.

2.3 Sample Preparation

In order to study the oxide layers formed in these corrosion conditions, the samples corroded must be cross sectioned and polished to reveal their microstructure. In order to ensure that the oxide layers are not lost during polishing, the cross sectioned samples are held together in a matrix of epoxy surrounded by a slotted molybdenum rod inside of a brass tube. This completed fixture measures 3mm in diameter by 1-2mm in thickness and, once assembled, is ready for mechanical polishing. A schematic version of
this sample preparation process is shown in Figure 2-4. In the beginning of the figure, the sample can be seen with 2 oxide layers on it: one on top, and one on bottom. In order to get the sample down to a size small enough to fit inside the final fixture, it is mechanically thinned as shown in Figure 2-4 a. Once thinned, the sample may be slid into the slotted Molybdenum rod as shown in Figure 2-4 b. In part c, this Molybdenum Rod-Sample fixture is then placed in the brass tubing with Gatan G-1 epoxy and allowed to harden. Once hardened, the entire fixture is sliced as shown in Figure 2-4 d to reveal the final cross sectioned sample shown in part e.

**Starting Materials:**
- Sample
- Slotted Molybdenum Rod
- Brass Tubing

**Process:**
- a. Sample is Mechanically Thinned
- b. Thinned Sample is inserted into Slotted Molybdenum Rod
- c. Fixture from part b is Placed into Brass Tubing with Epoxy
- d. Entire fixture is sliced to expose Sample cross section
- e. Finished Sample

**Figure 2-4:** Schematic representation of sample preparation process
Once the sample has been successfully cross sectioned, it is ready for mechanical polishing. Samples are affixed to a flat holder using a low melting temperature adhesive called Crystal Bond. They are then sanded using rough 600 grit silicon carbide paper until they are flat on both sides. Once this is achieved, one side of the sample is given a rough polish using Allied 1200 grit silicon carbide paper lubricated with water on a traditional polishing wheel, followed by 1 micron diamond paste and finally 0.05 micron colloidal silica both on nylon disks on a polishing wheel. Samples are then examined using an optical microscope to determine that they are free of scratches and show a mirror finish. Any scratches on the sample require repeated polishing until they are gone. Once the desired polish is achieved, the samples are cleaned in an ultrasonic bath of acetone, after which optical micrographs are taken for recording purposes. An optical micrograph of a final polished sample is shown in Figure 2-5. Once this has been completed, the samples are ready for further examination.

Figure 2-5: Optical Micrograph of a final polished cross sectional sample ready for examination
2.4 Sample Examination

The polished samples are examined using two techniques: a Scanning Electron Microscope (SEM) at Penn State equipped with Energy Dispersive Spectroscopy (EDS), and the Microbeam Synchrotron line at Argonne National Laboratories analysis featuring $\mu$-X-ray Fluorescence ($\mu$-XRF) and $\mu$-X-ray diffraction ($\mu$-XRD). These two facilities provide data which complement one another and help to identify specific features in a given sample.

2.4.1 SEM Examination

The Scanning Electron Microscope used at Penn State is an FEI Quanta 200 ESEM (environmental scanning electron microscope) with an additional Backscattered Electron (BSE) detector. In order to image samples correctly in this microscope, samples are mounted onto metal stubs using carbon tape, and silver paint is applied to provide a conduction path and thus avoid charging. Both the silver paint and carbon tape can later be removed completely in an ultrasonic bath of acetone. Because the compositional contrast of the samples is of more interest than the topographic contrast, images are taken using the BSE detector. The BSE detector collects electrons which are elastically scattered by the nucleus of the sample’s atoms. This means that atoms with heavier nuclei will show up brighter than those with lighter nuclei. It also means that higher energy electrons from deep within the sample can be viewed, leading to lower spatial resolution than that of traditional secondary electron detectors.
To measure the composition, Energy Dispersive Spectroscopy (EDS) can also be performed. In EDS an energy spectrum of the x-rays emitted during inelastic scattering of the incident electrons on the sample is acquired. Analysis of this spectrum allows the determination of the chemical composition of an area approximately 3 to 5 µm in diameter [21]. While EDS can detect elements as small as Boron, to derive a composition from the raw spectra, proper calibration procedures and analysis are required. While the FEI Quanta has most of this automated, its results still have a large margin of error and are will only used in qualitative analysis in this thesis.

The ESEM used was also outfitted with an EDS mapping feature in which the user can create an elemental map of the SEM image being examined. This is done simply by taking EDS spectra from hundreds of points on a 2-D map determined by the user. The intensity of the peaks of interest (corresponding to elements of interest) are then laid out in the same user-defined map space, and can be compared to the original BSE image.

### 2.4.2 Microbeam Synchrotron Analysis

The main characterization technique utilized in this thesis, Microbeam Synchrotron Analysis, is performed at the Advanced Photon Source (APS) located at Argonne National Laboratories just outside of Chicago. There are several reasons this technique is uniquely suited to our goal of gathering detailed data from the individual sections of the oxide layer. First, the x-rays emitted by the synchrotron have extremely high brilliance over a wide variety of wavelengths. This means that phases which would be undetectable by traditional XRD (due to their low volume fraction) are more likely to
be visible using the synchrotron radiation. The specific beamline used at the synchrotron (2IDD) utilizes zone plate technology to focus the synchrotron radiation down to a spot size of 0.2µm. This micro beam is directed at the cross sectional sample at a fixed angle of 15 degrees which causes it to have a footprint on the sample of 0.2µm x 2µm. Using a fixed angle CCD screen and fluorescence detector, both μ-X-Ray Diffraction and μ-X-Ray Fluorescence data can be simultaneously collected from this footprint. The sample is held on a motorized stage which can be moved very precisely, allowing the user to effectively “step” the beam along the sample gathering data from individual layers, interfaces, and any other regions of interest.

A diagram of the synchrotron setup is given in Figure 2-6. At the bottom of the Figure is a sample with incident x-ray beam hitting it, creating the 0.2µm x 2µm footprint. This produces both diffraction and fluorescence information which is collected by the CCD camera and fluorescence detector respectively.
Using the motorized stage, the beam is “stepped” in increments of 0.2µm or 0.25µm along the cross sectioned oxide layer as demonstrated in Figure 2-7. At each step, the beam is held in place and data is acquired for 30 seconds by the fluorescence detector, and 1 minute by the diffraction detector. These acquisition times are chosen in order to give a strong signal without saturating the detectors. The beam is then stepped to the next location, and the process is repeated until the entire area of interest has been covered.

Figure 2-6: Setup of μ-XRF and μ-XRD collection technique
The data for this thesis was collected at two different times, during two different trips to the synchrotron source. Alloy 3 was examined during a synchrotron run in July 2006, and the data for the remaining alloys was collected in August of 2007. Data was collected July 2006 with a step size of 0.25\(\mu\)m, and with a step size of 0.2\(\mu\)m in August 2007. The remaining differences in the data collected at these two times will be discussed in section 2.4.2.2. Once all of the data is collected, it then has to be converted into a form which can more easily be analyzed.

2.4.2.1 \(\mu\)-X-Ray Fluorescence Data

The \(\mu\)-XRF data is collected as a spectrum of energy versus intensity by a Ge(Li) Canberra solid state detector. Energy windows, called regions of interest (ROI’s) are then
defined on this spectrum based on which elements and corresponding emission lines (e.g. Fe Kα, Mo Lα, etc.) the researchers wish to investigate. In the case of this thesis, ROI’s are placed for 14 elemental lines listed in Table 2-5 along with their energies and established ROI’s [23]. It can be seen in the table that in some cases certain elements will not be distinguishable from one another. For instance, the ROI for molybdenum spans from 2.15-2.55 keV, whereas the ROI for lead goes from 2.26-2.40 keV. Since the ROI for lead is completely contained within the ROI for molybdenum, it will not be possible for the researchers to differentiate between the two using the fluorescence data alone.

Table 2-5: Fluorescence line energies and their regions of interest

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Line</th>
<th>Line Energy (keV)</th>
<th>ROI (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>Kα</td>
<td>1.49</td>
<td>1.38</td>
</tr>
<tr>
<td>Silicon</td>
<td>Si</td>
<td>Kα</td>
<td>1.74</td>
<td>1.66</td>
</tr>
<tr>
<td>Yttrium</td>
<td>Y</td>
<td>Lα</td>
<td>1.92</td>
<td>1.85</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Mo</td>
<td>Lα</td>
<td>2.29</td>
<td>2.15</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>Mα</td>
<td>2.35</td>
<td>2.26</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>Kα</td>
<td>2.96</td>
<td>2.80</td>
</tr>
<tr>
<td>Titanium</td>
<td>Ti</td>
<td>Kα</td>
<td>4.51</td>
<td>4.35</td>
</tr>
<tr>
<td>Vanadium</td>
<td>V</td>
<td>Kα</td>
<td>4.95</td>
<td>4.79</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>Kα</td>
<td>5.41</td>
<td>5.26</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>Kα</td>
<td>5.90</td>
<td>5.76</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>Kα</td>
<td>6.40</td>
<td>6.25</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>Kα</td>
<td>6.93</td>
<td>6.81</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>Kα</td>
<td>7.48</td>
<td>7.35</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>Kα</td>
<td>8.05</td>
<td>7.81</td>
</tr>
</tbody>
</table>

Some of the elements chosen for detection by μ-XRF were found to be either not present in the samples researched or did not fluoresce with sufficient intensity to be detected. These elements are aluminum, silicon, yttrium, argon, and titanium. Other
weakly fluorescing elements have ROI’s too close to emission energies of two very strongly fluorescing elements: iron and chromium, which dominate the fluorescence spectrum due to their high content in the alloys. As a result, data for vanadium, manganese, and cobalt appears identical to that of their strongly fluorescing neighbors, and is therefore meaningless. The K-lines and ROI’s for all of these elements are shown in Figure 2-8. It can be seen that, due to their close proximity, vanadium will be dominated by chromium. Also, since the ROI for manganese contains the chromium Kβ line, it too will be dominated by chromium. Cobalt’s ROI is located in between the iron Kα & iron Kβ lines, so it is dominated by iron.

Figure 2-8: K-lines and ROI’s (shown in yellow) for vanadium, chromium, manganese, iron, and cobalt
The fluorescence data is collected in arbitrary units, and it not normalized. As a result, the fluorescence data in this thesis will be qualitative, and used primarily to expand on and deepen understanding of $\mu$-x-ray diffraction data.

2.4.2.2 $\mu$-X–Ray Diffraction Data

The diffraction data for each spot is collected as images taken by a CCD screen and saved as .tiff images in which each pixel has an intensity value corresponding to the phases present. In July of 2006, Alloy 3 data was taken with the CCD’s 2 theta value (shown in Figure 2-6) at approximately 30 degrees, at a distance of about 37 cm from the sample. The August 2007 data taken for the other samples, however, was taken at a 2 theta angle of 32 degrees with a distance to the CCD of approximately 40 cm. The major difference introduced by this is the angular range of the diffraction data, which is illustrated in Table 2-6. These ranges are quite close, and both include the high-intensity bcc iron peak we are looking for, as well as all four of the major magnetite and spinel peaks we expect to find.

Table 2-6: 2$\theta$ Angular ranges of diffraction data taken for each sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date Taken</th>
<th>Distance to CCD</th>
<th>CCD 2$\theta$ Angle</th>
<th>2$\theta$ Angular Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 3</td>
<td>July 2006</td>
<td>37.2 cm</td>
<td>30$^\circ$</td>
<td>23.122$^\circ$-38.826$^\circ$</td>
</tr>
<tr>
<td>HT-9 DELTA</td>
<td>August 2007</td>
<td>40.0 cm</td>
<td>32$^\circ$</td>
<td>24.100$^\circ$-38.985$^\circ$</td>
</tr>
<tr>
<td>HT-9 DELTA Annealed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HT-9 IPPE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Once all of the diffraction patterns are acquired, they must be put into a format which can be analyzed and understood. To accomplish this, data taken in July of 2006 is analyzed using the program called 2DConvert developed by A.Yilmazbayhan as described in detail in her thesis [22]. The result of this program is a plot of diffracted intensity peaks versus 2 theta angle. A schematic of this process can be seen in Figure 2-9. In the first part of the figure, the initial 2-D diffraction pattern is shown. The middle of the figure shows the same diffracted image with the region to be integrated superimposed over it. The final portion of Figure 2-9 shows the final plot of diffracted intensity versus 2-theta angle. In many cases, these peaks will sit atop a slowly rising background such as those shown in Figure 2-10. This background is removed manually during the diffraction peak analysis described in section 2.4.2.2.1.

Data collected in August of 2007 is analyzed using a different program developed at Argonne National Laboratories called CCD sum Sdiapp. The major difference between these two programs is that CCD sum Sdiapp neglects to take the Lorentz-Polarization factor into account. As a result, this is then done manually by dividing the

Figure 2-9: Schematic representation of the tiff images being processed into intensity versus two theta data.
intensity seen at any given 2-theta angle by the Lorentz-Polarization factor given in Eq. 2.3 [22].

Figure 2-10 shows a comparison between the same data set processed by 2DConvert and CCD sum Sdiapp. It shows that, apart from a small difference in the background levels (probably due to a difference in the models used by the two programs to remove background) the size, shape, and location of the peaks are all the same. Analysis of these peaks yields the same results regardless of which program is used, since this background is later manually removed using PeakFit.

\[ LP_{\text{correction}} = \frac{0.01 + 1.99 \cos^2(2\theta)}{\sin(\theta)} \]  

Eq. 2.3

Figure 2-10: Comparison of tiff image processing program outputs.
2.4.2.2.1 Diffraction Peak Analysis

In order to analyze the diffraction peaks obtained from the 2DConvert and CCD sum Sdiapp processing, a commercial program called PeakFit 4.0 [24] is used. First, the slowly rising background shown in Figure 2-10 is removed manually using the program’s background fitting algorithm. Once the background is removed, the diffraction peaks are manually fitted using non-normalized Pearson VII peaks, taking care to ensure that these peaks are realistic. Pearson VII peaks are ideal for this process since they are continuous distributions which have no skewness, are of variable kurtosis, and their intensity can be integrated to obtain a finite answer. In Figure 2-11, a small section of fitted diffraction data is shown. The dark blue line is the data, and the first apparent peak in it has a slight skewness to it. To fit this apparent peak, 2 Pearson VII peaks are required, located at 29.86 degrees and 30.00 degrees. These peaks represent two individual phases of two different compounds, specifically Fe$_3$O$_4$[311] and FeCr$_2$O$_4$[311] – the 100% intensity phases of their structures. The second apparent peak in the figure, on the other hand, is symmetric and requires only one peak to fit correctly. It represents Fe$_3$O$_4$[222] which is only an 8% intensity peak of that structure. Typically, using this method obtains an overall fit of the data with a coefficient of determination ($R^2$) value of over 0.99, where $R^2$ represents a proportion of the variability in the data that is accounted for by the fitted peaks.
Once all of the peaks for each diffraction pattern from a sample are fit and analyzed in the manner described above, they are placed into a 3D contour plot as illustrated in Figure 2-12. These 3-D contour plots are valuable, as they illustrate the phases found at each location in the sample. Unfortunately, the 3D contour plot does not allow us to see the difference between closely-spaced peaks from phases such as the Fe$_3$O$_4$ [311] and FeCr$_2$O$_4$ [311] peaks. Therefore, to properly illustrate the findings from the $\mu$-XRD data, a combination of both Intensity vs. 2$\theta$ plots and 3D contour plots is used.

Figure 2-11: Sample fitting of peaks using PeakFit
2.4.2.2 Diffraction Peak Information

Once all of the peaks have been fit, they are ready to be analyzed. Several pieces of information are available from each of these peaks. As mentioned before, the peak position can be correlated with a lattice distance and assigned a phase and an orientation.
accordingly. These are found using previously obtained standards called powder
diffraction files.

A second piece of information in each peak is its full-width, half-max (FWHM).
Sharper diffraction peaks with a smaller FWHM are associated with larger or more
textured grains, whereas peaks which are broader and have larger FWHM’s are
associated with smaller, or less textured grains. Another piece of information we get from
a peak is its magnitude. Within a given phase, different crystallographic orientations of
that phase will yield different x-ray intensities. Powder diffraction files contain known
diffracting intensities for each of these crystallographic orientations from a randomly
oriented sample. Deviations from these expected intensities indicate that the sample is
has preferred crystallographic orientations or is textured. Peak intensity can also be used
to qualitatively determine phase content.
Chapter 3

Experimental Results

This chapter presents the experimental results for the alloys studied using the methods detailed in Chapter 2. A summary of the corrosion conditions and examination performed, as discussed in Chapter 2, is given in Table 3-1.

Table 3-1: Comparison of corrosion and examination conditions for alloys discussed

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Metal</th>
<th>Corrosion Loop</th>
<th>Corrosion Temp. (°C)</th>
<th>Corrosion Time (hours)</th>
<th>Microbeam Step Size (µm)</th>
<th>Microbeam 2θ Angular Range</th>
<th>µ-XRD Processing Program</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-9 DELTA</td>
<td>HT-9</td>
<td>DELTA</td>
<td>500</td>
<td>666</td>
<td>0.2 µm</td>
<td>24°-39°</td>
<td>CCD sum Sdiapp</td>
</tr>
<tr>
<td>HT-9 DELTA Annealed</td>
<td>HT-9</td>
<td>DELTA</td>
<td>500</td>
<td>666</td>
<td>0.2 µm</td>
<td>24°-39°</td>
<td>CCD sum Sdiapp</td>
</tr>
<tr>
<td>HT-9 IPPE</td>
<td>HT-9</td>
<td>IPPE</td>
<td>550</td>
<td>3000</td>
<td>0.2 µm</td>
<td>24°-39°</td>
<td>CCD sum Sdiapp</td>
</tr>
<tr>
<td>T91</td>
<td>T91</td>
<td>DELTA</td>
<td>500</td>
<td>666</td>
<td>0.2 µm</td>
<td>24°-39°</td>
<td>CCD sum Sdiapp</td>
</tr>
<tr>
<td>Alloy 3</td>
<td>Model</td>
<td>DELTA</td>
<td>500</td>
<td>666</td>
<td>0.25 µm</td>
<td>23°-39°</td>
<td>2DConvert</td>
</tr>
</tbody>
</table>

In this chapter, each of the five samples will be discussed individually. For each of the samples, first the overall oxide structure and visible features will be discussed in conjunction with Scanning Electron Microscope (SEM) images and Energy Dispersive Spectroscopy (EDS) maps, if applicable. After this, the Microbeam X-ray Fluorescence (µ-XRF) data will be introduced and discussed, followed by the fully processed Microbeam X-ray Diffraction (µ-XRD) data. Some samples were also examined using Transmission Electron Microscopy (TEM) by a previous student researcher [25], and this data will be used to inform the discussion of the current data. A summary will follow for
3.1 Examination of Oxide Layers Formed on HT-9 DELTA after 666 hours of exposure to 500°C Lead-Bismuth Eutectic

HT-9 DELTA, the first sample in Table 3-1, was corroded in the Los Alamos National Laboratory (LANL) DELTA loop at 500°C for 666 hours as described in Section 2.2. 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.

3.1.1 Scanning Electron Microscope Examination of HT-9 DELTA

Figure 3-1 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 9.5 µm thick in total. The sub-layers in this oxide are referred to as the inner oxide layer (the layer which connects to the metal) and the outer oxide layer (the layer which connects to the inner oxide layer, but not the metal). It is believed that the inner-outer oxide layer interface is coincident with the initial metal surface, with the inner layer formed by inward diffusion of oxygen, and the outer layer formed by outward diffusion of iron [26].
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 [25]. These regions of preferential oxidation along

Figure 3-1: Scanning electron micrograph of oxide layers formed on HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic.
grain boundaries are shown in purple on Figure 3-1. Areas with lath oriented favorably to oxide advancement then oxidize, creating the “wavy” appearance of the interface.

The inner oxide layer also exhibits slight porosity, as indicated by the arrows in Figure 3-1. 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 the outer oxide layer is not affected by the metal’s microstructure [27] [28]. 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 3-1: 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 [25] [28].

3.1.2 Energy Dispersive Spectroscopy Mapping of HT-9 DELTA

Figure 3-2 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 inner 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 Kα map given in Figure 3-2. The bismuth and lead Lα 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.
3.1.3 Microbeam X-Ray Fluorescence Examination of HT-9 DELTA

Figure 3-3 shows the fluorescence data obtained using microbeam synchrotron radiation for the major alloying elements, iron and chromium, from the oxide layers formed on HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic.

Figure 3-2: Energy dispersive spectroscopy maps from oxide layers formed on HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic.
shown in Figure 3-1. 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 3-3: Iron and chromium microbeam x-ray fluorescence data from oxide layers formed on HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic.
X-Ray fluorescence data from minor contaminants and alloying elements (lead and nickel, respectively) are shown in Figure 3-4. 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, but it does show a noticeable increase in the inner half of the outer oxide. This corresponds to the bright spots observed in the scanning electron micrograph which were previously identified in Figure 3-2 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 researchers came to the preliminary conclusion that this was due to nickel diffusion away from the inner oxide towards the metal during oxide formation [26]. 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 3-4 that this is not the case. Instead, nickel fluorescence intensity remains constant both in the metal, as well as after the inner oxide-metal interface enrichment, and then shows a second enrichment in the inner half of the outer oxide. This means that the mechanism proposed by Zhang et al. does not entirely explain the behavior of nickel during the lead-bismuth corrosion of 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.
3.1.4 Microbeam X-Ray Diffraction Examination of HT-9 DELTA

As the \( \mu \)-XRF data is collected, \( \mu \)-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 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 3-5 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 0.2µm 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 3-5: Summary of data obtained using microbeam synchrotron radiation on oxide layers formed on HT-9 DELTA 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 versus 2-theta angle versus distance into the sample. Indexed peaks are indicated as well as approximate distance between layers. The asterisks denote locations of individual diffraction patterns discussed later in this section.
3.1.4.1 Metal Region

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. There is only one visible peak for the bcc iron phase in this angular range as seen in Table 3-2. Chromium carbide, on the other hand, has three observable peaks in this angular range, as seen in Table 3-3. It should be noted that while the chromium carbide peak identified is only 0.01° different from expected, the bcc iron peak is located 0.14 degrees lower than where it should be. This is likely due to chromium substitution in the bcc iron lattice slightly increasing the d-spacing, leading to a lower observed 2 theta angle. The value for the bcc Cr d-spacing is also given in Table 3-2.

Table 3-2: Expected peaks for bcc Fe (Ferrite) and bcc Cr structure in the studied angular range (PDF: 00-006-0696)

<table>
<thead>
<tr>
<th>bcc Fe d-spacing (Å)</th>
<th>2 theta Angle</th>
<th>Relative Intensity</th>
<th>(h k l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0268</td>
<td>37.56°</td>
<td>100%</td>
<td>(1 1 0)</td>
</tr>
<tr>
<td>bcc Cr d-spacing (Å)</td>
<td>2 theta Angle</td>
<td>Relative Intensity</td>
<td>(h k l)</td>
</tr>
<tr>
<td>2.0577</td>
<td>36.98°</td>
<td>100%</td>
<td>(1 1 0)</td>
</tr>
</tbody>
</table>

Table 3-3: Expected peaks for fcc Cr$_{23}$C$_6$ (chromium carbide) in the studied angular range (PDF: 04-007-5437)

<table>
<thead>
<tr>
<th>Cr$_{23}$C$_6$ d-spacing (Å)</th>
<th>2 theta Angle</th>
<th>Relative Intensity</th>
<th>(h k l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3814</td>
<td>31.81°</td>
<td>23%</td>
<td>(4 2 0)</td>
</tr>
<tr>
<td>2.1739</td>
<td>34.94°</td>
<td>28%</td>
<td>(4 2 2)</td>
</tr>
<tr>
<td>2.0496</td>
<td>37.13°</td>
<td>100%</td>
<td>(5 1 1)</td>
</tr>
</tbody>
</table>
Vegard’s law states that there is an approximately linear relationship between the lattice parameter of a crystal lattice and the atomic concentration of constituent elements. Equation Eq. 3.1 shows where $a$ is the lattice parameter and $x$ is the atomic percentage of iron in the HT-9 matrix. Solving Eq. 3.1 for the lattice parameter observed in the metal layer of the HT-9 sample taking only major alloying elements (chromium and iron) into account yields a composition of 75 at% Fe, 25 at% Cr. This is similar to the actual composition of HT-9 which is approximately 87 at% Fe and 12.4 at% Cr. Deviation from expected is probably due to the non-inclusion of the minor alloying elements in the calculation.

$$a_{HT-9} \approx x \cdot a_{Fe} + (1-x) \cdot a_{Cr}$$ \hspace{1cm} \text{Eq. 3.1}$$

In the metal layer, only one chromium carbide peak, located at 37.14° and corresponding to the (5 1 1) reflection, is observed. This may be due to either the lower relative intensity of the other two orientations (23 and 28%), or due to the sampling problem, since the grain size is bigger than the beam size and the carbides could be oriented preferentially in the HT-9 sample, resulting in only a few peaks being visible.

Both the bcc Fe (1 1 0) and Cr$_2$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 previous TEM findings by Siwy [25]. He observed bright field contrast coming from groups of narrow elongated grains in the inner oxide, and concluded that they were an inter lath phase of either retained austenite or ferrite. A bright field contrast image of the oxide layers is given in Figure 3-6 along with a schematic showing the location of these retained metal structures.
From the peaks observed in the microbeam synchrotron diffraction patterns, we can identify these grains as a mixture of bcc iron and chromium carbides.

Figure 3-6: TEM bright field image from oxide layers formed on HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic with schematic of inner oxide region (region A) containing dashed lines representing retained metal grains in the inner oxide [25].
Figure 3-5 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 \( \text{Fe}_3\text{O}_4 \), \( \text{FeCr}_2\text{O}_4 \), or a combination of the two, however in the contour map in Figure 3-5 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. The expected peaks for both the \( \text{Fe}_3\text{O}_4 \) magnetite and \( \text{FeCr}_2\text{O}_4 \) spinel phases are given in Table 3-4.

Table 3-4: Expected peaks for \( \text{Fe}_3\text{O}_4 \) (magnetite) and \( \text{FeCr}_2\text{O}_4 \) (spinel) in the studied angular range (PDFs: 04-008-8147, 04-006-2807)

<table>
<thead>
<tr>
<th>( \text{Fe}_3\text{O}_4 )</th>
<th>2 theta Angle</th>
<th>Relative Intensity</th>
<th>( \text{h k l} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.9688</td>
<td>25.40°</td>
<td>29%</td>
<td>(2 2 0)</td>
</tr>
<tr>
<td>2.5318</td>
<td>29.88°</td>
<td>100%</td>
<td>(3 1 1)</td>
</tr>
<tr>
<td>2.4240</td>
<td>31.24°</td>
<td>7%</td>
<td>(2 2 2)</td>
</tr>
<tr>
<td>2.0992</td>
<td>36.23°</td>
<td>21%</td>
<td>(4 0 0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \text{FeCr}_2\text{O}_4 )</th>
<th>2 theta Angle</th>
<th>Relative Intensity</th>
<th>( \text{h k l} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.9621</td>
<td>25.46°</td>
<td>33%</td>
<td>(2 2 0)</td>
</tr>
<tr>
<td>2.5261</td>
<td>29.95°</td>
<td>100%</td>
<td>(3 1 1)</td>
</tr>
<tr>
<td>2.4185</td>
<td>31.31°</td>
<td>7%</td>
<td>(2 2 2)</td>
</tr>
<tr>
<td>2.0945</td>
<td>36.31°</td>
<td>19%</td>
<td>(4 0 0)</td>
</tr>
</tbody>
</table>

Although the observation of the \( (\text{Fe,Cr})_3\text{O}_4 \) oxide phase, an oxide, in the metal region may appear strange, these phases are often observed in the metal because of 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 irregular appearance, as seen in the SEM image in Figure 3-1. These oxide phases slowly
appear in the metal layer and grow stronger as they traverse the metal towards the inner oxide.

Figure 3-7 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. This pattern was taken from 3.2µm into the HT-9 DELTA sample, as denoted by the first asterisk (*) in Figure 3-5. In Figure 3-7, it can be seen that there are 5 peaks present: three corresponding to the strongest diffracting orientations of Fe$_3$O$_4$, 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$_3$O$_4$ magnetite, with no evidence of the FeCr$_2$O$_4$ spinel phase in the µ-XRD data until about 9 µm into the sample (well into the inner oxide layer).

It can be seen in part (a) of Figure 3-7 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$_3$O$_4$ 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$_3$O$_4$, 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.
3.1.4.2 Inner Oxide Layer

The inner oxide layer of the HT-9 DELTA sample exhibits diffraction peaks consistent with a mixture of Fe$_3$O$_4$, FeCr$_2$O$_4$, Cr$_2$O$_3$, bcc iron, and Cr$_{23}$C$_6$ phases.

Figure 3-8 shows a diffraction pattern taken from 9.2 µm into the sample, in the inner oxide as indicated by the second asterisk in Figure 3-5. 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 3-7 (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.
The four observed peaks of the Fe$_3$O$_4$ 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$_2$O$_4$ spinel peaks are become visible and are shown in Figure 3-8 b with the purple dotted lines. The FeCr$_2$O$_4$ 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. In general, these spinel phases were least an order of magnitude smaller than the magnetite phase. The relative peak intensities of the magnetite and spinel phases corresponded well to their expected relative intensities shown in Table 3-4.

TEM analysis of this same region also suggested that its composition is dominated by a mixture of the Fe$_3$O$_4$ and FeCr$_2$O$_4$ phases with some retained metal grains. Figure 3-9 shows a bright field image and corresponding diffraction pattern taken from a highly oriented region of equiaxed grains in the inner oxide. These grains proved
to be (Fe,Cr)$_3$O$_4$ as expected. The long thin grains in Figure 3-9 indicated with the white arrows are the same retained metal grains shown previously in Figure 3-6 [25].

![Figure 3-9: TEM bright field image (a) and corresponding diffraction pattern (b) from a (Fe,Cr)$_3$O$_4$ grain within the inner oxide with a zone axis of [1-11] from HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic. Arrows indicate retained metal grains. [25]](image)

Along with retained bcc iron, this sample also shows carbide peaks in its inner oxide. In addition to the (5 1 1) peak, a second Cr$_{23}$C$_6$ (4 2 0) peak (at about 31.82°) appears midway through the inner oxide and extends for about 1-2 µm in the inner oxide, as shown in Figure 3-5. A small peak (circled in purple in Figure 3-8) is also present at 34.93°, but it is not clear if this should be indexed as the Cr$_{23}$C$_6$ (4 2 2) peak, expected at 34.94°, or the Cr$_2$O$_3$ (1 1 3) peak, expected at 34.92°. Both phases have other peaks present in this region, and as Figure 3-10 shows, the diffracted intensity seen at 34.93° has characteristics similar to both of the phases. It consists of both a low-intensity ring, as well as higher intensity “spots.” Intensities seen from other Cr$_{23}$C$_6$ peaks also exhibit similar “spots,” while that from Cr$_2$O$_3$ (1 0 4) has the characteristics of a low intensity.
ring. Since they are not distinguishable, the intensity seen at 34.93° will be taken to be a mixture of the Cr$_2$C$_6$ (4 2 2) peak and the Cr$_2$O$_3$ (1 1 3) peak.

As a result of this assumption, two Cr$_2$O$_3$ peaks, (1 1 0) and (1 1 3), are identified in Figure 3-8 b, and a third, (1 0 4), can be seen further on in the inner oxide as evidenced in Figures 3-5 and 3-10. The (1 1 0) peak (located at 30.52°) is not labeled in the diffraction patterns because its diffracted intensity is much lower and is obscured by

Figure 3-10: Diffraction pattern taken from 11.2 µm into HT-9 DELTA in the inner oxide after 666 hours of exposure to 500°C lead-bismuth eutectic.
nearby (Fe,Cr)$_3$O$_4$ (3 1 1) peaks (located at 29.88 and 29.95°). It can, however, be easily identified during the peak fitting process as well as the contour map in Figure 3-5.

All peaks from the Cr$_2$O$_3$ phase identified have very low intensity, and represent only three of the five possible Cr$_2$O$_3$ peaks at this angular range, shown in Table 3-5. Due to the already low intensity of the peaks, it is little surprise that the peaks with the lowest relative intensities, (0 0 6) and (2 0 2), are not observed. The other peaks are observed, but with relative intensities different from those in the powder diffraction file. This may be due either to their overlap with nearby peaks, or to the phase being highly textured. Since the peak at (1 0 4) in Figure 3-10 exhibits more of a spot pattern than a ring, and TEM studies did not reveal any large Cr$_2$O$_3$ grains in the oxide structure, it is likely that the Cr$_2$O$_3$ grains are highly textured, hence the deviation from expected intensities.

Table 3-5: Expected peaks for Cr$_2$O$_3$ (chromium oxide) in the studied angular range (PDF: 04-009-2109)

<table>
<thead>
<tr>
<th>Cr$_2$O$_3$ d-spacing (Å)</th>
<th>2 theta Angle °</th>
<th>Relative Intensity</th>
<th>(h k l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6650</td>
<td>28.35°</td>
<td>100%</td>
<td>(1 0 4)</td>
</tr>
<tr>
<td>2.4797</td>
<td>30.52°</td>
<td>90%</td>
<td>(1 1 0)</td>
</tr>
<tr>
<td>2.2657</td>
<td>33.48°</td>
<td>6%</td>
<td>(0 0 6)</td>
</tr>
<tr>
<td>2.1751</td>
<td>34.92°</td>
<td>27%</td>
<td>(1 1 3)</td>
</tr>
<tr>
<td>2.0457</td>
<td>37.17°</td>
<td>5%</td>
<td>(2 0 2)</td>
</tr>
</tbody>
</table>

Fluorescence data in Figure 3-5 shows that further on in the inner oxide layer the chromium content increases even further, giving rise to more intense FeCr$_2$O$_4$ and Cr$_2$O$_3$ 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.
3.1.4.3 Outer Oxide Layer

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 3-5 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 3-11 shows a diffraction pattern and a peak fit from the inner half of this region (closer to the inner oxide), located 13.4µm into the sample as indicated by an asterisk in Figure 3-5. The fit in Figure 3-11 b shows that the FeCr$_2$O$_4$ and Cr$_2$O$_3$ peaks have entirely disappeared, whereas the Fe$_3$O$_4$ peaks are more intense. The Fe$_3$O$_4$ 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. These have been observed using both TEM and SEM to be columnar, and to measure approximately 0.4µm wide by 2µm long [25]. 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.
Two new peaks are also identified in Figure 3-11, and these are associated with an fcc Pb-Bi phase. As shown earlier, the inner 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, as seen in Table 3-6. 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 thesis, we will identify this phase as the fcc (Pb, Bi) phase.

Figure 3-11: (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.
It is worth noting that the location of the fcc \((\text{Pb,Bi})\) \((2\ 0\ 0)\) peak is very close to the location of the \(\text{Cr}_2\text{O}_3\) \((1\ 1\ 0)\) peak \(30.52\degree\). Since, according to the fluorescence data, there is no chromium in the outer oxide where the bright spots are present, and no lead or bright spots in the inner oxide where there is chromium, it is safe to assume that the \~30.5\degree\ peak belongs to \(\text{Cr}_2\text{O}_3\) \((1\ 1\ 0)\) in the inner oxide, and to fcc \(\text{Pb-Bi}\) \((2\ 0\ 0)\) in the outer oxide. This is confirmed by the similar locations of the other peaks of these phases.

### Table 3-6: Fcc Pb-Bi phases corresponding to peak locations in the studied angular range (PDFs: 04-005-9303, 04-003-0604, and 04-004-6681)

<table>
<thead>
<tr>
<th>(\text{Pb}) d-spacing (Å)</th>
<th>2 theta Angle</th>
<th>Relative Intensity</th>
<th>((h\ k\ l))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8522</td>
<td>26.45\degree</td>
<td>100%</td>
<td>((1\ 1\ 1))</td>
</tr>
<tr>
<td>2.4701</td>
<td>30.64\degree</td>
<td>48%</td>
<td>((2\ 0\ 0))</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(\text{Pb}_{17}\text{Bi}_3) d-spacing (Å)</th>
<th>2 theta Angle</th>
<th>Relative Intensity</th>
<th>((h\ k\ l))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8677</td>
<td>26.31\degree</td>
<td>100%</td>
<td>((1\ 1\ 1))</td>
</tr>
<tr>
<td>2.4835</td>
<td>30.47\degree</td>
<td>48%</td>
<td>((2\ 0\ 0))</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(\text{Pb}_3\text{Bi}) d-spacing (Å)</th>
<th>2 theta Angle</th>
<th>Relative Intensity</th>
<th>((h\ k\ l))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8702</td>
<td>26.29\degree</td>
<td>100%</td>
<td>((1\ 1\ 1))</td>
</tr>
<tr>
<td>2.4857</td>
<td>30.44\degree</td>
<td>49%</td>
<td>((2\ 0\ 0))</td>
</tr>
</tbody>
</table>

3.1.5 HT-9 DELTA Summary

A sample of HT-9 was corroded in the DELTA loop at Los Alamos National Laboratory for 666 hours in 500°C lead-bismuth eutectic, and the resulting oxide layers were examined using a variety of techniques. Techniques discussed were: scanning electron microscopy, energy dispersive spectroscopy, transmission electron microscopy,
micro x-ray fluorescence, and micro x-ray diffraction. The sample exhibited a duplex oxide consisting of an inner and an outer oxide layer each with their own sublayers.

Table 3-7 summarizes some of the microstructural characteristics of this oxide found using the techniques listed above. Chemical compositions are given relative to the average chemical composition of the alloy, which is set equal to 1. These compositions are averaged over each individual region, as shown in Figure 3-12.

Table 3-7: Summary of findings for oxide layers formed on HT-9 DELTA after 666 hours of exposure to 500°C lead-bismuth eutectic.

<table>
<thead>
<tr>
<th>Metal Region</th>
<th>Inner Oxide (4.0µm)</th>
<th>Outer Oxide (5.5µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inner Oxide (3.2 µm)</td>
<td>Cr Enrichment (0.8µm)</td>
</tr>
<tr>
<td>Observations</td>
<td>Dense, uneven interface with inner oxide</td>
<td>Porous, small grains with retained metal lath</td>
</tr>
<tr>
<td>Average Chemical Composition</td>
<td>Fe: 1</td>
<td>Cr: 1.46</td>
</tr>
<tr>
<td>Diffracted Phases</td>
<td>bcc Fe, Cr$_2$C$_6$, Fe$_3$O$_4$</td>
<td>bcc Fe, Cr$_2$C$_6$, Fe$_3$O$_4$, FeCr$_2$O$_4$</td>
</tr>
</tbody>
</table>

*bcc Fe* in outer oxide likely a result of CCD collection error
Later, these findings will be compared to those for the two other HT-9 samples, as well as the T-91 sample and Alloy 3.

### 3.2 Examination of Oxide Layers Formed on HT-9 DELTA Annealed after 666 hours of exposure to 500°C Lead-Bismuth Eutectic

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, as described in section 2.1.3. HT-9 DELTA Annealed was heat treated at 1060 °C for 1 hour, then air cooled, followed by an anneal at 730 °C for 2 hours, and another air cooling. 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.

### 3.2.1 Scanning Electron Microscope Examination of HT-9 DELTA Annealed

Figure 3-13 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 µm thick containing an inner and outer oxide. Just as in the HT-9 DELTA sample, the inner layer exhibits some porosity as well oxidation along lath boundaries advancing into the bulk metal. This layer’s interface with the metal is wavy and its morphology is dictated by the original structure of the metal, just as in the case of the HT-9 DELTA sample, as well as similar samples corroded in supercritical water.

The interface between the inner oxide and the outer oxide is also slightly wavy. Since this interface represents the original metal surface, this unevenness may be a result of liquid metal dissolution occurring during initial startup of the corrosion experiments, or of the surface of the metal not being perfectly flat when it was placed in the loop. The outer oxide layer in Figure 3-13 also contains structures resembling those seen in the oxide layers of HT-9 DELTA. The outer oxide consists of two sublayers: the first is filled with bright “spots” which are absent in the outermost half of the layer. The outer oxide layer is dense with occasional cracks or missing pieces (such as the one seen at the top of the SEM image in Figure 3-13).
3.2.2 Microbeam X-ray Fluorescence Examination of HT-9 DELTA Annealed

Figure 3-14 shows the fluorescence data for major alloying elements, iron and chromium, obtained during the scan of the oxide layers shown in Figure 3-13 at APS. In the metal, the iron and chromium concentrations remain relatively constant until 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 extra 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 levels of iron similar to those seen in the metal. In this layer, phases containing chromium are expected to disappear.

Figure 3-14: Iron and chromium microbeam x-ray fluorescence data from oxide layers formed on HT-9 DELTA Annealed after 666 hours of exposure to 500°C lead-bismuth eutectic.

Fluorescence data from the minor alloying and contaminating elements lead and nickel is given in Figure 3-15. The fluorescence signal from nickel was weaker than those
emitted by iron and chromium due to its low content in the alloy. The lead fluorescence signal is fairly weak and noisy, but does show a distinct peak in the inner 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 inner half of the outer oxide.

Figure 3-15: Lead and nickel microbeam x-ray fluorescence data from oxide layers formed on HT-9 DELTA Annealed after 666 hours of exposure to 500°C lead-bismuth eutectic.
The nickel fluorescence signal starts off constant in the metal, then shows an 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.

### 3.2.3 Microbeam X-Ray Diffraction Examination of HT-9 DELTA Annealed

Figure 3-16 shows the contour plot of the diffracted intensities as a function of 2-theta angle and location from diffraction patterns taken in 0.2\(\mu\text{m}\) steps across the oxide layers formed on HT-9 DELTA Annealed. The following sections will discuss these diffraction results in detail for each layer of the sample.
Figure 3-16: 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 the 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.
3.2.3.1 Metal Region

In the metal region near the oxide, several peaks are visible, while 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 likely seen in the metal region due to the preferential oxidation along the metal lath boundaries observed ahead of the oxide front. These peaks were indexed as solely the $\text{Fe}_3\text{O}_4$ phase, and their intensities increase dramatically closer to the inner oxide region.

No diffraction peaks from either ferrite or carbides were observed in the diffraction patterns from the metal region. The likely explanation for this is that the metal was annealed, reducing stresses at grain boundaries and giving the lathes a more closely 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 it is possible that this peak would not be visible in the small region probed. Similarly, the carbides in this region may have adopted different orientations than the three observable ones in this angular range. TEM studies or further XRD data over a wider angular range or with greater sampling of the metal would be needed to confirm or refute this.

3.2.3.2 Inner Oxide Region

Both magnetite ($\text{Fe}_3\text{O}_4$) and spinel ($\text{FeCr}_2\text{O}_4$) peaks are observed from the very beginning of the inner oxide region; however, the spinel peaks are once again about an order of magnitude smaller than the magnetite peaks. The relative intensities of the diffraction peaks in both phases are close to what would be expected from a randomly
oriented sample, with the exception of the Fe$_3$O$_4$ (4 0 0) and the FeCr$_2$O$_4$ (4 0 0) peaks. Both of these peaks show diffraction signals that are slightly stronger than would be expected in a randomly oriented sample. Only one Cr$_2$O$_3$ peak (the (1 1 0)) is observed during the examination of this sample, and only in a small region 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 the HT-9 DELTA Annealed sample, the annealing process may have intensified this effect. The presence of carbides in the inner oxide could indicate that uncorroded metal is present in the inner oxide as well, however without further studies, 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 3-17 shows a full peak fit from the inner oxide near the inner oxide-outer oxide interface, denoted by the first asterisk in Figure 3-16. Although the strongest Cr$_2$O$_3$ and FeCr$_2$O$_4$ signals come from this section of the sample, they are still much smaller than those observed in the HT-9 DELTA sample. It is worth noting that the diffraction pattern in Figure 3-17 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 (ROI) 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 would not strongly affect which peaks are seen, but in the case of highly oriented phases like the carbides, these inconsistencies can arise.
A new peak not observed in HT-9 DELTA is also present in this diffraction pattern. The peak diffracts at approximately 28.12°, and it shows up as a spot pattern, indicating that it is coming from a single grain. As shown in Figure 3-18, this new peak actually diffracts with the exact same spot pattern (with varying intensities) through the metal, inner, and outer oxide layers – a total distance of 6.6 µm. Such diffraction behavior would mean that the peak is either coming from several grains with the exact same orientation, or from one 6.6 µm long grain. No such grains were ever observed in any of the SEM or optical microscopy studies done, and attempts made to index it yielded the (1 0 4) orientation of hematite, Fe₂O₃, as the only possible candidate given known elements and potential contaminants in this oxide.

Figure 3-17: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 4.6 µm into HT-9 DELTA Annealed’s inner oxide layer after 666 hours of exposure to 500°C lead-bismuth eutectic.
While normally magnetite (Fe$_3$O$_4$) develops during the corrosion process, hematite (Fe$_2$O$_3$) has also been observed forming in oxygen-rich environments. However, since this sample was corroded in the same environment as the HT-9 DELTA sample, it would be unlikely that one alloy, but not the other, would develop the phase. Fe$_2$O$_3$ has three expected peaks in this angular range, but only one is seen in the diffraction data. The powder diffraction data for the Fe$_2$O$_3$ phase is given in Table 3-8. Only the (1 0 4) 100% intensity peak is seen, while the (1 1 0) 73% intensity peak and the (1 1 3) 19% intensity peak are not observed. Given all of this information, it is believed that the peak seen at 28.12° does not in fact diffract from the Fe$_2$O$_3$ phase, but could be from a
contaminant on the surface, or from another unknown source. Other possible
identifications for this peak were explored and ruled out, including likely contaminants
such as silicon carbide and diamond. Without further study, the peak remains unindexed.

Table 3-8:  Fe\textsubscript{2}O\textsubscript{3} Hematite peak locations (PDF: 04-008-7625)

<table>
<thead>
<tr>
<th>Fe\textsubscript{2}O\textsubscript{3} d-spacing (Å)</th>
<th>2 theta Angle</th>
<th>Relative Intensity</th>
<th>(h k l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6815</td>
<td>28.17°</td>
<td>100%</td>
<td>(1 0 4)</td>
</tr>
<tr>
<td>2.5040</td>
<td>30.22°</td>
<td>73%</td>
<td>(1 1 0)</td>
</tr>
<tr>
<td>2.1936</td>
<td>34.62°</td>
<td>19%</td>
<td>(1 1 3)</td>
</tr>
</tbody>
</table>

3.2.3.3 Outer Oxide Region

After the inner oxide region comes a sharp interface with the outer oxide. As seen
in the fluorescence data in Figure 3-14, the outer oxide is formed only from iron, with
some nickel and lead enrichments in the inner half of it. Similar to HT-9 DELTA, the
inner half of HT-9 DELTA Annealed’s outer oxide contains strong Fe\textsubscript{3}O\textsubscript{4} peaks as well
as both of the fcc Pb-Bi phase’s peaks. Unlike HT-9 DELTA, HT-9 DELTA Annealed
exhibits a strongly diffraction unknown peak that is largest in the inner half of the outer
oxide, but continues into the outer half of the outer oxide as well.

As expected from the location of the bright spots in the SEM, and from 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 inner half of the outer oxide. A diffraction pattern and fitted peaks
from this region of the outer oxide (6.0µm into the sample, as denoted by an asterisk in
Figure 3-16) is given in Figure 3-19. While difficult to see due to its low intensity, the fcc
Pb-Bi peak (1 1 1) does form a spotted ring, while the (2 0 0) peak is simply spots, indicating that these peaks may be diffracting from larger or textured grains.

Because of its very large grain sizes in the outer oxide, diffracted peaks from Fe$_3$O$_4$ vary dramatically in intensity. As explained previously, this is 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.

**3.2.4 HT-9 DELTA Annealed Summary of Findings**

An annealed sample of HT-9 was corroded in the DELTA loop at Los Alamos National Laboratory for 666 hours in 500°C lead-bismuth eutectic, and the resulting oxide layers were examined using a variety of techniques, including: scanning electron microscopy, micro x-ray fluorescence, and micro x-ray diffraction. The sample exhibited
a duplex oxide consisting of an inner and an outer oxide layer, each with sublayers of their own. Table 3-9 summarizes some of the microstructural characteristics of this oxide found using the techniques listed above. Chemical compositions are given relative to the chemical composition of the alloy (baseline metal content for each element = 1).

Table 3-9: Summary of findings for oxide layers formed on HT-9 DELTA Annealed after 666 hours of exposure to 500°C lead-bismuth eutectic.

<table>
<thead>
<tr>
<th>Metal Region</th>
<th>Inner Oxide (3.0 µm)</th>
<th>Outer Oxide (4.2 µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observations</td>
<td>Inner Oxide Layer (3.0 µm)</td>
<td>Pb-Bi layer (2.4µm)</td>
</tr>
<tr>
<td>Dense, uneven interface with inner oxide</td>
<td>Porous, small grains with retained metal lath</td>
<td>Dense, large equiaxed grains with bright spots</td>
</tr>
<tr>
<td>Average Chemical Composition</td>
<td>Fe: 1 Cr: 1 Ni: 1 Pb: 1</td>
<td>Fe: 0.80 Cr: 1.50 Ni: 1.03 Pb: 1.01</td>
</tr>
<tr>
<td>Diffracted Phases</td>
<td>Fe$_3$O$_4$ FeCr$_2$O$_4$ Cr$_2$C$_6$ Cr$_2$O$_3$</td>
<td>Fe$_3$O$_4$ fcc Pb-Bi</td>
</tr>
</tbody>
</table>

While very similar to the HT-9 DELTA sample, the HT-9 DELTA Annealed sample did show some key differences. Firstly, it did not show an additional chromium enrichment in the inner oxide near the inner-outer oxide interface, probably due to more of the chromium in the sample being sequestered in carbides from the annealing process. As a result, no chromium-containing phases were observed to increase in intensity near this region. In general, this sample exhibited a lower intensity of peaks associated with the presence of FeCr$_2$O$_4$ and even more notably, Cr$_2$O$_3$ phase than the HT-9 DELTA sample.

Another difference from the HT-9 DELTA sample was that the HT-9 DELTA Annealed sample did not exhibit a (1 1 0) bcc Fe peak in the diffraction data, likely due
to increased grain size or highly oriented grains as a result of the annealing process. 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 that the previous two.

### 3.3 Examination of Oxide Layers Formed on HT-9 IPPE after 3000 hours of exposure to 550°C Lead-Bismuth Eutectic

The last sample of HT-9 studied in this thesis comes from the same stock as the HT-9 DELTA samples discussed in the previous sections, but it was corroded at a higher temperature for a longer period in the IPPE loop, as described in section 2.2. 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.

#### 3.3.1 Scanning Electron Microscope Examination of HT-9 IPPE

Figure 3-20 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 µm 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 the lath grain structure of the metal with preferential oxidation proceeding along grain boundaries, then attacking favorably oriented grains first resulting in a wavy appearance. The outer oxide layer in Figure 3-20, 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 show the two sublayers seen in the previous samples, being instead a single layer of columnar grains. The layer also shows a lower concentration of the bright spots previously associated with the presence of the fcc lead-bismuth phase.

Finally, the layer’s interface with the lead bismuth coolant is very uneven and shows signs of liquid metal 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 liquid metal dissolution of the outer oxide layer, resulting in a different ratio of outer to inner oxide layer thickness than the previous samples. The SEM image in Figure 3-20 shows this has resulted in an uneven outer oxide-coolant interface.
Figure 3-20: Scanning electron micrograph of oxide layers formed on HT-9 IPPE after 3000 hours of exposure to 550°C lead-bismuth eutectic.

### 3.3.2 Microbeam X-ray Fluorescence Examination of HT-9 IPPE

Figure 3-21 shows the fluorescence data for iron and chromium obtained during the examination of this sample at APS. As observed in the other HT-9 samples, iron and chromium levels are fairly constant in the metal until the inner oxide-metal interface. Unlike the other samples, at this interface there is a significant chromium enrichment and depletion of iron. Further on in the inner oxide, the iron content remains decreased and
chromium content higher than that in the bulk metal. Just as in the previous HT-9 samples, the outer oxide contains only iron.

Figure 3-22 shows the equivalent fluorescence data for lead and nickel. It can be seen that the lead fluorescence signal for this sample does not rise above the noise level, indicating little lead was present in the section of the outer oxide layer scanned. Nickel on the other hand, is enriched in the metal just ahead of the inner oxide layer, followed by a depletion in the rest of the oxide. There is also a small nickel enrichment about midway through the inner layer. This enrichment is not associated with any feature in particular.
except for being located just past the highest chromium enrichment. It is not clear at this point if this nickel enrichment has anything to do with the chromium enrichment.

Figure 3-22: Lead and nickel microbeam x-ray fluorescence data from oxide layers formed on HT-9 IPPE after 3000 hours of exposure to 550°C lead-bismuth eutectic.

3.3.3 Microbeam X-Ray Diffraction Examination of HT-9 IPPE

Figure 3-23 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 the HT-9 IPPE oxide layers.
Figure 3-23: 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 the 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.
3.3.3.1 Metal Layer

In the metal layer several major peaks are visible, the most notable of which is a very strongly diffracting ferrite \((1 \ 1 \ 0)\) peak. This peak continues onto the inner oxide layer indicating that there is some uncorroded metal within the inner oxide. Also similar to the previous two samples, the metal layer contains all four \(\text{Fe}_3\text{O}_4\) peaks which steadily increase 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 \(\text{Cr}_2\text{C}_6\) carbides seen in the two previous HT-9 samples, the peaks are consistent with \(\text{Cr}_7\text{C}_3\) carbides. The powder diffraction information for \(\text{Cr}_7\text{C}_3\) is given in Table 3-10.

Only the most intense diffraction orientation for \(\text{Cr}_7\text{C}_3\), \((1 \ 5 \ 1)\), is seen in the metal. The second most intense, \((1 \ 1 \ 2)\) is seen later on in the inner oxide, and the smallest \((1 \ 5 \ 0)\) and \((0 \ 6 \ 0)\) peaks are never observed. Since these are smaller magnitude peaks, they may be lost in the noise, or the carbides may be highly oriented causing the other peaks not to appear. Although the \((1 \ 5 \ 1)\) \(\text{Cr}_7\text{C}_3\) peak is somewhat overshadowed in the contour plot by the very intense Ferrite \((1 \ 1 \ 0)\) peak, this peak can be seen in the peak fits, such as the one shown in Figure 3-24 taken from a location 2.6\(\mu\)m into the sample.

<table>
<thead>
<tr>
<th>(\text{Cr}_7\text{C}_3) d-spacing (Å)</th>
<th>2 theta Angle</th>
<th>Relative Intensity</th>
<th>((h \ k \ l))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2969</td>
<td>33.01°</td>
<td>33%</td>
<td>((1 \ 5 \ 0))</td>
</tr>
<tr>
<td>2.1231</td>
<td>35.80°</td>
<td>46%</td>
<td>((1 \ 1 \ 2))</td>
</tr>
<tr>
<td>2.0489</td>
<td>37.15°</td>
<td>100%</td>
<td>((1 \ 5 \ 1))</td>
</tr>
<tr>
<td>2.0256</td>
<td>37.59°</td>
<td>13%</td>
<td>((0 \ 6 \ 0))</td>
</tr>
</tbody>
</table>
Following the metal is the inner oxide region. The very beginning of the inner oxide shows the highest chromium concentrations, and, not surprisingly, is also where the highest intensities of peaks associated with the chromium-containing phases Cr$_2$O$_3$ and FeCr$_2$O$_4$ are seen. Two peaks associated with the Cr$_7$C$_3$ carbide phase were identified in this region. A diffraction pattern taken from this section of the oxide is given with peaks identified in Figure 3-25. It should be noted that the Cr$_2$O$_3$ peaks appear to diffract in ring patterns rather than spots, and the full width half max of these peaks (as determined by the peak fitting process) are broad. These two things indicate that the Cr$_2$O$_3$ phase has smaller grains and no strong preferential orientations. All of the Cr$_2$O$_3$ peaks become progressively weaker as the beam moves 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) Cr$_2$O$_3$ peak which briefly reappears about 13 µm into the oxide layer).

![Diffraction pattern and integrated intensity](image)

Figure 3-25: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 8.2 µm into HT-9 IPPE’s inner oxide region after 3000 hours of exposure to 550°C lead-bismuth eutectic.

Similar to the Cr$_2$O$_3$ peaks, the carbide peaks are visible for only a short distance into the inner oxide layer, and by 9 µm in they are gone. The peaks from the FeCr$_2$O$_4$ spinel phase, however, continue with about the same intensity through the remainder of the inner oxide, stopping at the outer oxide at the same location where the chromium fluorescence intensity drops off.

In addition to the chromium-containing phases, the inner oxide also displays the (1 1 0) bcc Fe peak, as well as all four of the Fe$_3$O$_4$ peaks expected in this angular range. The intensity of the bcc iron peak decreases further into the sample, until about 14 µm where it disappears. The Fe$_3$O$_4$ peaks, however, are visible throughout the entire inner oxide, increasing in intensity near the Fe-enriched outer oxide. Their relative intensities stay fairly close to what would be expected from randomly oriented grains. The diffracted
intensity of these peaks appears in ring patterns, meaning that in the inner oxide, the grains of the Fe₃O₄ phase are fairly small and not highly textured.

### 3.3.3.3 Outer Oxide Region

The HT-9 IPPE sample exhibited an outer oxide consisting of only one layer, unlike HT-9 DELTA or HT-9 DELTA Annealed, each which showed 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. However, electron dispersive spectroscopy was used to confirm that lead and bismuth are in fact present in the outer oxide of this sample. An electron dispersive spectroscopy map of the oxide layer in the sample is shown in Figure 3-26. The light blue arrows in the figure indicate areas of lead and bismuth enrichment, which appear as bright spots in the SEM image.

While EDS does confirm presence of lead and bismuth, there are several possible reasons the fcc Pb-Bi phase might not show up in diffraction images. Fewer bright spots are seen in the HT-9 IPPE SEM image seen in Figure 3-20, indicating that there is less lead and bismuth than in the previous two samples. It is possible that the area in the oxide scanned during the experiment may have missed these Pb-Bi areas entirely, or that their concentrations were so low that they did not diffract strongly enough to be seen in the diffraction patterns. It is also possible that the fcc Pb-Bi phase was formed in an orientation that does 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$_3$O$_4$ 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

Figure 3-26: Energy dispersive spectroscopy maps from outermost oxide layer formed on HT-9 IPPE after 3000 hours of exposure to 550°C lead-bismuth eutectic. Arrows indicate areas of enriched lead and bismuth.
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 3-27 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°.

![Diffraction pattern and peak fit](image)

Figure 3-27: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 22.6 µm into HT-9 IPPE’s outer oxide region after 3000 hours of exposure to 550°C lead-bismuth eutectic.

In a similar manner as in the two HT-9 samples previously discussed, the Fe$_3$O$_4$ peaks in HT-9 IPPE vary dramatically in intensity throughout the outer oxide layer, and are very narrow in shape. Both of these observations are consistent with Fe$_3$O$_4$ diffracting from either large or highly oriented columnar grains in the outer oxide as seen in the SEM image in Figure 3-20.
### 3.3.4 HT-9 IPPE Summary of Findings

An annealed sample of HT-9 was corroded in the DELTA loop at Los Alamos National Laboratory for 666 hours in 500°C lead-bismuth eutectic, and the resulting oxide layers were examined using a variety of techniques. The techniques discussed were: scanning electron microscopy, energy dispersive spectroscopy, micro x-ray fluorescence, and micro x-ray diffraction. The sample exhibited a duplex oxide consisting of an inner and an outer oxide layer, each with sublayers of their own. Table 3-11 summarizes some of the microstructural characteristics of this oxide, found using the techniques listed above. Chemical compositions are given relative to the chemical composition of the alloy (baseline metal content for each element = 1).

Table 3-11: Summary of findings for oxide layers formed on HT-9 IPPE after 3000 hours of exposure to 550°C lead-bismuth eutectic.

<table>
<thead>
<tr>
<th>Metal Region</th>
<th>Inner Oxide (12.5µm)</th>
<th>Outer Oxide (6.7µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr Enrichment</td>
<td>Inner Oxide Layer</td>
<td>Cr Enrichment</td>
</tr>
<tr>
<td>(1.4µm)</td>
<td>(11.1µm)</td>
<td>(1.4µm)</td>
</tr>
<tr>
<td>Observations</td>
<td>Porous, small grains with retained metal lath</td>
<td>Porous, small grains with retained metal lath</td>
</tr>
<tr>
<td>Average Chemical Composition</td>
<td>Fe: 0.76</td>
<td>Fe: 0.78</td>
</tr>
<tr>
<td></td>
<td>Cr: 1.75</td>
<td>Cr: 1.56</td>
</tr>
<tr>
<td></td>
<td>Ni: 0.64</td>
<td>Ni: 0.45</td>
</tr>
<tr>
<td></td>
<td>Pb: 1.01</td>
<td>Pb: 1.02</td>
</tr>
<tr>
<td>Diffracted Phases</td>
<td>Fe₃O₄</td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td></td>
<td>bcc Fe</td>
<td>bcc Fe</td>
</tr>
<tr>
<td></td>
<td>Cr₃C₃</td>
<td>FeCr₂O₄</td>
</tr>
<tr>
<td></td>
<td>Fe₃O₄</td>
<td>Cr₂O₃</td>
</tr>
</tbody>
</table>

Compared with the two previously discussed HT-9 DELTA samples, HT-9 IPPE exhibits several differences. Firstly, the oxide layers in HT-9 IPPE are much thicker than those in 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, while 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 the corrosion process. In addition, HT-9 IPPE’s outer oxide layer contained no sublayers, and the single layer present contained less lead and bismuth than the other HT-9 samples.

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 shows a similar enrichment at its inner oxide-outer oxide layer, while HT-9 DELTA Annealed did not exhibit an especially high chromium enrichment at all. Finally, HT-9 IPPE’s carbide phase identified was Cr$_7$C$_3$ instead of the Cr$_2$3C$_6$ seen in previous samples.

### 3.4 Examination of Oxide Layers Formed on T91 after 666 hours of exposure to 500°C Lead-Bismuth Eutectic

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 [29] found that T91 exposed to flowing LBE at 470°C developed the expected two-layer oxide, the outer layer being porous and the inner layer compact. They found that this outer layer was primarily Fe$_3$O$_4$ whereas the inner layer was composed of the metal’s alloying elements in their near-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 Fe₃O₄ and (Fe,Cr)₃O₄ [29]. Our results will confirm and extend those of Barbier and Rusanov.

### 3.4.1 Scanning Electron Microscope Examination of T91

Similar to the T91 sample in the previous study, this T91 exhibits a contiguous oxide layer which is approximately 7.2 µm thick and contains an inner and outer oxide. Figure 3-28 shows a scanning electron microscope image taken using backscattered electrons 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 outer oxide – inner oxide interface (representing the initial metal’s pre-corrosion surface) is straight as would be expected. The inner oxide – metal interface is discontinuous, showing signs of preferential oxide advancement along particular directions similar to the interfaces seen in the previous HT-9 samples. It is unknown if this preferential oxidation extends along the grain lath boundaries as in HT-9, or if the uneven corrosion is due to a different factor, such as grain orientation.
In the SEM image in Figure 3-28, the outer oxide of T91 exhibits two sub-layers similar to what was seen in the HT-9 DELTA and HT-9 DELTA Annealed samples. In the SEM image, it can be seen that the inner half of the outer oxide layer contains a high density of the bright spots seen in the previous HT-9 samples, and identified as lead and bismuth. Lead and bismuth are also seen on the outermost edge of the oxide, likely left behind after removal from the corrosion loop. Unlike previous samples which had dense outer oxides, however, T91’s outer oxide layer is highly porous.
3.4.2 Microbeam X-ray Fluorescence Examination of T91

Figure 3-29 shows the microbeam x-ray 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 corresponding increase in chromium content, with an especially high peak of chromium just before the inner-outer oxide interface. The outer oxide shows only iron, indicating that the outer oxide is formed by outwards iron migration. In the inner half of the outer oxide layer, the iron fluorescence intensity dips down slightly, the rises again. This is likely caused by porosity seen mainly in the inner half of the outer oxide layer.
Figure 3-29: Iron and chromium microbeam x-ray fluorescence data from oxide layers formed on T91 after 666 hours of exposure to 500°C lead-bismuth eutectic.

Figure 3-30 shows the lead and nickel fluorescence data from the T91 sample. Not surprisingly, the lead signal shows an enrichment in the inner half of the outer oxide, as well as on the outer surface, 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.
As in all of the previous samples, the nickel fluorescence signal in Figure 3-30 shows a small enrichment near 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 compared to 0.57 weight percent in HT-9. It will be shown later in the examination of Alloy 3 that this nickel peak in the outer oxide actually comes from the coolant, not the steel, so its height indicates simply indicates high deposition of nickel in this region by the coolant.

Figure 3-30: Lead and nickel microbeam x-ray fluorescence data from oxide layers formed on T91 after 666 hours of exposure to 500°C lead-bismuth eutectic.
3.4.3 Microbeam X-Ray Diffraction Examination of T91

Figure 3-31 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’s oxide layers.
Figure 3-31: Summary of data obtained using microbeam synchrotron radiation on oxide layers formed on T91 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 the 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.
3.4.3.1 Metal Region

In the metal layer the most intense peak is that from bcc iron (1 1 0), which, as usual, although it drops off in intensity, continues into the inner oxide. This indicates that there are packets of uncorroded metal remaining in the inner oxide layer as also seen in the HT-9 samples. All four of the Fe$_3$O$_4$ magnetite peaks are also present, again likely due to the uneven nature of the inner oxide-metal interface. The intensity of these four peaks increases closer to the inner oxide layer.

Small carbide peaks are seen in the metal layer, however they do not really manifest until the inner oxide. Since carbides in previous samples have been highly oriented, it is little surprise that their peaks would appear inconsistently in the sample, with varying intensities. Also, T91 has only 8.26wt% chromium whereas HT-9 has 11.95%, so fewer chromium carbides would be expected in T91.

3.4.3.2 Inner Oxide Region

As mentioned above, 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. The fact that they do not appear in the expected relative intensities is consistent with the characteristics of a highly oriented phase. It can be seen in Figure 3-31 that both peaks appear to continue into the outer oxide layer, but as will be explained in more detail later, both peaks deviate substantially from their initial positions, and in opposite directions, indicating the presence of two completely different phases in the outer oxide.
In addition to chromium carbides and ferrite, the inner oxide layer also shows large magnetite peaks, and spinel peaks about an order of magnitude smaller. These spinel peaks grow ever weaker as they get closer to the inner-outer oxide interface. Simultaneously, several low-intensity Cr$_2$O$_3$ peaks appear, and grow stronger as the beam is scanned towards this interface. The Cr$_2$O$_3$ 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 would not necessarily indicate the location of the strongest enrichment of carbides if we know that they are highly oriented).

A diffraction pattern and peak fit from the chromium enriched area is shown in Figure 3-32. In this figure, the intensity of the Cr$_2$O$_3$ (1 0 4) and (1 1 0) peaks are fairly low, making them difficult to detect. The peaks corresponding to carbide phases, however, are intense, and diffract as spots, rather than rings, providing further backing for the interpretation that they are from 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.
3.4.3.3 Outer Oxide Region

The outer oxide, is again mostly comprised of iron with some lead and nickel enrichments. In this layer, the chromium-rich phases disappear and increased intensity of Fe$_3$O$_4$ magnetite peaks is observed. 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 are visible in the region corresponding to the inner half of the outer oxide. Unlike in these other samples, two additional peaks are seen in positions very close to those of the previously observed carbide peaks. It is not believed that these peaks come from the carbides, however, because a) there is no chromium fluorescence signal in 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 if this were the case. Figure 3-33 shows 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 indicates that these peaks in the outer oxide are not from carbide phase.

Since the outer oxide contains very large pores, it is possible that materials used in the polishing process might become lodged in some of those pores. The polishing process described back in Section 2.3 involved silicon carbide paper, 1 µm diamond paste and 0.05 µm colloidal silica. Using this information, the peak seen at ~37.1 degrees could be identified as diamond from the diamond paste used in the polishing process. The peak at 32.0 degrees, however, remains unindexed.

The powder diffraction file for diamond in the angular range studied can be found in Table 3-12. Diamond only has one peak in this angular range, and it is located at 37.23
degrees, representing the (1 1 1) orientation of the phase. Since there are no other diamond peaks in the studied angular range, it is not possible to provide further evidence using other peaks that the peak at 37.1 degrees is diamond.

Table 3-12: Diamond (C) peak locations (PDF: 01-075-0410)

<table>
<thead>
<tr>
<th>Diamond d-spacing (Å)</th>
<th>2 theta Angle</th>
<th>Relative Intensity</th>
<th>(h k l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0538</td>
<td>37.23°</td>
<td>100%</td>
<td>(1 1 1)</td>
</tr>
</tbody>
</table>

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 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 3-34. 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, suggesting that they come from trapped particles as well.
The outermost part of the outer oxide is mainly composed of strongly diffracting Fe$_3$O$_4$ magnetite peaks, as well as the continued unindexed peak at 32.0º. As in previous samples, these Fe$_3$O$_4$ peaks vary dramatically in relative intensity, and likely diffract from large grains.

### 3.4.4 T91 Summary of Findings

A sample of T91 was corroded in the DELTA loop at Los Alamos National Laboratory for 666 hours in 500°C lead-bismuth eutectic, and the resulting oxide layers were examined using a variety of techniques. Techniques discussed were: scanning electron microscopy, micro x-ray fluorescence, and micro x-ray diffraction. The sample exhibited a duplex oxide consisting of an inner and an outer oxide layer each with sublayers of their own. Table 3-13 summarizes some of the microstructural characteristics of this oxide found using the techniques listed above.
compositions are given relative to the chemical composition of the alloy (baseline metal content for each element = 1).

Table 3-13: Summary of findings for oxide layers formed on T91 after 666 hours of exposure to 500°C lead-bismuth eutectic.

<table>
<thead>
<tr>
<th>Metal Region</th>
<th>Inner Oxide (2.6µm)</th>
<th>Outer Oxide (4.6µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inner Oxide (1.4µm)</td>
<td>Cr Enrichment (1.2µm)</td>
</tr>
<tr>
<td><strong>Observations</strong></td>
<td>Dense, uneven interface with inner oxide</td>
<td>Slightly porous, small grains with retained metal</td>
</tr>
<tr>
<td><strong>Average Chemical Composition</strong></td>
<td>Fe: 1 Cr: 1 Ni: 1 Pb: 1</td>
<td>Fe: 0.86 Cr: 1.39 Ni: 0.76 Pb: 1.01</td>
</tr>
<tr>
<td><strong>Diffracted Phases</strong></td>
<td>Fe$_3$O$_4$ bcc Fe</td>
<td>Fe$_3$O$_4$ bcc Fe FeCr$_2$O$_4$ Cr$_2$C$_6$</td>
</tr>
</tbody>
</table>

Although T91’s oxide layers and main diffraction peaks were similar to those seen in the HT-9 samples, there were a few key differences. The chromium-containing phases in T91 were of much lower relative intensity than those in the HT-9 samples, and did not continue through much of the inner oxide layer. This is consistent with the fact that 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 becoming trapped in the pores.
3.5 Examination of Oxide Layers Formed on Alloy 3 after 666 hours of exposure to 500°C Lead-Bismuth Eutectic

Alloy 3 is a purely ferritic model alloy created from 91wt% iron and 9wt% chromium. While its chromium content is similar to that found in T91, it lacks the other alloying elements used to stabilize other phases such as martensite, as well as add strength.

The sample was corroded in flowing LBE in the DELTA loop for 666 hours at 500°C. The alloy was examined at APS in June 2006 using a 0.25 µm step size. Although a slightly different angular range was examined than the other alloys discussed (see Table 3-1), the difference was small and should not have any effect on the findings for this sample.

3.5.1 Scanning Electron Microscope Examination of Alloy 3

Figure 3-35 shows an overall view of the oxide layers formed on Alloy 3 during corrosion. Unlike previous alloys studied, Alloy 3’s oxide layer 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. This delaminating of the oxide layers may have been due either to spalling during corrosion or liquid metal penetration via cracks in the oxide layers. It is also not clear if the oxide layer delaminated during corrosion or cooling, but presence of lead and bismuth found in the open gap by this work as well as previous researchers suggests that this happened while
the sample was still in contact with the liquid LBE during corrosion. 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 µm in total. The inner oxide/outer oxide interface exhibits some porosity, which was also seen in TEM studies by Andrew Siwy [25]. Bright field images of the overall oxide layer as well as this interface are shown in Figure 3-36. The interface between the inner and outer oxide layers consists of smaller grains with pores corresponding to the locations of grain

Figure 3-35: Scanning electron micrograph of oxide layers formed on T91 after 666 hours of exposure to 500°C lead-bismuth eutectic.
boundaries. The outer oxide near this interface shows large equiaxed grains which become longer and more columnar farther from the interface. The inner oxide also shows columnar grains, but they are much shorter and smaller than those seen in the outer oxide. The oxides overall do not appear to be highly textured, nor do the grains seem to show any preferential orientation [25].

TEM studies found that, unlike all of the previous samples, Alloy 3 exhibited a uniform oxidation front into the metal, likely because there was not martensitic lath boundaries for the oxidation to proceed along. Also different from most of the previous samples (with the exception of HT-9 IPPE) the outer oxide of Alloy 3 appears to consist

Figure 3-36: Bright field transmission electron microscope images of oxide layers formed on T91 after 666 hours of exposure to 500°C lead-bismuth eutectic [25].
of only a single layer. It does, however, still contain the bright spots indicative of LBE contamination throughout. Overall, both oxide layers are cracked and inhomogeneous.

3.5.2 Microbeam X-Ray Diffraction Examination of Alloy 3

Figure 3-37 shows the fluorescence signals from iron and chromium (the only alloying elements in the sample). In the metal the iron and chromium contents are constant, then both drop off as the beam falls into the oxide-metal 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 increases, although not to levels above those seen in the metal as with previous samples.
Figure 3-37: Iron and chromium microbeam x-ray fluorescence data from oxide layers formed on Alloy 3 after 666 hours of exposure to 500°C lead-bismuth eutectic.

Figure 3-38 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 3-38 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 is unlikely since no nickel or nickel-containing substances are used in these processes. The third, and most likely
explanation, is that the nickel was deposited there by the coolant. It is known that the lead-bismuth coolant tends to leach nickel out of the alloys that make up the loop 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 contamination in the coolant would also deposit. In light of this observation, it is possible that nickel enrichments in the outer oxides of previous samples may also have resulted from deposition by the coolant.

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.

3.5.3 Microbeam X-Ray Diffraction Examination of Alloy 3

Figure 3-39 shows the contour plot of the diffracted intensities from phases as a function of 2-theta angle and location taken in 0.25µm steps across Alloy 3’s oxide layers.
Figure 3-39: Summary of data obtained using microbeam synchrotron radiation on oxide layers formed on Alloy 3 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 the sample. Indexed peaks are indicated as well as approximate distance between oxide layers. The asterisk denotes the location of the diffraction pattern discussed further on in this section.
3.5.3.1 Metal Region

At the beginning of the metal region an extremely strong bcc Fe (1 1 0) peak is observed. Strangely, this peak continues throughout all of the oxide layers, and even out into the epoxy. This may be due to the actual presence of ferrite out this far, or, more likely it could be an artifact. This is backed up by TEM studies which did not observe the bcc ferrite phase anywhere outside of the metal layer [25]. Because this data was taken in June of 2006, it was taken using an older CCD that was replaced before the rest of the diffraction data discussed in this thesis was taken. The older CCD was more prone to saturation, and since the bcc Fe (1 1 0) peak was incredibly intense, it is likely that it saturated the CCD, causing it to seem as though it the phase were present when it was not.

Magnetite (Fe$_3$O$_4$) peaks are also present in the metal region, indicating that there is some oxidation occurring deeper into the metal than indicated by SEM and TEM results. There are no carbide peaks present, which is expected since carbon was not an alloying element used in Alloy 3. There are, however, two Cr$_2$O$_3$ 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 powder diffraction information for rhombohedral bismuth is given in Table 3-14.

Table 3-14: Rhombohedral bismuth (Bi) peak locations (PDF: 00-044-1246 )

<table>
<thead>
<tr>
<th>Bi d-spacing (Å)</th>
<th>2 theta Angle</th>
<th>Relative Intensity</th>
<th>(h k l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.369</td>
<td>31.98°</td>
<td>27%</td>
<td>(1 0 4)</td>
</tr>
<tr>
<td>2.273</td>
<td>33.37°</td>
<td>29%</td>
<td>(1 1 0)</td>
</tr>
<tr>
<td>2.032</td>
<td>37.47°</td>
<td>5%</td>
<td>(0 1 5)</td>
</tr>
</tbody>
</table>
Previous TEM studies identified a grain of this exact same bismuth phase in this sample as well, but the grain was observed in the gap in between the metal and inner oxide [25]. 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 small areas are sampled by both the TEM and the synchrotron, and the bismuth phase is distributed throughout multiple regions of the sample.

3.5.3.2 Gap between Metal Region and Inner Oxide Region

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 ~30.5º peak appears. This peak had previously been indexed as either Cr$_2$O$_3$ (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 locations of chromium and lead/bismuth were mutually exclusive, this sample has them both located in this same region. Since there are no other Cr$_2$O$_3$ peaks in this region, and the other fcc Pb-Bi peak appears at the same location, it is logical to conclude that the peak at 30.5 º is diffracting from fcc Pb-Bi (1 1 1) and not Cr$_2$O$_3$ (1 1 0) in this region.

3.5.3.3 Inner Oxide 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 four magnetite peaks, and both fcc Pb-Bi
peaks. A diffraction pattern taken and its corresponding peak fit from 6.0 µm this region is given in Figure 3-40. It can be seen that the magnetite diffracts 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.

![Diagram of diffraction pattern and integrated intensity versus 2-theta plot.](image)

Figure 3-40: (a) Diffraction pattern and (b) corresponding integrated intensity versus 2-theta plot from 6.0 µm into Alloy 3’s inner oxide region after 666 hours of exposure to 500°C lead-bismuth eutectic.

None of the previously examined samples exhibited peaks from the fcc Pb-Bi phase in the inner oxide. Since the oxide has delaminated, and the inner oxide is porous, the liquid metal seen in the gap region could easily seep into those pores, resulting in the presence of the fcc Pb-Bi phase here.

Further on in the inner oxide, from about 6.75 to 8.0 µm, there is also the rise of some spinel phase. As in all of the previous samples, the spinel peaks are about an order of magnitude smaller than the magnetite peaks. As the chromium content of the sample
decreases heading towards the outer oxide, so does the presence of the spinel peaks, disappearing entirely in the outer oxide.

### 3.5.3.4 Outer Oxide Region

The outer oxide of the sample contains magnetite peaks and 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 [25]. It is little surprise then that the Fe₃O₄ 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.

### 3.5.4 Alloy 3 Summary of Findings

A sample of model Alloy 3 was corroded in the DELTA loop at Los Alamos National Laboratory for 666 hours in 500°C lead-bismuth eutectic, and the resulting oxide layers were examined using a variety of techniques. Techniques discussed were: scanning electron microscopy, transmission electron microscopy, micro x-ray fluorescence, and micro x-ray diffraction. The sample exhibited a duplex oxide, but this oxide was separated from the metal by a large gap, indicating that the oxide layers may
have spalled or delaminated due to liquid metal ingress. The inner and outer oxide layers did not show sublayers. Table 3-15 summarizes some of the microstructural characteristics of this oxide found using the techniques listed above. Chemical compositions are given relative to the chemical composition of the alloy (baseline metal content for each element = 1).

Table 3-15: Summary of findings for oxide layers formed on Alloy 3 after 666 hours of exposure to 500°C lead-bismuth eutectic

<table>
<thead>
<tr>
<th>Metal Region</th>
<th>Gap Region (1.7µm)</th>
<th>Inner Oxide (2.6µm)</th>
<th>Outer Oxide (4.6µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Observations</strong></td>
<td>Dense, large grains with no martensite</td>
<td>Open with assorted debris</td>
<td>Small pores, small-medium grains</td>
</tr>
<tr>
<td><strong>Average Chemical Composition</strong></td>
<td>Fe: 1</td>
<td>Cr: 1</td>
<td>Ni: 1</td>
</tr>
<tr>
<td><strong>Diffraeted Phases</strong></td>
<td>Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt; bcc Fe</td>
<td>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; Bi</td>
<td>Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt; bcc Fe</td>
</tr>
<tr>
<td></td>
<td>fcc Pb-Bi</td>
<td>fcc Pb-Bi FeCr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td></td>
</tr>
</tbody>
</table>

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 appeared in new and sometimes seemingly sporadic places when compared to previous samples. In TEM studies, it did not show preferential oxidation along grain boundaries, 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, likely due to an artifact in data collection. Alloy 3 also differed from other alloys in that it
exhibited the fcc Pb-Bi phase throughout the inner oxide as well as in the outer oxide. It also exhibited a new bismuth phase not seen in any previous sample.

Because there was no carbon present, no carbides were seen in Alloy 3. It also had the lowest occurrence of chromium-containing oxide phases, especially where they would be expected in the chromium-enriched inner oxide region. Since Alloy 3 and T91 had similar chromium content, it would be expected that they would exhibit similar intensities of chromium-containing phases. This would lead to the conclusion that the other alloying elements in alloys like T91 somehow encourage the formation of or stabilize chromium containing oxides, whereas chromium remains in the bcc iron matrix in Alloy 3.
Chapter 4

Discussion and Conclusions

As part of the continuing efforts to develop new and innovative power plant designs for the future of nuclear power production, materials for use in the lead cooled fast reactor were studied in this thesis. These materials were ferritic-martensitic steels intended for use as fuel cladding and other reactor internal components. These steels were investigated in order to better understand their corrosion mechanisms, and to use this information to determine ways in which the alloy microstructure might be optimized to improve corrosion behavior.

In this thesis, the oxidation layers formed on five samples of ferritic-martensitic steel were investigated after being corroded in a flowing lead-bismuth eutectic environment under one of two sets of conditions. These samples were cross-sectioned and polished, then investigated using a variety of techniques including scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), synchrotron radiation micro x-ray fluorescence (µ-XRF), and synchrotron radiation micro x-ray diffraction (µ-XRD). Table 4-1 summarizes the corrosion conditions and characterization methods used for each of the samples.
Table 4-1: Corrosion conditions and examination methods for samples studied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Corrosion Loop</th>
<th>Corrosion Time (hours)</th>
<th>Corrosion Temperature (°C)</th>
<th>Characterization Tools</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-9 DELTA</td>
<td>DELTA</td>
<td>666</td>
<td>500</td>
<td>SEM, EDS, TEM*, µ-XRF, µ-XRD</td>
</tr>
<tr>
<td>HT-9 DELTA Annealed</td>
<td>DELTA</td>
<td>666</td>
<td>500</td>
<td>SEM, µ-XRF, µ-XRD</td>
</tr>
<tr>
<td>HT-9 IPPE</td>
<td>IPPE</td>
<td>3000</td>
<td>550</td>
<td>SEM, EDS, µ-XRF, µ-XRD</td>
</tr>
<tr>
<td>T91</td>
<td>DELTA</td>
<td>666</td>
<td>500</td>
<td>SEM, µ-XRF, µ-XRD</td>
</tr>
<tr>
<td>Alloy 3</td>
<td>DELTA</td>
<td>666</td>
<td>500</td>
<td>SEM, TEM*, µ-XRF, µ-XRD</td>
</tr>
</tbody>
</table>

*TEM results obtained from A. Siwy’s Master of Science Thesis [25].

4.1 Summary of Findings

From the characterization techniques employed, numerous similarities and differences were found between the alloys studied. A summary of the findings is given in Table 4-2, and a discussion of their similarities and differences for each region is given in the following sections.
### Table 4-2: Summary of Findings for Alloys studied

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Metal Region</th>
<th>Inner Oxide</th>
<th>Cr Enrichment (0.8μm)</th>
<th>Pb-Bi layer (2.4μm)</th>
<th>Outermost layer (3.1μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-9 DELTA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Observations</td>
<td>Dense, uneven interface with inner oxide</td>
<td>Porous, small grains with retained metal lath</td>
<td>Porous, small grains</td>
<td>Dense, large equiaxed grains with bright spots</td>
<td>Dense, large columnar grains</td>
</tr>
<tr>
<td>Average Chemical Composition</td>
<td>Fe: 1</td>
<td>Cr: 1</td>
<td>Ni: 1.05</td>
<td>Pb: 1.03</td>
<td>Fe: 0.76</td>
</tr>
<tr>
<td>Diffraeted Phases</td>
<td>FeO₄</td>
<td>bcc Fe</td>
<td>C₃₃₃₄</td>
<td>Fe₃C₄</td>
<td>FeO₄</td>
</tr>
<tr>
<td>HT-9 DELTA Annealed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Observations</td>
<td>Dense, uneven interface with inner oxide</td>
<td>Porous, small grains with retained metal lath</td>
<td>Porous, small grains with retained metal lath</td>
<td>Dense, large equiaxed grains with bright spots</td>
<td>Dense, large columnar grains</td>
</tr>
<tr>
<td>Average Chemical Composition</td>
<td>Fe: 1</td>
<td>Cr: 1</td>
<td>Ni: 1.03</td>
<td>Pb: 1.01</td>
<td>Fe: 0.80</td>
</tr>
<tr>
<td>Diffraeted Phases</td>
<td>FeO₄</td>
<td>bcc Fe</td>
<td>C₃₃₃₄</td>
<td>Fe₃C₄</td>
<td>FeO₄</td>
</tr>
<tr>
<td>HT-9 IPPE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Observations</td>
<td>Dense, uneven interface with inner oxide</td>
<td>Porous, small grains with retained metal lath</td>
<td>Porous, small grains with retained metal lath</td>
<td>Dense, large columnar grains with some bright spots</td>
<td></td>
</tr>
<tr>
<td>Average Chemical Composition</td>
<td>Fe: 1</td>
<td>Cr: 1</td>
<td>Ni: 1.04</td>
<td>Pb: 1.01</td>
<td>Fe: 0.76</td>
</tr>
<tr>
<td>Diffraeted Phases</td>
<td>FeO₄</td>
<td>bcc Fe</td>
<td>C₃₃₃₄</td>
<td>Fe₃C₄</td>
<td>FeO₄</td>
</tr>
<tr>
<td>T91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Observations</td>
<td>Dense, uneven interface with inner oxide</td>
<td>Slightly porous, small grains with retained metal</td>
<td>Slightly porous, small grains with retained metal</td>
<td>Large pores, equiaxed grains with bright spots</td>
<td>Dense, large columnar grains</td>
</tr>
<tr>
<td>Average Chemical Composition</td>
<td>Fe: 1</td>
<td>Cr: 1</td>
<td>Ni: 1.07</td>
<td>Pb: 1.01</td>
<td>Fe: 0.86</td>
</tr>
<tr>
<td>Diffraeted Phases</td>
<td>FeO₄</td>
<td>bcc Fe</td>
<td>C₃₃₃₄</td>
<td>Fe₃C₄</td>
<td>FeO₄</td>
</tr>
<tr>
<td>Alloy 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Observations</td>
<td>Dense, large grains with no martensite</td>
<td>Open with assorted debris</td>
<td>Small pores, small-medium grains</td>
<td>Dense, large equiaxed, then columnar grains</td>
<td></td>
</tr>
<tr>
<td>Average Chemical Composition</td>
<td>Fe: 1</td>
<td>Cr: 1</td>
<td>Ni: 0.77</td>
<td>Pb: 2.51</td>
<td>Fe: 0.79</td>
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<tr>
<td>Diffraeted Phases</td>
<td>FeO₄</td>
<td>bcc Fe</td>
<td>Cr₂₃₅</td>
<td>Bi</td>
<td>FeO₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.1.1 Metal Region

The metal region for each of the alloys was typically dense with no porosity. All of the metal regions studied exhibited diffraction peaks consistent with the presence of Fe$_3$O$_4$, although oxide grains were not always apparent in SEM images from these regions. The Fe$_3$O$_4$ phase seen in this region exhibited small grain sizes and random orientations, and increased in intensity closer to the inner oxide region.

All alloys showed nickel enrichment at the metal-inner oxide interface, except for Alloy 3 which did not contain nickel as an alloying element. There was evidence of preferential oxidation along grain boundaries ahead of the oxide front into the metal for all of the alloys except Alloy 3 likely because it had large ferrite grains rather martensitic lath along of which much of the preferential oxidation occurred. Alloy 3 was also different from the other alloys in showing peaks from a pure bismuth phase as well as Cr$_2$O$_3$ in the metal region. The presence of the bismuth phase is believed to be caused by spalling of the oxide layers, leaving a space for liquid metal coolant to accumulate. Cr$_2$O$_3$ was observed in this alloy very close to the gap region, and coincided with the location of the emergence of Fe$_3$O$_4$ peaks, likely from oxidation of metal beneath the spalled oxide layers.

HT-9 DELTA Annealed was the only alloy in which the (110) bcc Fe peak was not observed in scans of its metal region, likely because the grains were not properly oriented for this peak to be visible. Diffraction peaks associated with carbides were observed in the metal region only for HT-9 DELTA, but they were also seen in the inner oxides of other alloys.
4.1.2 Inner Oxide Layer

Each of the alloys studied exhibited a duplex oxide which consisted of an inner and an outer layer. The interface between these two layers was, for the most part, straight, and represented the location of the initial metal surface. All of the inner oxide layers studied exhibited small-sized equiaxed grains around 300 nm in diameter, and some porosity, presumably due to egress of iron to form the outer oxide layer. Consistent with iron egress, all of the alloys studied showed an inner oxide depleted in iron and enriched in chromium.

The inner oxide layers exhibited primarily peaks associated with Fe$_3$O$_4$ containing varying amounts of FeCr$_2$O$_4$ and Cr$_2$O$_3$. While the Fe$_3$O$_4$ phase was randomly oriented, phases containing chromium in this region tended to be textured exhibiting diffraction peaks with intensities differing from those that would be expected from a randomly oriented sample.

Four of the five inner oxides also contained carbides: Cr$_{23}$C$_6$ in HT-9 DELTA, HT-9 DELTA Annealed, and T91, and Cr$_7$C$_3$ in HT-9 IPPE. Alloy 3 did not contain any carbon, and therefore did not form carbides. Three of the inner oxides also contained regions with especially high chromium content. These were HT-9 DELTA, HT-9 IPPE, and T91. HT-9 DELTA and T91 showed this chromium concentration peak at the inner oxide-outer oxide boundary, whereas HT-9 IPPE had the chromium concentration peak at the metal-inner oxide boundary. In these regions of especially high chromium content the highest diffracted intensity of Cr$_2$O$_3$ and chromium carbides were observed. In the remainder of the layer, the highest intensity chromium containing phase was typically
FeCr$_2$O$_4$. For alloys without chromium enrichment peaks (HT-9 DELTA Annealed and Alloy 3), diffracted peaks from chromium-containing phases did not exhibit outstanding variation in intensity over the inner oxide layer.

All of the oxides with a lath microstructure in the metal showed retained metal lath grains in the inner oxide. This indicates that the likely oxide front advancement mechanism is for preferential grain boundary oxidation to occur followed by selective oxidation of the laths.

### 4.1.3 Outer Oxide Layer

All of the alloys studied exhibited an outer oxide layer comprised mainly of Fe$_3$O$_4$ magnetite. The outer oxide grains tended to be large and columnar, approximately 400 nm wide and 1000 nm long. The outer oxides were comprised mainly of iron and oxygen, showing no chromium or chromium-containing phases. The outer oxides were enriched in nickel and lead enrichments, including Alloy 3 which did not even have nickel as one of its alloying elements. These nickel and lead enrichments were determined to have been deposited by the coolant into the outer oxide layer, and were visible as bright spots in the SEM images. All of the outer oxides showed wavy interfaces with the coolant, which was taken as evidence of oxide dissolution occurring during the corrosion process.

While most of the alloys showed dense outer oxide layers, the outer oxide formed on T91 showed pores, some of which were large enough to trap diamond particles used in the polishing process. Three of the outer oxides (HT-9 DELTA, HT-9 DELTA Annealed, and T91) also contained sublayers, the inner half of which contained an fcc Pb-Bi phase,
and the outer half was comprised solely of Fe$_3$O$_4$. HT-9 IPPE’s outer oxide layer did not contain sublayers, but since this alloy experienced weight loss over its last 1000 hours of corrosion, it is unclear if this is because the outermost layer was never formed, or because the outermost layer was dissolved by the coolant. Alloy 3 also did not show an outermost sublayer, and due to its extensive spalling it is not possible to say if the outermost layer formed and spalled off, or never formed at all. Alloy 3 was also the only alloy to exhibit a pure bismuth phase in its outer oxide.

### 4.2 Conclusions

A study was performed of oxide layers formed on ferritic-martensitic steels and a model alloy during exposure to flowing lead bismuth eutectic coolant. The oxide layers formed on these alloys were examined using a combination of SEM, EDS, and the unique technique of microbeam synchrotron radiation diffraction and fluorescence. Supporting TEM examinations were also performed in another study.

The corrosion mechanism proposed in this thesis is one similar to (although not identical to) that experienced by ferritic-martensitic steels in other (gaseous and water-based) environments. In general, the oxide layers appear to have been formed by the simultaneous ingress of oxygen ($O^2-$) and egress of iron ($Fe^{2+}$) across the inner oxide - outer oxide interface, which corresponds to the original metal surface. The result of this is an outer oxide layer enriched in iron, and an inner oxide layer with a relative enrichment of chromium, as well as pores left behind were iron has left the inner oxide.
The outer oxide layers are formed entirely of Fe$_3$O$_4$ and contaminates from the coolant, while the inner oxide layers are formed primarily from Fe$_3$O$_4$, but also contain retained ferrite, carbides, and chromium oxides. Chromium oxides, specifically Cr$_2$O$_3$, have extremely low diffusion coefficients and are known barriers against diffusion oxygen and iron in these materials. They are considered protective in that they act to slow runaway oxidation. The largest concentrations of Cr$_2$O$_3$ tended to form a barrier close to the inner oxide-outer oxide interface for samples corroded in the DELTA loop. For the sample corroded in the IPPE loop, on the other hand, this Cr$_2$O$_3$ barrier was at the metal-inner oxide interface. The sample corroded in the IPPE loop was corroded at a temperature 50°C higher and for 2334 hours longer than the samples corroded in the DELTA loop, and it is possible that one or both of these differences could be related to the change in location of the Cr$_2$O$_3$ phase.

The model alloy, Alloy 3, was formed only from iron and chromium, and corroded under the same conditions as the HT-9 DELTA and the T91 samples. While the latter samples formed stable oxide layers, Alloy 3 spalled both its inner and outer oxide layers. The spalling seen on Alloy 3 suggests that the additional alloying elements in T91 and HT-9 are instrumental in the formation of stable oxide layers.

While not all oxide layers showed evidence of spalling, they all did experience at least some liquid metal dissolution, some evidence for which was seen in the form of uneven outer oxide-coolant interfaces. The outer oxide layers studied experienced lead, bismuth and nickel contamination in their outer oxide layers, presumably by trapping or ingress of the coolant. HT-9 IPPE, having been corroded for a longer time at a higher temperature than the other samples studied, actually experienced weight loss between
2000 hours and 3000 house or exposure presumably due to the continuous dissolution rate exceeding the oxide formation rate.

Studies performed in this thesis on oxide layers using microbeam synchrotron radiation granted us a unique and highly detailed view of the oxide characteristics as well as the oxidation mechanism of these ferritic-martensitic steels. The findings above are important in the continued study of materials suitable for use in internal components for the lead cooled fast reactor.

**4.3 Suggestions for Future Work**

In order to continue and expand on this study, not only longer corrosion times, but more samples corroded for those times would be ideal to get a better picture of dissolution behavior as well as long-term oxide behavior. Additional studies on the effects of different dissolved oxygen content in lead-bismuth eutectic would also help in controlling and changing oxidation rates of samples. Finally, given the preferential grain boundary attack seen in the samples examined, a study on grain boundary engineering might also help in slowing or changing oxidation rates.
Bibliography


Appendix

Powder Diffraction Data for All Phases Discussed (2-Theta Range of 25-38°)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Formula</th>
<th>PDF#</th>
<th>Structure</th>
<th>2-Theta angle (E=9.5 kEv)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Iron</strong></td>
<td>Fe</td>
<td>00-006-0696</td>
<td>Im-3m (229)</td>
<td>Ferrite</td>
</tr>
<tr>
<td>Cubic</td>
<td>d(Å)</td>
<td>I(f)</td>
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