Characterization and Drying of Oxyhydroxides on Aluminum Clad Spent Nuclear Fuel

Matthew Shalloo

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CHARACTERIZATION AND DRYING OF OXYHYDROXIDES ON ALUMINUM CLAD SPENT NUCLEAR FUEL

by

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Cheryl L. Addy, Vice Provost and Dean of the Graduate School
DEDICATION

Thank you to my academic advisor, Dr. Knight, for bringing me onto his team and guiding me through my graduate studies and research so far. I appreciate the trust he has had in my abilities and the opportunities he’s afforded me during this time.

To my family and friends who spent time with me and kept me motivated and focused during difficult periods of my work; I could not have completed this without your support.
ACKNOWLEDGEMENTS

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Additional assistance was received from the University of South Carolina Excellence in Nuclear Engineering Fellowship Program supported by a grant from the Nuclear Regulatory Commission (NRC-HQ-84-15-G-0022).
ABSTRACT

Research reactors such as the Advanced Test Reactor (ATR) and the High Flux Isotope Reactor (HFIR) employ aluminum-clad fuel elements made up of many thin plates with uranium dispersed within. In most engineering applications, aluminum is considered to have favorable corrosion characteristics. It forms a thin oxide layer [Al₂O₃] under atmospheric conditions that is impenetrable to oxygen thus stopping any further corrosion. However, both aluminum metal and Al₂O₃ react with water to form hydrous oxides which are less protective against further corrosion and form significantly thicker layers than oxidation in dry air. As a result, aluminum-clad spent nuclear fuel (ASNF) hosts chemisorbed bound water on the fuel surface. In addition, adsorbed or physiosorbed water contributes to the total water within the oxide layer. This is a challenge for sealed dry storage of ASNF because the physiosorbed water and water in the hydroxides could be released as free water at high temperature or decomposed by radiolysis leading to further corrosion and a buildup of pressure within the cannister. The goal of this research is to study the formation of lab-grown oxides on aluminum samples as surrogates for those on ASNF, characterize those oxide layers, and quantify the conditions necessary to remove bulk, physiosorbed, and chemisorbed water. This knowledge will be used to set parameters for full-scale drying studies of ASNF later on. Testing of aluminum oxide powder samples by Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA/DSC) has been performed on commercially available oxyhydroxide powders to determine the dehydroxylation temperatures to be expected in bulk tests. Gibbsite was
found to decompose at about 300°C while dehydroxylation for fine and coarse boehmite averaged around 520°C, and 440°C respectively.

Aluminum coupons of Al-1100, Al-5052, and Al-6061 were immersed in distilled water at 20°C, 50°C, and 100°C to produce a hydrated oxide layer. Bulk drying tests conducted via Thermogravimetric Analysis (TGA) on these aluminum-cladding surrogate samples found dewatering for 20°C, 50°C, and 100°C samples to initiate at modest temperatures below 100°C. The amount of water removed depended on a combination of the heating period and maximum temperature. However, even in low temperature TGA runs, the total amount of water removed matched closely with higher temperature runs as long as the low temperature was maintained for a sufficiently long time. Imaging by Scanning Electron Microscope (SEM) and analysis by X-Ray Diffraction (XRD) took place throughout the research for a detailed understanding of the microstructure and crystal structure at each stage of the process. Based on the findings from this work it is believed that the current drying process of vacuuming the drying canister to 5Torr and heating to 220°C for 35 to 45 minutes in air cyclically is insufficient for removing the maximum chemically bound water. Instead, the drying process should involve heating the spent fuel elements continuously to 220°C or more staying below the suggested maximum of 250°C, for about 5 hours either by forced gas circulation or under vacuum with external heating. Even using these parameters, it is uncertain if not unlikely that the water trapped in crystalline structures on the outermost surface was fully liberated. Rather, the evidence seems to suggest most of the mass loss seen in bulk drying tests is coming from the lower and/or the intermediate layers closer to the substrate’s surface.
PREFACE

This work was carried out in an effort to better understand the effectiveness of the current methods for drying aluminum-clad Spent Nuclear Fuel (ASNF) before placing it into interim dry storage casks. Quantified parameters necessary for maximum removal of bulk and chemisorbed water reported here will be used to justify experimental conditions for large-scale bulk drying tests which are in the planning process at this time.
# TABLE OF CONTENTS

Dedication ................................................................................................................................. iii
Acknowledgements .................................................................................................................... iv
Abstract .................................................................................................................................... v
Preface ......................................................................................................................................... vii
List of Tables .............................................................................................................................. ix
List of Figures ............................................................................................................................ x
List of Symbols .......................................................................................................................... xiii
List of Abbreviations ................................................................................................................ xiv
Chapter 1: Introduction ............................................................................................................. 1
Chapter 2: Literature Review ..................................................................................................... 3
Chapter 3: Methods ..................................................................................................................... 22
Chapter 4: Results & Discussion ............................................................................................... 37
Chapter 5: Conclusion ................................................................................................................. 91
References ................................................................................................................................... 102
LIST OF TABLES

Table 2.1: Corrosion layer thicknesses for untreated RERTR program fuels .................. 13
Table 2.2: Composition of Simulated Corrosion Products ........................................ 13
Table 3.1: Aluminum cladding surrogate treatments .................................................. 33
Table 4.1: TGA Results for 20°C Immersed Surrogates .............................................. 54
Table 4.2: TGA Results for 50°C Immersed Surrogates .............................................. 54
Table 4.3: TGA Results for 100°C Immersed Surrogates ............................................ 54
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Schematic of Aluminum plate fuel “window frame” assembly method</td>
<td>14</td>
</tr>
<tr>
<td>2.2</td>
<td>MTR fuel element design</td>
<td>14</td>
</tr>
<tr>
<td>2.3</td>
<td>HFIR Fuel Element Design</td>
<td>15</td>
</tr>
<tr>
<td>2.4</td>
<td>Crystalline Structure of Al(OH)3</td>
<td>15</td>
</tr>
<tr>
<td>2.5</td>
<td>Layer Stacking of Al(OH)3</td>
<td>16</td>
</tr>
<tr>
<td>2.6</td>
<td>Bayerite Somatoid</td>
<td>17</td>
</tr>
<tr>
<td>2.7</td>
<td>Hexagonal polynuclear chain of gelatinous alumina hydroxide</td>
<td>18</td>
</tr>
<tr>
<td>2.8</td>
<td>TEM of lath-like Boehmite grown at 200°C from Pseudo-Boehmite</td>
<td>19</td>
</tr>
<tr>
<td>2.9</td>
<td>SEM of Rhombic Boehmite grown at 200°C / 100% Humidity</td>
<td>20</td>
</tr>
<tr>
<td>2.10</td>
<td>Al2O3·H2O System</td>
<td>21</td>
</tr>
<tr>
<td>3.1</td>
<td>Al Surrogate sample with copper tape grounding</td>
<td>33</td>
</tr>
<tr>
<td>3.2</td>
<td>Empty SEM holder (left) &amp; SEM sample grounded to holder (right)</td>
<td>34</td>
</tr>
<tr>
<td>3.3</td>
<td>Scanning Electron Microscope Diagram</td>
<td>35</td>
</tr>
<tr>
<td>3.4</td>
<td>DSC Reference and Sample Crucibles</td>
<td>36</td>
</tr>
<tr>
<td>3.5</td>
<td>Oxyhydroxide powders for STA</td>
<td>36</td>
</tr>
<tr>
<td>3.6</td>
<td>Diagram of DSC crucibles and heaters</td>
<td>37</td>
</tr>
<tr>
<td>3.7</td>
<td>Diagram of Bragg’s Law for analyzing crystal structure</td>
<td>37</td>
</tr>
<tr>
<td>3.8</td>
<td>TGA-only crucible loaded with 14x15mm Surrogate</td>
<td>38</td>
</tr>
<tr>
<td>4.1</td>
<td>20°C Water / 36 Days – Cross Section from SRNL</td>
<td>55</td>
</tr>
<tr>
<td>4.2</td>
<td>20°C Water / 61 Days – Cross Section from SRNL</td>
<td>56</td>
</tr>
</tbody>
</table>
Figure 4.3: 20°C Water / 36 Days - Bayerite Somatoids

Figure 4.4: 20°C Water / 36 Days – Layered Structure

Figure 4.5: 20°C Water / 36 Days – Tabular structure (6061-RT-022619-7-I)

Figure 4.6: 50°C Water / 31 Days / Polished (1100-50-71318-2)

Figure 4.7: 50°C Water / 31 days / Polished (1100-50-71318-2)

Figure 4.8: 50°C Water / 29 Days - Bayerite (1100-50-2618)

Figure 4.9: 50°C Water / 112 Days – Bayerite & Boehmite (5052-50-31518)

Figure 4.10: 50°C Water / 31 days / Desiccated – Smooth (6061-50-121717)

Figure 4.11: 100°C Water / 7 Days - Boehmite (1100-100-32718-I)

Figure 4.12: 100°C Water / 7 Days - Needle-like boehmite (1100-100-32718-I)

Figure 4.13: 100°C Water / 7 Days – Hydroxide network (1100-100-32718-HW)

Figure 4.14: 100°C Water / 41 Days - 20°C Water / 2 Days (1100-100-11718)

Figure 4.15: 100°C Water / 49 Days - 20°C Water / 10 Days (6061-100-42318)

Figure 4.16: 100°C Water / 20 Days - 20°C Water / 28 Days (6061-100-111118)

Figure 4.17: Blocky boehmite found ATR simulated specimen

Figure 4.18: Pit in corrosion layer of ATR endbox sample

Figure 4.19: TGA & DSC of Gibbsite Powder to 1000°C

Figure 4.20: DSC curves for three powder samples to 1000°C

Figure 4.21: Powder XRD of Gibbsite heated to 450 and 600°C

Figure 4.22: Powder XRD of Gibbsite heated to 230, 450, and 600°C

Figure 4.23: TGA & DSC of Fine Boehmite Powder to 1000°C

Figure 4.24: Powder XRD of Fine Boehmite heated to 400 and 1000°C

Figure 4.25: TGA & DSC of Coarse Boehmite Powder to 1000°C
Figure 4.26: Powder XRD of Coarse Boehmite heated to 300 and 1000°C .................. 76
Figure 4.27: TGA of 20°C Water Immersion Aluminum Surrogates .................. 77
Figure 4.28: SEM of Al surrogate dried at 500°C in TGA (RT0226a) .................. 78
Figure 4.29: SEM of Al surrogate dried at 500°C in TGA (RT0226j) .................. 79
Figure 4.30: SEM of Al surrogate dried at 500°C in TGA (RT0226a) .................. 80
Figure 4.31: SEM of Al surrogate dried at 260°C in TGA (RT0226b) .................. 81
Figure 4.32: SEM of Al surrogate dried at 260°C in TGA (RT0226b) .................. 82
Figure 4.33: SEM of Al surrogate dried at 200°C in TGA (RT0226e) .................. 83
Figure 4.34: SEM of Al surrogate dried at 200°C in TGA (RT0226e) .................. 84
Figure 4.35: SEM of 50°C Al surrogate dried at 500°C in TGA (MT0315a) ........ 85
Figure 4.36: SEM of 50°C Al surrogate dried at 500°C in TGA (MT0315a) ........ 86
Figure 4.37: SEM of 100°C Al surrogate dried at 500°C in TGA (HT0327a) ..... 87
Figure 4.38: SEM of 100°C Al surrogate dried at 260°C in TGA (HT0327b) .... 88
Figure 4.39: SEM of ATR Boehmited plate dried at 500°C in TGA (HTATRa) ... 89
Figure 4.40: SEM of ATR Boehmited plate dried at 500°C in TGA (HTATRa) ... 90
**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>X-Ray Wavelength</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Incident X-Ray angle</td>
</tr>
<tr>
<td>$d$</td>
<td>Separation distance of crystalline planes</td>
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<tr>
<td>W</td>
<td>Watt</td>
</tr>
<tr>
<td>m</td>
<td>Meter</td>
</tr>
<tr>
<td>$\mu$m</td>
<td>Micrometer</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
<td>--------------------------------------------------</td>
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<tr>
<td>ANL</td>
<td>Argonne National Laboratory</td>
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<tr>
<td>ASNF</td>
<td>Aluminum-Clad Spent Nuclear Fuel</td>
</tr>
<tr>
<td>ATR</td>
<td>Advanced Test Reactor</td>
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<tr>
<td>DOE</td>
<td>Department of Energy</td>
</tr>
<tr>
<td>DOS</td>
<td>Department of State</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>FRR</td>
<td>Foreign Research Reactor</td>
</tr>
<tr>
<td>HEU</td>
<td>High-Enriched Uranium</td>
</tr>
<tr>
<td>HFIR</td>
<td>High Flux Isotope Reactor</td>
</tr>
<tr>
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<td>Idaho National Laboratory</td>
</tr>
<tr>
<td>MTHM</td>
<td>Metric Tons of Heavy Metal</td>
</tr>
<tr>
<td>MTR</td>
<td>Materials Test Reactor</td>
</tr>
<tr>
<td>RERTR</td>
<td>Reduced Enrichment for Research and Test Reactors</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SNF</td>
<td>Spent Nuclear Fuel</td>
</tr>
<tr>
<td>SRNL</td>
<td>Savannah River National Laboratory</td>
</tr>
<tr>
<td>STA</td>
<td>Simultaneous Thermal Analysis</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravitmetric Analysis</td>
</tr>
<tr>
<td>USC</td>
<td>University of South Carolina</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
</tbody>
</table>
Chapter 1

INTRODUCTION

Aluminum is employed as a cladding material by several research reactors such as the Advanced Test Reactor (ATR) and the High Flux Isotope Reactor (HFIR) for its low neutron absorption cross section and high thermal conductivity. The combination of these properties allows for extremely high neutron flux while maintaining modest fuel and coolant temperatures. However, aluminum’s favorable corrosion characteristics in air do not follow into water. The thin layer of aluminum oxide which normally impedes further corrosion reacts with water to form hydrates of alumina. This chemically bound water is less easily removed than the bulk water present upon removal from a spent fuel pool. The hydrates will not only trap water on the fuel surface, but they are capable of developing in much greater quantities than that which forms in air. This buildup can lead to several issues for extended storage; complete dewatering before interim dry storage may not be achievable. For example, radiolysis of the bound water in a dry storage cask can generate hydrogen. The radiolytically produced hydrogen would build up which can make for a flammable environment in the cask and increase pressure toward the cask design limit. Therefore, the motivation to pursue this topic is found in the need to quantify the necessary parameters for removing as much water as possible from the ASNF element surfaces in preparation for interim dry storage. To achieve this goal, aluminum cladding surrogates were treated in water at different temperatures to form lab-grown oxide layers which were studied by Scanning Electron Microscope for microstructure characterization.
and present phases were ascertained by thin-film X-Ray Diffraction (XRD). Powder samples of hydrates alumina underwent Simultaneous Thermal Analysis (STA) to record decomposition temperatures and quantifying water removal. These were also analyzed by XRD at varying points in the heating process to confirm phase transformations found by STA experiments. Finally, bulk drying of the aluminum surrogates was conducted via Thermogravimetric Analysis (TGA) which provided more practical dehydration temperatures as well as precise mass-loss measurements.
Chapter 2

LITERATURE REVIEW

Aluminum and its alloys are widely used as structural materials in many mechanical and chemical systems. Aluminum has very good corrosion resistance in air and water due to the formation of oxides and hydroxides in these environments which form a passivating corrosion layer. The oxides and hydroxides of aluminum, sometimes interchangeably referred to simply as oxides or as oxyhydroxides, have in turn been studied alongside the metal for mining and refining as well as for laboratory purposes.

In research reactors that operate at low temperature and power in contrast to power reactors, aluminum is used for in-core applications. In many of these research reactors worldwide, aluminum is the fuel cladding material. The interest with respect to this work lies in the behavior of aluminum oxides when exposed to a water environment and the removal of that chemically bound water from the metal substrate’s surface. The motivation for removal is driven by the need to limit the impact of chemically bound water on the long-term dry storage of such fuel in sealed cannisters [1]. To build on what is already known of these processes, the current understanding must be established.

Aluminum is useful as a cladding material for dispersion-type nuclear fuels for several reasons. It has a high thermal conductivity of 237 W/m·K [2] and a low neutron absorption cross section of 0.231 barns [3]. These two factors together allow for operation at a reasonable power density and at tolerable temperatures for aluminum.
Dispersing the fuel within thin plates of aluminum ensures maximized heat flow between the fuel-cladding and cladding-coolant interfaces. The ability to operate at high flux lends this type of composite material to employment in research reactors in the U.S. such as the High Flux Isotope Reactor (HFIR), Materials Test Reactor (MTR), and Advanced Test Reactor (ATR) along with numerous others internationally. These designs are useful in a wide array of research applications such as radioisotope production, materials irradiation, and physics model validation studies. In a research reactor, all of these endeavors can be accomplished much more safely, quickly, and economically than in a commercial reactor. Ceramic fuel such as U$_3$O$_8$, UAl$_x$, or U$_3$Si$_2$ are most common and they are mixed with aluminum powder which acts as a mechanical matrix for the fuel meat. This mixture is then pressed into a briquette and sandwiched between solid aluminum plates (window frame method) before being rolled and welded shut. An exploded view of the configuration is shown in Figure 2.1 [5]. The fuel element geometry beyond these basic plates can differ significantly. MTR fuel elements are assembled parallel to each other lengthwise in a stacking formation as seen in Figure 2.2 [5] making it one of the more practical fabrication options. On the other end of the spectrum, HFIR fuel was designed for extremely high neutron flux even in comparison to other research reactors requiring it to have a more complex geometry of curved fuel plates which facilitate such conditions in the center of the cylindrical assembly seen in Figure 2.3 [6].

The downside of using aluminum as a cladding for dispersion fuels is that water can be trapped on its surface as it corrodes in water. The low density and thermal conductivity of these hydrates can lead to reduction of coolant flow in the gaps between plates and in localized temperature spikes on the cladding surface. The presence of
physiosorbed and chemisorbed water can also present concerns for spent nuclear fuel in an interim or long-term sealed storage. One of the primary issues is that this water can undergo radiolysis where ionizing radiation breaks the bonds in H\textsubscript{2}O and setting off a series of chemical reactions involving several ionized species [7]. The release of hydrogen gas is the main concern in this context. Hydrogen may not react quickly but could lead to a buildup of pressure which is flammable in the presence of oxygen and could push the container’s internal pressure toward its design limit. A study on the production of hydrogen due to radiolysis of chemisorbed water in aluminum hydroxides showed radiolytic yield of hydrogen in dry and humid conditions for the hydroxide film. This shows the importance of accounting for residual water and hydroxides in dry fuel storage systems as highlighted in the ASTM standard guide for dry storage [8].

In addition to domestically utilized aluminum-based spent fuel, the U.S. also accepts ASNF from foreign research reactors. While ASNF only makes up a small portion of DOE spent fuel mass measured in metric tons of heavy metal (MTHM), it accounts for roughly 30% of the nearly 3,500 spent fuel cannisters located at several spent fuel management complexes across the country [9]. Most of that ASNF is from foreign research reactors [10]. In 1996, the U.S. Department of Energy (DOE) and Department of State (DOS) started The Foreign Research Reactor Spent Nuclear Fuel (FRR SNF) Acceptance Program in an effort to return U.S. origin high-enriched Uranium (HEU) as part of a non-proliferation policy [11]. This program is projected to accept about 10,060 ASNF assemblies by the end of the agreement in 2029 [11]. The present disposition pathway is to receive and store this fuel in the L Basin (wet storage) at the Savannah River Site (SRS) to await processing in the H-Canyon into a glass waste form.
through a process called vitrification. The vitrified waste is then to be stored on-site pending ultimate disposal in a federal repository. Drying and placement of this fuel into sealed, road-ready cannisters is an alternative disposition pathway for which additional work to address gaps in the technologies and technical bases is needed [1].

While there are many different aluminum hydroxides that can be found in nature or synthesized in a laboratory, the predominant crystalline hydrates known to grow on immersed aluminum are Bayerite/Gibbsite \([\text{Al(OH)}_3]\) and Boehmite \([\text{AlOOH}]\) [12]. This agrees with findings from a recent study on the oxide growth on aluminum fuel plates from the Reduced Enrichment for Research Reactors (RERTR) tests RERTR-6 and 7A which were conducted in the Advanced Test Reactor (ATR) [13]. Recent work in characterization of the materials stored in L Basin at SRS have also shown such hydroxides [14].

Bayerite, also written as \([\text{Al}_2\text{O}_3(\text{H}_2\text{O})_3]\), is an aluminum hydroxide rarely found in nature but is a polymorph of Gibbsite, a common component of bauxite ores. It shares a similar structure, and essentially the same thermophysical properties [15]. Bayerite and gibbsite are 34.64% water by atomic mass and typically form at modest temperatures in a water or saturated water environment [13]. Boehmite, also written as \([\text{Al}_2\text{O}_3(\text{H}_2\text{O})]\), is more commonly found in nature and is only 15.02% water by atomic mass [15]. The development of each phase in water is strongly tied to each phase’s solubility and the ambient water temperature. In neutral pH \((4.5 – 8.5)\) solution which is typical of a research reactor or spent fuel pool, the solubilities are very low [15]. At temperatures below approximately 100°C, Bayerite is the least soluble and thus the predominant phase although boehmite may be found within this domain as well [12]. Moderate temperatures
above 100°C but not exceeding 330°C the system solubility will tend to favor boehmite
growth instead [15].

Understanding the crystal structure of the aluminum hydroxides in question can
be valuable in establishing the processes that occur as they decompose thereby observing
the result of drying aluminum-clad fuel elements at the molecular level. The crystal
structure of Gibbsite and Bayerite is a network of Al-OH octahedra (Figure 2.4) [15]
which are arranged in an AB-BA and AB-AB sequence respectively [15] (Figure 2.5)
[17]. A 2002 study of aluminum hydroxide crystal structures found that the Bayerite base
unit comprised of eight Al-OH octahedra held together by shared hydrogen bonds
contrary to previous claims that it only included four such units [18]. The development
of larger Bayerite crystals tends to favor the formation of somatoids, layered stacks of
Al(OH)$_3$ platelets forming hour-glass, cone, or spindle shapes as shown in Figure 2.6
[15]. Gibbsite crystals tend to develop as alumina gels age into hexagonal rings which
stack onto each other (Figure 2.7) [15]. Boehmite’s crystal structure also begins with
octahedral Al-OH units which form in pairs [18]. Bulk boehmite crystallization can take
on several different shapes dependent on the conditions of formation and the precursor.

Heating gibbsite or pseudo-boehmite in water above 100°C at 1 atm results in
exceedingly narrow lath-like boehmite crystals of varied length and only several units of
boehmite thick [15] which is shown in Figure 2.8 [19]. At higher pressure and
temperature or by using bayerite as the precursor, the crystals will take on a rhombic or
occasionally hexagonal structure as seen in Figure 2.9 [20].

The current knowledge of aluminum corrosion in water starts with the widely
understood development of a disordered aluminum oxide [Al$_2$O$_3$] layer which forms in
air and passivates the metal preventing further corrosion. This occurs because of a Pilling-Bedworth ratio of 1.29 [19] meaning the density of the oxide layer is only slightly less than that of the metal substrate thus preventing incomplete coverage or over-coverage which could result in surface cracking. Exposure to water will quickly lead to dissolution of the passivating layer resulting in the growth of Pseudo-Boehmite [15], [22], a nearly x-ray indifferent, poorly crystalized oxyhydroxide similar to boehmite but with excess water sometimes retaining up to 30% water by atomic mass [15]. Pseudo-boehmite crystals have been reported to be on the order of about 2.5nm long [15] making them difficult to detect through microscopy. It is believed to be a transitional phase before the reprecipitation of the dissolved Al$_2$O$_3$ layer into ordered hydroxides. After the pseudo-boehmite layer has been established, precipitation of well-crystallized Bayerite or Boehmite will commence atop the gelatinous layer depending mainly on temperature, and pH as mentioned above. At modest temperatures (T < 375K) Bayerite is the most stable solid in the Al$_2$O$_3$·H$_2$O system [15]. Somatoids of bayerite will tend to form on the outermost surface of the oxide layer and eventually overtaking the whole exterior but never penetrating or replacing that lower layer perhaps until considerable time passes [23]. These small yet abundant crystals described previously as stacks of Al(OH)$_3$ platelets form the characteristic roughly cylindrical and sometimes hour-glass structures seen in Figure 2.6 [15]. At moderate temperatures (375 < T < 640K), well-crystalized boehmite will form on top of the pseudo-boehmite instead as it becomes the most stable phase [15]. As discussed previously, with pseudo-boehmite as the precursor, needle-shaped boehmite tends to form but higher temperatures and pressures seem to allow for larger, rhombic structures to grow. This proposed hierarchy for hydroxide growth in a
water environment is supported by the phase diagram of the Al₂O₃·H₂O system in Figure 2.10 [15].

The thickness of these corrosion layers varies greatly with each fuel element’s history. A study at Argonne National Lab (ANL) found that fuel plates with about a one-micron pre-film developed at 185°C and 1Mpa that were subsequently irradiated in ATR for 90 or 135 days developed oxyhydroxide layers between 0.4 and 13.4µm thick [13]. Several corrosion layer thicknesses found on various aluminum fuel elements from the RERTR fuel testing program, none of which were pre-filmed, can be found in Table 2.1 ranging from 12 to 45 microns [24]. The thinner corrosion layer on the ATR samples can be attributed to the pretreatment they received which has proven affective for preventing corrosion-related fuel performance issues in high power density research reactors [24].

The temperatures at which the stages of thermal decomposition occur for aluminum’s oxyhydroxides are influenced by several factors, but they are mainly defined by the heating rate used during thermal analysis. Because of this, discussing the dewatering of such materials as an event that occurs within a specific temperature range is most accurate. A group at the University Mohamed Boudiaf of M’sila in Algeria conducted thermal analyses using a heating rate of 20°C/min and concluded that Gibbsite decomposes in three stages; partial endothermic dehydroxylation into boehmite around 246°C, strong endothermic transformation into amorphous χ-Alumina at about 312°C, and some residual endothermic decomposition of Boehmite along-side phase transformation into γ-Alumina at 542°C. Most of the mass loss, roughly 25% of the initial sample mass or 75% of the chemically bound water, was recorded during the second stage [25]. Wefers and Misra reported similar findings and stated that fine-particle
Gibbsite (<1µm) undergoing thermal analysis only showed one endothermic reaction around 200°C but in coarser samples, the newly formed alumina would revert back into boehmite within the larger particles due to water vapor presence from the initial reaction [15]. Bayerite dehydroxylation was found to be nearly identical to Gibbsite with some boehmite formation in larger particles and transformation to highly disordered η-alumina between 227 and 347°C [15]. Lower dehydroxylation at a temperature as low as 100°C has been reported for this trihydrate under vacuum conditions [26]. Lippens reported that pseudo-boehmite and well-crystallized boehmite tend to thermally decompose into γ-alumina somewhere between 270 – 300°C and 350 – 400°C respectively [27]. The crystal structure of aluminum hydroxides during calcination undergoes a pseudomorphic transition i.e., the microstructure does not visibly change and thus is nearly undetectable by SEM even if hydroxyls have been thermally removed [28]. The use of XRD can be useful for identifying the structured α-alumina after thermal decomposition but the transition aluminas tend to be more elusive.

Studies on the bulk drying of ASNF surrogates have been conducted in the past few decades to get an idea of the efficacy of the current drying process options. To this end, an effort at INL in 1996, utilizing a full-size mock-up of the drying and canning station to be used, developed a simulated corrosion product consisting of clays commonly found in the Idaho desert soil mixed with commercially available Pseudo-Boehmite [Al₂O₃·1.3H₂O], the composition of which can be seen in the first column of Table 2.2 [29]. Several sets of drying parameters were tested involving varied periods of vacuuming between 30 minutes and 6 hours sometimes baking at 100°C in 1 atm of air for 2 hours after vacuuming. The conclusion was that unheated vacuuming beyond 4
hours did not yield more than 28% mass loss relative to the original oxide mass while adding the 2-hour bake at 100°C achieved a mass loss of up to 62% [29]. Given that the physically bound water made up about 64% of the simulated corrosion product, this implies incomplete drying of bulk water and almost certainly no dewatering of the chemically bound water in the Pseudo-Boehmite which accounted for an additional ~2% of the corrosion product mass. Therefore, the conclusion was that this process is not effective for removing all of the bulk water let alone the bound water in the corrosion layer. A similar study was conducted again at INL in a half-scale mock-up this time heated by PID controlled band-heaters outside the chamber [30]. This 1998 series of experiments adopted the same type of simulated corrosion product with a slightly different composition which is shown in the second column of Table 2.2 [30]. This work used thermogravimetry to analyze the simulated corrosion product before and after testing for a deeper understanding of the practicality of the drying regimen. Additionally, the drying process was altered to involve four consecutive cycles of vacuuming down to 5 Torr, holding for 35 to 45 minutes depending on the iteration, then backfilling with inert gas and heating to 220°C with the external band heaters [30]. The post-drying TGA results from sections the researchers deemed “dry” still lost more than 14% of their post-test mass, sometimes significantly more, again indicating that very little chemically bound water was liberated from the pseudo-boehmite in this drying process [30]. Attempts to characterize the corrosion products after drying were futile. A different study at Lockheed Idaho Technologies Company in 1995 investigated scrapings from ATR fuel elements in wet storage by running them through a TGA up to 500°C. They found that the microstructure did not seem to have changed relative to pre-drying samples. XRD of
the same specimens yielded results that suggested dehydroxylation led to a transformation into a mostly amorphous transition alumina with some possible indications of Diaspore [AlOOH] and Bayerite [Al(OH)$_3$] but with very little certainty [31]. Both of these outcomes further demonstrate the known pseudomorphic transformation that takes place in the dehydroxylation process of these corrosion products [31].
Table 2.1: Corrosion layer thicknesses for untreated RERTR program fuels

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Alloy</th>
<th>Thickness (µm)</th>
<th>Water pH</th>
<th>Coolant outlet Temp. (°C)</th>
<th>Surface Heat flux (W cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORR</td>
<td>AlMg2</td>
<td>24</td>
<td>5-6.3</td>
<td>53</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>AG3NE</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6061</td>
<td>24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HFR</td>
<td>AG5NE</td>
<td>45</td>
<td>6.70</td>
<td>55</td>
<td>120</td>
</tr>
<tr>
<td>RGAS</td>
<td>AlMg2</td>
<td>40</td>
<td>6.5-7.0</td>
<td>54</td>
<td>60</td>
</tr>
<tr>
<td>NRU</td>
<td>6102</td>
<td>35</td>
<td>5.5-6.5</td>
<td>70</td>
<td>250</td>
</tr>
<tr>
<td>JMTR</td>
<td>AlMg2</td>
<td>20</td>
<td>5.5-6.0</td>
<td>45</td>
<td>100</td>
</tr>
<tr>
<td>IVV-2M</td>
<td>AlMg2</td>
<td>25</td>
<td>6</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>SAV-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RA3</td>
<td>6061</td>
<td>12</td>
<td>5.0-6.2</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>OSIRIS</td>
<td>AG2NE</td>
<td>35</td>
<td>6</td>
<td>47</td>
<td>130</td>
</tr>
</tbody>
</table>

Table 2.2: Composition of Simulated Corrosion Products

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Percent of Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1996</td>
</tr>
<tr>
<td>Bentonite</td>
<td>Dry</td>
</tr>
<tr>
<td></td>
<td>31</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>27</td>
</tr>
<tr>
<td>Pseudo-boehmite</td>
<td>42</td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 2.1: Schematic of Aluminum plate fuel “window frame” assembly method

Figure 2.2: MTR fuel element design
Figure 2.3: HFIR Fuel Element Design

Figure 2.4: Crystalline Structure of Al(OH)3
Figure 2.5: Layer Stacking of Al(OH)3
Figure 2.6: Bayerite Somatoid
Figure 2.7: Hexagonal polynuclear chain of gelatinous alumina hydroxide

\[ 6[\text{Al}(\text{H}_2\text{O})_3^{3+}] \rightarrow 12\text{H}^+ - 12\text{H}_2\text{O} \rightarrow \text{Al}_6(\text{OH})_{12}^{8+} \cdot 12\text{H}_2\text{O} \]

\[ \text{Al}_{10}(\text{OH})_{32}^{3+} \cdot 16\text{H}_2\text{O} \]

\[ \text{Al}_{32}(\text{OH})_{92}^{14+} \cdot 28\text{H}_2\text{O} \]

\[ \text{Al}_{54}(\text{OH})_{150}^{4+} \cdot 36\text{H}_2\text{O} \]

Ref: Hsu and Bates 1964
Hem and Roberson 1967
Nail, White and Hem 1976
Figure 2.8: TEM of lath-like Boehmite grown at 200°C from Pseudo-Boehmite
Figure 2.9: SEM of Rhombic Boehmite grown at 200°C / 100% Humidity
Figure 2.10: Al2O3-H2O System
Chapter 3

METHODS

Aluminum Cladding Surrogates

Coupons of aluminum alloys commonly found in research reactors such as Al-1100, 5052, and 6061 were treated and analyzed by the SRNL team before being delivered to USC. Most were quarter-circle sections with a radius of about 1.5” and a thickness of about 1/8” as seen in (Figure 3.1). The treatment involved immersion in distilled water at 20°C, 50°C, or 100°C for periods between 7 and 112 days. This was performed to grow hydrated oxide layers on the aluminum coupons. These were characterized and used as test specimens in this work. It should be noted that although there was a particular surface of interest for the hydrated oxide layer, there was some exposure to water for the backside of each sample as they were laid on the bottom of the immersion chamber. Among the twelve aluminum cladding surrogates, seven were polished on the main water-exposed face before immersion and the others were left as fabricated. After the immersion, most were taken out, dried by Kim wipe, and briefly air-dried before being placed in a bag for storage. One was removed and left in a container with Drierite chemical desiccant to maintain low relative humidity, and three were left in room temperature water for 2, 10, and 28 days after their heated submersion. Table 2.2 summarizes the different treatments for each of the twelve samples. They are referred to
throughout the paper as bulk samples, surrogate samples, and aluminum surrogates interchangeably.

**Scanning Electron Microscopy**

*Working Principles*

Scanning Electron Microscopy (SEM) was performed for each of the surrogate samples before any other treatment to establish the pre-drying surface condition of each one. The microscopes employed were the Tescan Vega3 SEM, and Zeiss Ultra Plus Field Emission SEM. Both of these instruments work by resistively heating a tungsten filament which consequently ejects electrons producing an electron beam. The expelled electrons are then directed down toward the sample. During the electrons’ descent, they are manipulated in three or more stages. Firstly, a high voltage electric field, typically adjustable between 5-40kV, accelerates them toward the target. After acceleration, the electrons are focused toward a particular area on the sample by a magnetic field in a fashion similar to photons being focused by an optical lens. The third stage of this process is carried out by the scanning coils which use a variable electric field to direct the electron beam in a zig zag known as a raster scanning pattern. The possible extra stages in newer SEMs are extra magnetic lenses for improving the accuracy of the beam. When the electrons finally reach the sample material, they normally backscatter elastically at an angle close to the angle of incidence (assuming a perpendicular angle of incidence relative to the sample surface) or they penetrate the material and produce secondary electrons which are most often detected at small angles relative to the sample surface. A diagram of a generic scanning electron microscope setup can be found in Figure 3.3 [32] where the location of the electron detectors visually demonstrates where each type of
electron is expected. The information collected from the detectors is used to render an image of the sample surface. Higher-end SEMs including those used in this work often use data collected from several detectors for a more accurate rendering and better clarity.

Sample Preparation

The sample preparation protocol for SEM was to apply a carbon-black sticker to a metal sample holder for adhesion and electrical conduction to the base then firmly pressing the sample down from the sides so the surface structures were not affected. Some samples had a piece of copper tape connecting the surface to the base to increase the flow of electrons into the grounded base of the sample carrier as mentioned above. Figure 3.2 shows an unloaded sample holder with carbon black sticker applied and the underside showing how the copper tape grounds the surface to the sample holder. The same preparation procedure was used when examining the samples after they had undergone the heated drying process. Given the observed surface condition however, none of these were grounded with copper tape as it was unnecessary given that they had more metal substrate exposure and it could have altered the loose, post-drying oxide film condition even more-so than in their pre-drying condition.

Operation

Operating an SEM can vary in difficulty depending on the complexity of the instrument. The Tescan Vega3 was the primary SEM used in this research partly because of its user-friendly interface and robust design. The Zeiss FESEM was slightly more sophisticated but operates on the same principles, so the following explanation applies to both. The two SEMs operate under vacuum to reduce electron interactions with the chamber’s atmosphere. After signing into the operating software and loading the sample,
the imaging parameters must be set before the first image can be displayed. The
accelerating voltage is set, the magnification is initially minimized, and the scanning
speed is set to a moderately high rate which reduces the image quality but gives a near
real-time image making it easier to focus. Once the initializing parameters are set, the
instrument can be activated to begin the flow of electrons from the filament. To focus the
image, the working distance parameter, used in calculations performed by the computer
to render the image, and the actual distance from the focal point of the electron beam to
the sample surface must be the same. To do so, the desired working distance parameter is
set to the desired quantity, usually 5-8mm, and the sample stage is slowly raised until the
image is moderately clear. From there, the best practice is to magnify the image greater
than desired and focus as well as possible by adjusting the working distance parameter.
Upon zooming out, the image should be very clear. To capture an image, the scanning
speed is reduced significantly to refine the image.

Sample Surface Charging

When studying the surrogate samples via SEM, it was found that the non-
conductive oxide layer caused significant charging on the sample surface making it
difficult to collect highly focused images in many cases. Charging typically occurs when
examining a non-conductive material because the electrons fired at the specimen get
absorbed by the sample material without producing secondary electrons, backscattering,
or passing through to the sample holder. This buildup of electrons repels the electron
beam resulting in bright spots, streaking, and difficulty focusing. Some solutions
successfully used to combat this problem include the following:
• Grounding the sample surface to the holder with copper tape.
• Using a low acceleration voltage (5-10kV) to decrease penetration.
• Frequently changing the frame of reference to reduce electron buildup.
• Reducing the beam intensity to spread the electrons across a broader area.
• Sputter coating with gold to make the surface conductive.

Among these options for reducing charging effects, sputter coating was most effective although it could only be employed on samples which were not destined for further analysis to avoid skewing the data by introducing a foreign material. The main reason why it was so helpful was because the other solutions typically resulted in lower image quality. The accelerating voltage in particular had a strong effect on image quality because a lower voltage results in lower electron penetration and thus fewer secondary electrons being generated for an image.

Simultaneous Thermal Analysis of Powders

*Working Principles*

Simultaneous thermal analyses (STA) were performed on commercially produced gibbsite \([\text{Al(OH)}_3]\) (15µm), coarse boehmite \([\text{AlOOH}]\) (77µm), and fine boehmite (7µm) using a Netzsch STA 409 CD. One part of STA is Thermogravimetric Analysis (TGA) where a sample is weighed during a heating or cooling cycle to detect mass change due to decomposition, evaporation, oxidation, and so on. In this context, mass loss due to dehydroxylation is the concern. The second is Differential Scanning Calorimetry (DSC) where two crucibles, one loaded and one empty (Figure 3.4), are heated in a furnace and their temperatures are carefully controlled to ensure they are the same throughout the heating program. A diagram of such a setup is shown in (Figure 3.6) [33]. The difference
in heat required to maintain the sample crucible at a given temperature relative to the empty reference is calculated which reveals the heat flow in or out of the sample due to a chemical reaction or phase change. When working with such small masses in a closed system, the buoyant force of the internal atmosphere comes into play. As the furnace temperature increases, the density of the heated, flowing gas decreases reducing the buoyant force. This is illustrated in the TGA curve as an increase in mass which is not actually a chemical effect. There are measures to mitigate this effect discussed in the operations section.

**Sample Preparation**

The commercially produced oxyhydroxide powders were kept in vials to prevent moisture from reaching them as seen in (Figure 3.5). Most powdered samples were between 20-60mg, greater mass being optimal for ensuring the sample mass overshadowed the buoyancy effect. Several powder samples were left in a vacuum desiccator overnight but no change in their behavior was recorded so that was not practiced in subsequent experiments.

**Operation**

Powdered samples were loaded into the sample crucible and placed atop the sample carrier visible in Figure 3.4. A vented lid was used in some tests, but most were conducted without one and no significant difference was detected. Upon loading a sample, the chamber pressure was reduced by a two-stage vacuum system down to about $6.4 \times 10^{-4}$ mbar then refilled to ambient pressure with dry, high-purity Argon. Upon reaching ambient pressure, the chamber was continuously purged with 100mL/min of Argon throughout the test as per the manufacturer’s suggestion to prevent oxygen
presence from affecting results. To combat the buoyancy effect referred to earlier, a baseline run can be performed simply by running the instrument with identical heating parameters to the test of interest but with no sample loaded. The resultant TGA curve is then subtracted from the sample’s curve to remove the buoyant effect acting on the crucible. However, the sample itself has its own effect on the TGA reading which cannot be corrected easily. Since the DSC crucibles were so small, the buoyant effect was negligible for powder samples of sufficient mass. The data from each test was post-processed in Netzsch’s proprietary Proteus Analysis software to calculate reaction onset temperatures, peak temperatures, and periodic TG readings. After each analysis, the powdered samples were preserved in glass scintillation vials for further investigation as needed.

Data Interpretation: DSC

Understanding DSC results requires knowledge of the material being studied so the user can anticipate what type of reactions to expect and familiarity with what the raw data that it generates. As mentioned previously, the DSC sample carrier maintains each of the crucibles at a constant temperature throughout the heating cycle. Therefore, if the sample undergoes an exothermic reaction, for example, the reaction is generating heat and increasing the temperature of the sample so it will require less heat than the empty reference will to maintain the same temperature. This difference in heat flow is recorded by the instrument and can be displayed graphically. Pertinent DSC information that can be calculated using Netzsch’s Proteus Analysis software includes the onset of the reaction where the spike begins, the average reaction temperature which can be estimated as the peak of the spike, and the reaction enthalpy which is calculated by integrating the spike.
In this work, the main focus was on the two reaction temperatures since the end goal involves suggesting a proper temperature to heat the used fuel.

**Data Interpretation: TGA**

Interpreting TGA data for homogeneous powder samples is straightforward as it simply displays the mass loss or gain in mg or percent of the initial mass, but it proved useful in several aspects with respect to this work. Firstly, if there was more than one reaction in close succession, the TGA curve was helpful for determining which one was driving mass change. Additionally, the TGA data can be used to verify expected water content of certain samples such as the oxyhydroxide powders with known theoretical mass percent of water. Finally, this data set can be used to determine the sample mass at key points of a heating cycle so the user can make judgements about the expected quality and condition of the material being analyzed.

**X-Ray Diffraction**

**Working Principles**

X-Ray Diffraction (XRD) is a semi-qualitative analysis of crystalline phases in a sample performed by bombarding it with x-rays of known wavelength and angle. The x-rays are deflected by atoms in a lattice at an angle equal to the angle of the incident rays. As the angle of incidence is adjusted, a moving x-ray detector will identify constructive interference at angles for which the extra distance traveled by a ray deflected by a deeper crystal plane \([2dsin(\theta)]\) is a multiple of the x-ray’s own wavelength (see Figure 3.7 [32]). This phenomenon is named Bragg’s Law (Eq. 1) after its founder, Nobel Prize winner Lawrence Bragg. Knowing the wavelength, “\(\lambda\)”, and angle of detected
constructive interference, “θ”, one can use Bragg’s Law to calculate the interplanar spacing in the crystal formation, “d” for a particular crystal plane.

\[2d \sin 2\theta = n\lambda\] (Eq. 1)

Moreover, the intensity of the constructive interference will vary based on atomic positions in the crystal lattice and on the degree of crystallinity. A set of constructive interference angles along with the intensity of that interference, can thereby be interpreted as a sort of “finger-print” of a known crystal structure with that particular set of planar spacings and atomic positions. XRD was conducted throughout the experimental phase of this work on powders and bulk samples to deduce the phases present at different stages of thermal analysis. These were performed by a separate research group at the University of South Carolina in the Chemistry and Biochemistry Department. The analyses and peak matching were performed there then the diffraction patterns and XY data were delivered.

**Bulk Drying of Al Surrogates by TGA**

*Sample Preparation*

The same instrument used for STA of powders was employed for TGA of the aluminum surrogates. These experiments only yielded TGA data because the DSC-capable crucibles were too small to analyze a bulk sample large enough to be representative of the full surrogate surfaces. Sample preparation began with the cutting of the immersion surrogates to a size that would fit inside the largest available TGA crucible seen in Figure 3.8. The early samples were cut to about 14mm in width and 15mm in length. Given the conical bottom of the TGA crucible, 14mm was the maximum width for the upper, cylindrical section but narrower samples were able to reach lengths of up to
24mm without protruding from the top. The cutting was performed using a Leco VC-50 Diamond Wafering Saw because of its dry-cutting capability. This way, no water or oil coolant was necessary which may have altered the sample’s corrosion layer. A slow cutting speed was typical to avoid heating the samples and to prevent the edges from developing large burrs. Once cut, samples were placed back into the bags in which their mother pieces were kept. One of the cut samples was left in tap water for 12 hours before analyzing and several others were left in a vacuum desiccator for 24 hours. The desiccated samples did not indicate any change relative to those analyzed in their as-cut condition, so the practice was not continued. The wet sample analysis was not included in this work as it diverges from the scope, but such tests will be conducted in future related work.

**Operation**

TGA-only experiments are run nearly identically to STA runs. The sample is first weighed, and its water-corroded surface area is measured. Then it’s loaded into the crucible and placed atop the sample carrier (Figure 3.8). Once the furnace is sealed, vacuum is achieved before backfilling and eventually purging continuously with Argon. The main distinction is that the larger crucible causes a more prominent buoyancy effect. Therefore, for each different temperature program, a correction run had to be conducted with an empty crucible which was then subtracted from the sample results. Thus, the resultant graphs presented for thermal analyses of aluminum surrogate samples are corrected versions rather than originals. It was noted above that the buoyant effect is not completely removed from the final outcome because the sample itself contributes to the phenomenon to some degree and this is especially true for the larger solid samples. At the
end of each experiment, the sample was unloaded and placed in a fresh bag. This practice was substituted for storage in clean glass scintillation vial instead to further protect the corrosion layers.

Data Interpretation

Rationalizing the data generated by TGA of bulk samples with lab-grown oxide layers is more complicated than it is for powders. In this case, the samples are not homogeneous. There is a metal substrate, the treated surface with hydrates oxides and physiosorbed water, and the rest of the phases could have small amount of bound water that will contribute to the overall mass loss. The mass of the corrosion layer where most of the water is likely to be found is very small in comparison to the total sample mass. Another difficulty is that the corrosion products were not perfectly distributed so it is difficult to confidently report an areal density of water across the corrosion surface. That said the Netzsch Proteus Analysis software was once again used to determine the onset of mass loss, changes in the mass loss rate throughout the temperature program, and the final mass loss reading. When reading through the data, it was observed that the cooling section of each heating cycle was determined by a time period rather than a final temperature. This affected the final TGA reading because the buoyant effect lets off during the cooling period and if the final reading for each test is not at the same temperature then there will be some discrepancy. Thankfully, the decrease in mass loss reading toward the end of each test as a consequence of increased buoyancy was nearly linear with the decreasing temperature. This allowed for a simple linear extrapolation of the final mass reading at 20°C for all bulk TGA runs to avoid comparing readings with varied buoyancy forces on them.
Table 3.1: Aluminum cladding surrogate treatments

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Alloy</th>
<th>Temperature [°C]</th>
<th>Period [Days]</th>
<th>Grind/Polish</th>
<th>Post-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>6061-RT-022619-7-I</td>
<td>6061</td>
<td>20</td>
<td>36</td>
<td>600 Grit</td>
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<td>100</td>
<td>7</td>
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<td>100</td>
<td>49</td>
<td>Mirror</td>
<td>10 days at RT</td>
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</table>

Figure 3.1: Al Surrogate sample with copper tape grounding
Figure 3.2: Empty SEM holder (left) & SEM sample grounded to holder (right)
Figure 3.3: Scanning Electron Microscope Diagram
Figure 3.4: DSC Reference and Sample Crucibles

Figure 3.5: Oxyhydroxide powders for STA
Figure 3.6: Diagram of DSC crucibles and heaters

Figure 3.7: Diagram of Bragg’s Law for analyzing crystal structure
Figure 3.8: TGA-only crucible loaded with 14x15mm Surrogate
Chapter 4

RESULTS & DISCUSSION

Pre-TGA SEM

Recording the surface structure of samples with water immersion hydroxide layers is a key part of understanding the drying process as it allows a comparison of the microstructure before and after drying. The varied treatment of surrogates immersed in water led to a fairly broad array of resultant surface conditions. Based on literature, bayerite and gibbsite were expected on the lower temperature samples while boehmite was expected to dominate on surrogates immersed at 100°C. Some specimens were relatively easy to view in the SEM while others had such significant charging that only a handful of useful images were acquired unless they were sputter coated with gold. The degree of crystallinity was different among the sample population even within the same temperature group requiring the team to investigate treatment divergences.

Room Temperature Immersed Samples

The samples immersed in room temperature (20°C) water for 36 and 61 days developed the thickest corrosion layers of the whole lot at about 8 and 20µm respectively (Figure 4.1 & Figure 4.2). Two crystal structures were discovered thoroughly covering the sample surfaces. The first formations found were identified as bayerite somatoids by their characteristic smooth, narrow cylindrical shape (Figure 4.3). The larger of the two being nearly cylindrical but with a clearly noticeable layered arrangement (Figure 4.4).
Further inspection showed that these were made of extremely thin pseudo-hexagonal platelets (Figure 4.5) which are reminiscent of a description of maturing alumina gels that can develop into bayerite somatoids or gibbsite. This led to an observation that the layered structures sometimes resemble bunches of bayerite somatoids bound together like a bundle of sticks. Surface XRD only indicated bayerite presence which supports the notion that the two formations have the same crystal structure despite their differing microstructure. The smaller bayerite somatoids were measured to be about 1.5 to 3μm in length and 0.9 to 1.9μm in diameter. Length measurements of the layered structures were difficult to collect with any certainty because of their bases being implanted within the lower layer but it was estimated that they were between 6 and 8μm long and the typical diameter was between 3 and 4μm. The platelets they were comprised of tended to be around 0.7μm in diameter. The thicker oxide layers on these room temperature samples indicates the corrosion layer is not passivating as it is for those formed at higher water temperatures.

50°C Immersed Samples

The aluminum surrogates immersed in water at 50°C shared a similar structure to both of the other sets of surrogates but they more closely resembled the room temperature samples. Within this moderate temperature regime, both bayerite and boehmite were able to grow. The sample that was polished to 600 grit directly before its 31-day immersion was found to host scattered bayerite somatoids atop a significant amount of small, needle-like boehmite (Figure 4.6). On this sample, bayerite was sometimes seen sprawled in a circle around a pit while it was found closely packed together in other areas of the same sample (Figure 4.7). Analysis of another surrogate that was not polished before being
immersed for 29 days revealed a corrosion layer composition of mostly bayerite crystals (Figure 4.8). Even after long immersion, needle-like boehmite was found within the gaps between bayerite structures (Figure 4.9). The bayerite crystal sizes somewhat resembled measurements of the larger, layered structures found on room temperature samples although they tended to be smoother suggesting they are the same phase but perhaps the platelet stacking occurs more regularly at elevated temperature. The outlier within this group was 6061-50-121717 which was removed from the water after heating and placed in a sealed container with chemical desiccant for storage. This specimen did not have any of the bayerite structures seen among the others. Instead the surface was mostly covered in a smooth, mostly formless corrosion product (Figure 4.10) with a very small amount of needle-like boehmite inside hydroxide layer cracks. The phenomenon responsible for this is not certain but it likely occurred after desiccation as the hydroxide layer, which can act as a desiccant, absorbed water vapor from within its container as it was the only one out of the group to be absent of blocky bayerite formations.

100°C Immersed Samples

The crystalline structures found on aluminum surrogates immersed in water at 100°C had good agreement amongst the set although the differences in treatment led to some variation in overall surface condition. The surfaces were covered in ridges and valleys of minute crystalline structures in vast quantities which XRD analysis determined to be boehmite (Figure 4.11). Closer inspection revealed the needle-like structures described in literature (Figure 4.12). These formations, sometimes referred to as lath-like boehmite [19], are exceedingly thin and typically around 0.25µm long with diameters less than 0.05µm. While there was significant coverage by these thin formations, there
was also a sizable portion covered in amorphous globs of material which has not yet been identified as it is likely x-ray indifferent based on XRD results (Figure 4.13). As is indicated in Chapter 2, the lath-like crystals are known to develop under hydrothermal conditions with pseudo-boehmite as the precursor, so these results agree with findings from previous research efforts. The presence of amorphous formations on samples immersed for short periods further supports the idea that pseudo-boehmite is an intermediate phase that develops prior to crystalline bayerite and boehmite growth. The thickness of the corrosion layers on samples immersed at 100°C was around 1µm regardless of the immersion period which suggests the hydrous oxide film passivates the aluminum substrate at least somewhat effectively. With regard to the three that were left in water at room temperature after their heated immersions had completed, SEM studies showed progressive decomposition of the crystalline boehmite into a gel-like material. A comparison of the three samples left in water for 2, 10, and 28 days respectively after heating can be seen in Figure 4.14, Figure 4.15, and Figure 4.16. At 28 days in room temperature, it would seem that blockier structures begin to form somewhat resembling bayerite crystals. This change in morphology shows that the needle-like boehmite is not particularly stable in low temperature water.

**ATR Boehmited Plate**

As discussed in the literature review, ATR fuel elements are pre-treated with a thin film of about 1µm made up of boehmite by subjection to an autoclave at 185°C and 1MPa. Naturally, XRD on the ATR endbox sample confirmed that its surface layer was indeed boehmite, but the microstructure differed from the crystals seen on 100°C samples. In this case, the boehmite formations were blockier, perhaps rhombic in shape
and covered the surface very thoroughly held together by a continuous matrix similar to aggregate within concrete (Figure 4.17). Thorough corrosion layer coverage was to be expected considering the success operators of ATR and research reactors with similar power densities have had in using this pre-treatment to prevent runaway corrosion in the core. This corrosion layer hosted a number of pits which allowed for examining the inner structures. As seen in Figure 4.18, the microstructure did not seem to change with depth and none of the pits that were inspected reached down to the aluminum substrate demonstrating that these pits do not negatively affect the passivation of the metal.

**Simultaneous Thermal Analysis of Powders**

Simultaneous Thermal Analyses (STA) of powder samples were performed on commercially available aluminum oxyhydroxides to develop an understanding of the events which occur within the dehydroxylation processes for gibbsite and boehmite. A temperature range of 20-1000°C was employed with holds at different temperatures within the process for varying periods. The literature review revealed that the highest dehydroxylation for these powders would be slightly above 500°C for boehmite so exceeding that considerably was deemed appropriate for ensuring each expected reaction was detected. The gibbsite powder had a particle size of 15µm while the fine and coarse boehmite powders had particle sizes of 0.7µm and 77µm respectively.

**Gibbsite**

As discussed in the literature review, the thermal decomposition process of gibbsite and bayerite are nearly identical so the gibbsite powder provides an acceptable estimation of what will happen to bayerite during the drying process. While the exact dehydroxylation temperatures are dependent on several factors, the decomposition of
gibbsite powder typically began with an endothermic transformation from gibbsite to boehmite between 220 and 270°C which was quickly followed by a highly endothermic transformation to alumina between 280 and 365°C. These two reactions occurring in quick succession are evident in the DSC curve and a concurrent mass reduction in the TG curve (Figure 4.19). Such boehmite formation has been reported in literature when thermally analyzing large-particle gibbsite powder but not in finer samples [25]. The amount of boehmite which remained from this reaction tended to be considerable in experiments conducted at lower temperatures between 220 and 240°C with temperature hold times up to 8 hours to allow the mass loss to reach its maximum. The percentage of total mass lost was about 28.6% out of a possible 34.64% for these low temperature experiments. This indicates that over 17% of the sample’s initial water content remained. More significant mass loss was observed at higher temperatures such as 450°C, but complete dewatering was only seen in experiments where the final temperature achieved 600°C or more. When such temperatures were reached, a third reaction occurred between 500 and 535°C which is understood to be the dehydroxylation of the newly formed boehmite. Note in Figure 4.20 that the second reaction in the gibbsite curve coincides with the dehydroxylation of fine boehmite. Given the small crystal sizes found on the aluminum surrogates, this boehmite formation likely will not be a problem for drying.

Powder x-ray diffraction conducted on gibbsite powders heated to varying temperatures in the STA revealed that the degree of crystallinity diminished considerably with increasing temperature at least up to 600°C. Figure 4.21 shows the diffraction patterns of two such samples, one which was heated to 450°C and produced peaks characteristic of crystalline boehmite. The sample heated to 600°C had significantly
weaker peaks which matched up to crystalline alumina. Although the material was identifiable, the weak peaks are indicative of poor crystallinity and small particle size. Figure 4.22 further exemplifies this by comparing the previous two to a gibbsite sample heated only to 230°C which was not high enough to achieve dehydroxylation. This low temperature run left a large portion of well-formed gibbsite remaining which resulted in strong XRD peaks that dwarf those produced by the dehydroxylated samples. Further, this shows that alumina is likely still present in a transitional, x-ray indifferent phase in the 450°C sample despite boehmite being the only defined crystal structure.

*Fine Boehmite*

The fine and coarse boehmite powders acted quite differently from each other. The fine boehmite displayed two thermodynamic events within this temperature range. The first was a weak endotherm occurring between 355 and 400°C, averaging at about 390°C, and the second was the strongly endothermic dehydroxylation between 485 and 550°C with a typical average reaction temperature of about 520°C. Figure 4.23 displays the DSC and TG curves with respect to temperature. In this case, the decomposition reaction was less energetic than the gibbsite dehydration (Figure 4.20) because fewer bonds are broken in the process. This high decomposition temperature will surely make it difficult if not impossible to ever achieve full drying of the adherent oxyhydroxides.

Several of these fine boehmite samples were analyzed using XRD after heating to confirm the dehydroxylation temperature. It was confirmed that the first endotherm was not a decomposition reaction but some sort of reordering perhaps to either a different boehmite structure or an amorphous one. Therefore, the more energetic occurrence was verified as the transformation from boehmite to alumina. Figure 4.24 compares the XRD
spectra for two such samples heated to 400 and 1000°C. Note once more that the degree of crystallinity diminishes with increased temperature yet again. Comparing the scale with that of the gibbsite powder heated to 600°C however, the alumina signal is stronger for the fine boehmite which is a result of the higher final temperature leading to more organization of the newly formed alumina which is a phenomenon that has been observed in literature.

Coarse Boehmite

In experiments on coarse boehmite powders, one very noticeable difference from the others was that some of it would explode out of the crucible during the test. Thankfully this did not seem to significantly affect the TGA results as all of the powder landed on the sample carrier, so it was still being weighed. This is believed to have occurred because of localized pressure buildup within the larger particles while the boehmite energetically decomposes. The coarse boehmite experiments resulted in a three-stage dehydroxylation process. The first was believed to be bulk water removal with an average temperature of about 130°C that aligned with the initiation of slow mass loss. The second stage was a weak endotherm which occurred between 250 and 280°C. This early reaction was some sort of crystal reorganization similar to what was seen in the fine boehmite. Finally, the dehydroxylation occurred consistently around 440°C with relatively little variation in average reaction temperature (Figure 4.25). The decomposition for coarse boehmite was even less energetic than in its fine counterpart which is evident in Figure 4.20. It seems counterintuitive that the coarse boehmite decomposed at a lower average temperature but XRD data may be helpful in understanding why that is the case.
Powder XRD results for coarse boehmite heated to 300 and 1000°C is displayed in Figure 4.26. The most notable factor here is the very low intensity of the peaks in comparison with the two sets previously displayed for gibbsite and fine boehmite even for the sample only heated to 300°C. These intensities are a degree of magnitude lower. It’s uncertain why the crystallinity of these samples started off and remained so much poorer, but it may be one of the factors that caused the coarse boehmite to dehydrate at a lower temperature and less energetically than the fine boehmite.

**TGA of Aluminum Surrogates**

Bulk drying experiments took place in the same STA used in powder analyses using a TGA-only sample carrier so that mass loss could be recorded in real time while allowing for a reasonably sized bulk sample that would provide results characteristic of the overall surrogate sample surface. Still, the crucible was small compared to the surrogates, so they were cut into multiple pieces to fit and to accommodate several experiments for each surrogate chosen for analysis. Due to the high variability of treatment among the bulk samples and certain time constraints, not all of them have undergone TGA analysis in this stage of the research. Instead, several samples believed to be characteristic of their temperature groups were chosen for TGA and subsequently surface XRD. A heating rate of 5°C/min was kept constant for all of the tests to eliminate some uncertainty from the results. As mentioned in Chapter 3, baseline runs were used to correct sample data for the buoyancy effect within the furnace. Thus, data presented herein has been corrected as such. The graphical representations were also altered with a smoothing tool in the Proteus Analysis software to remove point discontinuities which occurred due to errant signals. This did not change the general shape or reading of the
curve. The final change in mass tabulated in this chapter was determined by assuming the reduction of the buoyant effect during the cooldown of each test was linear and solving for the mass loss at 20°C. This was necessary because the temperature of the final data point collected in each experiment varied slightly from test to test (e.g. final reading at 150°C vs 115°C). Using this method, the final mass losses are more comparable and not as skewed due to the furnace’s buoyancy effect.

**Room Temperature Samples**

The first set of surrogates studied in this stage of the project were those immersed in room temperature water for 36 days because they were most abundant and had thick corrosion layers at about 8µm. In each test, some mass loss was detected as low as 20°C. This low mass loss threshold is partially an artifact of the type of thermocouple affixed on the TGA sample carrier. Type-B thermocouples are best suited for high temperatures and although they are capable of providing measurements in lower ranges, they are particularly poor within the 0-50°C range. Additionally, the dry flowing argon atmosphere maintains a near-zero partial pressure of water within the furnace driving any loosely bound water to evaporate even before the boiling point. When samples were subjected to a heating cycle with a maximum temperature of 260°C or above, there was an increase in the rate of mass loss consistently between 220 and 224°C as seen in Figure 4.27. Some inconsistency in the water content from sample to sample was expected since the samples were different sizes and the corrosion layers were not completely uniform. Therefore, the water content was measured in mass per unit area [mg/cm²]. Even quantifying mass loss this way, however, was not perfect as it was observed that the areal water content was inversely proportional to the sample’s treated surface area among
samples heated to the same maximum temperature. This encouraged the use of larger samples for more generally representative results. The results from TGA runs on 20°C immersed surrogates are tabulated in Table 4.1.

When samples were heated to 500°C and held for 4 to 12 hours, the mass of water liberated normalized to the sample’s surface area was found to be between 0.92 and 0.98mg/cm². The slight variability is considered to be a result of non-uniform coverage of the hydroxide layer across each sample’s surface because there did not seem to be a discernable difference based on the temperature hold interval. In fact, mass loss was nearly complete before the hold temperature was reached in all 500°C experiments (Figure 4.27). Despite clearly defined mass loss, XRD on dried samples has been disappointing and thus it cannot be said with certainty that the specimens are entirely dry. Based on the lowering crystallinity of powdered samples with increased temperature, this is not particularly surprising as the aluminum metal signal certainly overshadows any peaks that the poorly developed surface structures may be contributing. SEM of 500°C samples revealed extensive surface cracking and spalling of the bayerite corrosion layer (Figure 4.28). The removal of the upper layer revealed a smooth underside (Figure 4.29) that matched the cracking pattern above. Exceptionally small particulates were discovered in between the cracks of the smooth intermediate layer (Figure 4.30). This widespread, seemingly random cracking that extends through two of the corrosion layers may be indicative of substantial water content in the lower layers which breaks free during the drying process. In TGA runs at 500°C some samples had material flaking off of them that was visible to the naked eye. This will need to be considered when drying
large quantities of ASNF are dried as a buildup may be an issue for worker safety if it is not properly addressed.

After collecting data on high temperature drying to get an idea for how much water could be removed while approaching aluminum’s melting point, lower temperatures needed to be investigated because the maximum suggested temperature for aluminum dispersion fuels during drying is 250°C which is a phase transition temperature for the metal substrate that could affect its structural integrity [35]. When the room temperature immersed specimens were heated to 260°C, the mass loss was similarly paced relative to the 500°C runs. Mass loss slowed down considerably before the hold started but carried on gradually during the hold as well. The calculated areal density of water was found to actually exceed results from higher temperature runs sometimes reaching nearly 1.2mg/cm² but again, this may simply be because of the small sample surface area. SEM images of samples dried at 260°C were very similar to the higher temperature drying experiments (Figure 4.31) but with more ragged cracks in the smooth, intermediate layer yet still showing the crystallites below it (Figure 4.32).

TGA runs performed at 220 and 200°C were expected to display progressively lower calculated surface water content but the main observed difference was that they lost mass more slowly over a period of about 6-8 hours. The calculated surface water content was comparable and even exceeded the 500°C runs on samples with low surface area. The one exception to this was the sample heated only to 200°C which released approximately 0.9mg/cm² despite sharing a similar treated surface area with the samples dried at higher temperature (Figure 4.27). That said, this is still not significantly lower than the others. The lower temperature heating programs still displayed a change in mass
loss rate below 220°C, as seen in Figure 4.27, which implies that the threshold
temperature for this reaction is not so concrete and that it can initiate at more modest
temperatures with time. XRD on these samples also came back inconclusive of any
crystalline structure presence just as with those heated to 500°C. SEM images of samples
heated to less than 260°C looked similar to those heated at higher temperatures but with
thinner crevices and less upper layer spalling (Figure 4.33). Also, the tiny crystallites
within the cracks were not revealed as clearly in some cases (Figure 4.34).

50°C Samples

Given that the crystalline structures populating the surface of the samples
immersed at 50°C were similar, yet perhaps better-formed, compared to those found on
room temperature samples, one could infer that the drying process might be similar. The
limited results so far indicate a surface water content between 0.22 and 0.65mg/cm²
(Table 4.2). The high variability is intuitively consistent with the treatment of the samples
as the lowest amount of water removed was from a sample that was desiccated while the
highest amount was from a sample that had an immersion period nearly 4 times longer
than the others (Table 3.1). A notable difference between these and the room temperature
samples is the thickness of the corrosion layer, so the slightly lower surface water content
makes sense given the thinner layer on these in comparison. Shown in the previous
section, SEM of room temperature samples dried in the TGA showed considerable
surface fissures and delamination revealing a smooth underlayer with exceedingly small
crystallites in between the cracks perhaps the crystals found in pseudo-boehmite now
visible after the excess water was driven off or a different crystal unidentified by XRD
thus far. SEM of the 50°C samples also showed such cracking (Figure 4.35), but no
delamination and the extremely small crystallites were seen directly below the bayerite layer (Figure 4.36). Based on these observations, it’s difficult to rationalize where the water is being liberated from and the contribution of each source. This is mainly due to the lack of microstructural change in the surface-layer crystal structures which could have undergone a pseudo-morphic transformation where they were indeed dehydroxylated, but the microstructure remained. This phenomenon is known to occur in aluminum hydroxides.

100°C Samples

Due to difficulties with the TGA during several of the experiments on 100°C immersed samples, the number of runs performed thus far is low. However, some valuable information can be gathered from the results, nonetheless. Once again, mass loss was detected at temperatures as low as 20°C due to both the Type-B thermocouple and the low vapor pressure within the furnace. In the 500°C TGA runs, mass loss was completed before the hold started just as in previous experiments. The final water liberated over the surface area was calculated to be 0.3 to 0.35mg/cm² with one outlier having lost 0.76mg/cm² during its TGA run (Table 4.3). This particular sample was left in room temperature water for nearly a month after its heated immersion period and it developed a formless corrosion layer free of well-defined crystals. During its heating program, it displayed an increase in mass loss rate at 220°C, exactly like the room temperature surrogates did. This strongly implies that the reaction detected at this temperature for the 20°C surrogates was actually the gelatinous lower layer rather than the crystalline bayerite. The disagreement with low-temperature immersion samples with respect to total surface water content is not remarkable since the surface structures were
only boehmite rather than bayerite and so the water removal may mostly be attributed to physiosorbed water. SEM revealed surface layer cracking similar to what was seen in the 50°C samples (Figure 4.37) where the crystalline structures did not seem to change at all (Figure 4.38). Given the high temperature required for decomposition of boehmite powders, this result makes sense. A common trait the 50 and 100°C surrogates share is a corrosion layer thickness of about 1µm. Even more compelling than the lack of crystalline transformation on the room temperature surrogates, it’s all but certain that the boehmite did not dehydroxylate even at 500°C since the amount of water removed was similar for both high and low temperature TGA runs. Thus, the mass loss must be attributed to intermediate and/or lower layer water content.

**ATR Boehmited Plate**

Knowing that ATR operators have had success in mitigating corrosion issues on fuel elements and core components by pre-filming the aluminum with a high temperature and pressure treatment, it could be deduced that very little free water or gelatinous hydroxide is present on its surface and that any chemically bound water is held strongly by the corrosion layer. When heating an ATR sample in the TGA to 500°C, mass loss began to overtake the buoyant effect at about 200°C but finished quickly. The calculated areal density of water was found to be about 0.2mg/cm², the lowest amount of all samples run thus far. SEM of the post-TGA sample showed very narrow cracks breaking apart the outer layer of boehmite (Figure 4.39). Closer inspection indicated no change in the microstructure as expected (Figure 4.40). Imaging by electron microscope was slightly easier for the dried sample likely suggesting the metal substrate was more accessible to incident electrons which reduced charging effects.
Table 4.1: TGA Results for 20°C Immersed Surrogates

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<tr>
<th>Mother Sample</th>
<th>6061-RT-022619-7-I</th>
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<th>6061-RT-022619-7-I</th>
<th>6061-RT-022619-7-I</th>
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<td>Post-Immersion Treatment</td>
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<td>Mass Loss [mg]</td>
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Table 4.2: TGA Results for 50°C Immersed Surrogates

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<th>1100-50-71318-2</th>
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Table 4.3: TGA Results for 100°C Immersed Surrogates

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Figure 4.1: 20°C Water / 36 Days – Cross Section from SRNL
Figure 4.2: 20°C Water / 61 Days – Cross Section from SRNL
Figure 4.3: 20°C Water / 36 Days - Bayerite Somatoids
Figure 4.4: 20°C Water / 36 Days – Layered Structure
Figure 4.5: 20°C Water / 36 Days – Tabular structure (6061-RT-022619-7-I)
Figure 4.6: 50°C Water / 31 Days / Polished (1100-50-71318-2)
Figure 4.7: 50°C Water / 31 days / Polished (1100-50-71318-2)
Figure 4.8: 50°C Water / 29 Days - Bayerite (1100-50-2618)
Figure 4.9: 50°C Water / 112 Days – Bayerite & Boehmite (5052-50-31518)
Figure 4.10: 50°C Water / 31 days / Desiccated – Smooth (6061-50-121717)
Figure 4.11: 100°C Water / 7 Days - Boehmite (1100-100-32718-I)
Figure 4.12: 100°C Water / 7 Days - Needle-like boehmite (1100-100-32718-I)
Figure 4.13: 100°C Water / 7 Days – Hydroxide network (1100-100-32718-HW)
Figure 4.14: 100°C Water / 41 Days - 20°C Water / 2 Days (1100-100-11718)
Figure 4.15: 100°C Water / 49 Days - 20°C Water / 10 Days (6061-100-42318)
Figure 4.16: 100°C Water / 20 Days - 20°C Water / 28 Days (6061-100-111118)
Figure 4.17: Blocky boehmite found ATR simulated specimen
Figure 4.18: Pit in corrosion layer of ATR endbox sample
Figure 4.19: TGA & DSC of Gibbsite Powder to 1000°C

Figure 4.20: DSC curves for three powder samples to 1000°C
Figure 4.21: Powder XRD of Gibbsite heated to 450 and 600°C

Figure 4.22: Powder XRD of Gibbsite heated to 230, 450, and 600°C
Figure 4.23: TGA & DSC of Fine Boehmite Powder to 1000°C

Figure 4.24: Powder XRD of Fine Boehmite heated to 400 and 1000°C
Figure 4.25: TGA & DSC of Coarse Boehmite Powder to 1000°C

Figure 4.26: Powder XRD of Coarse Boehmite heated to 300 and 1000°C
Figure 4.27: TGA of 20°C Water Immersion Aluminum Surrogates
Figure 4.28: SEM of Al surrogate dried at 500°C in TGA (RT0226a)
Figure 4.29: SEM of Al surrogate dried at 500°C in TGA (RT0226j)
Figure 4.30: SEM of Al surrogate dried at 500°C in TGA (RT0226a)
Figure 4.31: SEM of Al surrogate dried at 260°C in TGA (RT0226b)
Figure 4.32: SEM of Al surrogate dried at 260°C in TGA (RT0226b)
Figure 4.33: SEM of Al surrogate dried at 200°C in TGA (RT0226e)
Figure 4.34: SEM of Al surrogate dried at 200°C in TGA (RT0226e)
Figure 4.35: SEM of 50°C Al surrogate dried at 500°C in TGA (MT0315a)
Figure 4.36: SEM of 50°C Al surrogate dried at 500°C in TGA (MT0315a)
Figure 4.37: SEM of 100°C Al surrogate dried at 500°C in TGA (HT0327a)
Figure 4.38: SEM of 100°C Al surrogate dried at 260°C in TGA (HT0327b)
Figure 4.39: SEM of ATR Boehmitied plate dried at 500°C in TGA (HTATRa)
Figure 4.40: SEM of ATR Boehmited plate dried at 500°C in TGA (HTATRa)
Chapter 5

CONCLUSIONS

Adherent aluminum hydroxides develop on the surface of aluminum-clad nuclear fuel during operation and wet storage trapping water on the cladding surface that is not easily removed by the vacuum drying process typically employed for commercial fuel drying. Before the fuel elements can be placed into interim or long-term dry storage, both bulk and chemically bound water must be removed to the greatest extent possible to mitigate additional corrosion of the aluminum cladding along with pressurization and flammability due to radiolytic hydrogen production within the dry storage containers. To build on the current scientific understanding of the drying process for ASNF, aluminum cladding surrogate samples were treated by temperature-controlled immersion in water to form adherent hydroxide layers characteristic of those found on ASNF. The surface morphology of those corrosion layers was studied firstly by SEM to establish the materials, crystalline and non-crystalline, cultivated during each treatment regimen. Oxyhydroxide powders were analyzed by simultaneous thermal analysis to quantify the parameters necessary for full decomposition of each phase and to guide small-scale bulk drying experiments. Bulk drying tests were conducted by thermogravimetric analysis to allow for real-time mass measurement during the drying process. X-ray diffraction was utilized throughout the experimental phase of this work for phase determination of both powders and surrogate surfaces at different points in the two heating procedures. The objective was to use data collected in this work to come up with the parameters necessary
for maximum drying of ASNF without exceeding a suggested maximum cladding temperature of 250°C to prevent any phase changes in the aluminum. This information will then be used to guide future experiments utilizing full-scale drying equipment and surrogate fuel assemblies.

**Aluminum Cladding Surrogate Surface Morphology**

*20°C Immersion Surrogates*

Immersing aluminum surrogates in room temperature water for 36 and 61 days resulted in substantial corrosion layers between 8 and 20µm thick. Cross-sectional observation determined that this was a 3-layer formation beginning with a thin, cracked layer contacting the aluminum substrate. The next section is a sizable, smooth intermediate layer that may be a gelatinous alumina like pseudo-boehmite. Finally, an outer layer of well-formed aluminum hydroxide crystals thoroughly covers the exposed surface. Bayerite dominated this outer surface of small crystals taking form as small cylindrical structures called somatoids, or as layered conglomerations of Al(OH)₃ platelets. XRD only identified bayerite on these samples indicating that the larger formations may be accumulations of the smaller crystals. This 3-layered structure and bayerite dominance at low temperature has been observed in literature.

*50°C Immersion Surrogates*

Aluminum cladding surrogates immersed in water at 50°C for 29 to 112 days developed varied corrosion layers due to changes in treatment. On all of them there was a mixture of needle-like boehmite and bayerite somatoids similar to those seen on room temperature samples. Polishing before immersion facilitated much less bayerite growth and a more thorough covering by needle-like boehmite. This type of boehmite is known
to develop at elevated temperatures with pseudo-boehmite as a precursor which aligns with the idea that pseudo-boehmite forms early in the water-corrosion process before crystals begin to precipitate on top of it. The bayerite developed on the unpolished samples were nearly pellet-shaped with smooth sides but were similar in size to the layered structures found on room temperature samples. Surface XRD confirmed both bayerite and boehmite’s presence as expected. In the one longer immersion, the bayerite covered the surface more thoroughly. One of the 50°C surrogates was desiccated after its immersion had concluded and its surface morphology lacked the large amounts of well-formed crystals which may indicate that the removal of loosely bound or bulk water had a strong influence on the microstructure of the surface layer.

100 °C Immersion Surrogates

Surrogates immersed in 100°C water were thoroughly covered in ridges and valleys of needle-like boehmite. Aside from having seen the thin boehmite on 50°C samples, XRD confirmed that boehmite was the only crystalline phase for these samples. The thickness of hydroxide layers for this lot were rather thin at about 1µm and displayed a 2-layer structure when examined along the cross-section rather than 3. Three of the six samples immersed at 100°C were left in room temperature water for 2, 10, or 28 days after their heated immersions had finished. Examination of these three revealed a progressive dissolution of the needle-like boehmite to a point where the sample left for 28 days in room temperature water after heated immersion was nearly featureless aside from a wavy, smooth outer surface which suggests the needle structures are not stable in room temperature water.
**ATR Boehmited Plate**

A piece of ATR endbox was obtained for analysis. These are pre-filmed at high temperature and pressure to develop a protective layer of boehmite. The pre-treatment has proven effective at preventing corrosion-related fuel performance issues in ATR and similar reactors. The structures found on this sample were blocky, sometimes rhombic, structures that seemed to be embedded within a continuous matrix like aggregate in concrete. This layer hosted quite a few pits but those never reached the aluminum substrate interface and the blocky structures are visible down to the bottom of the pits. XRD confirmed only boehmite presence on this surrogate which aligned well with SEM studies.

**Powder Analyses of Oxyhydroxide Powders**

**Gibbsite**

The gibbsite powder used in STA experiments had a typical particle size of about 15µm. The dehydroxylation of gibbsite into alumina was found to occur in two nearly simultaneous stages. First, partial dehydroxylation from gibbsite to boehmite occurred between 220 and 270°C presumably because of hydrothermal conditions inside the large particles preventing full dehydroxylation to alumina [15], [25]. Quickly proceeding after was the highly energetic dehydroxylation from gibbsite to alumina beginning around 215°C with a typical average reaction temperature of about 300°C. The newly formed boehmite did not dehydroxylate until about 520°C in most cases so it had sizeable impact on the final mass loss when the experiment’s max temperature was below that. In one such experiment where the temperature was held at 260°C, the mass loss stopped after a few hours but approximately 17% of the total water content of the powder remained in
the sample as boehmite. Powder XRD showed an inverse relationship between the max
temperature in an experiment and the degree of crystallinity observed for the powder
suggesting the alumina formed in the decomposition process does not have a widespread,
uniform structure. This is consistent with literature which has repeatedly demonstrated
dehydroxylation to result in poorly crystallized transition aluminas.

Fine Boehmite

One of the two types of boehmite used for powder analyses is fine boehmite with
a particle size of about 0.7µm. This material displayed two thermodynamic events within
the heating process. The first was a very weak endotherm which XRD showed was not a
phase transformation. The second, stronger endotherm seen in the DSC data with an
average temperature of about 520°C was the dehydroxylation into alumina. The energy of
this reaction was much smaller than that of the gibbsite powder decomposition because
there are roughly 66% fewer water molecules to liberate. This reaction aligned with the
second dehydroxylation seen in gibbsite powders caused by newly formed boehmite.
XRD of fine boehmite heated to 400 and 1000°C showed a decreasing level of
crystallinity with increased temperature. This agrees with findings in literature that
intermediate phases between hydrated aluminum oxides and α-alumina are poorly formed
and nearly x-ray indifferent.

Coarse Boehmite

The other type of boehmite studied was coarse boehmite for which STA detected
three endothermic events. The first was removal of bulk water with an average
temperature slightly above 100°C and accompanied by gradual mass loss. The second
was a restructuring which did not coincide with any changes in the mass loss rate.
Finally, dehydroxylation to alumina commenced with an average temperature of about 440°C. This reaction was even less energetic than the fine boehmite decomposition. XRD analysis showed that the crystallinity of this powder was very poor even before dehydroxylation. Compared to the gibbsite and fine boehmite, the peak intensities were at least a degree of magnitude weaker.

**Bulk Drying of Aluminum Cladding Surrogates by TGA**

To detect any discrepancies between the dehydroxylation of powders and that of adherent hydroxides on actual pieces of aluminum, the cladding surrogates were cut and subjected to different drying temperatures for varying periods in a TGA. Measuring the mass as the water was removed allowed for an understanding of mass loss rate throughout the process and a precise measurement of total mass loss.

*20 °C Immersion Surrogates*

The room temperature surrogates studied in the TGA were those immersed for 36 days. Drying at 500°C resulted in liberation of water between 0.92 and 0.98mg/cm². During these high temperature runs, mass loss initiated at temperatures below 100°C which is believed to be free water removal. An increase in mass loss rate was observed consistently between 220 and 224°C which is likely some sort of dehydroxylation. This same type of rate increase was still visible when more modest maximum temperatures were used such as 200 and 220°C. In these lower temperature runs, the calculated areal density of water that was liberated came out to be comparable if not exceeding what was seen in the 500°C samples. In cases where it seemed more water was removed at lower temperature however, the sample surface areas tended to be smaller. The similarity in overall mass loss indicates that either the dehydroxylation of bayerite on the outermost
layer is not occurring or, more likely, its contribution to the overall mass loss is dwarfed by the water being drawn out of the lower and intermediate layers. This is additionally supported by the cracked and spalled surface condition after drying experiments. The cracking did not seem to follow a pattern which further points toward water ejection as the cause. The significant delamination of the upper layer should be noted as it could accumulate in the drying container and become an issue that needs to be addressed when drying large quantities of ASNF. While pre-TGA surface XRD confirmed the presence of bayerite, post-TGA XRD only indicated aluminum metal which suggests there was indeed dehydroxylation at least to some extent into an amorphous and/or extremely small particle-size alumina.

50 °C Immersion Surrogates

While the population of these 50°C surrogates dried in the TGA is limited, the information collected is valuable for comparison with the other groups. The amount of surface water removed varied quite a bit falling between 0.22 and 0.65mg/cm². The variability can be attributed to the different treatment before and after the samples were dried via heated immersion. The sample that only yielded 0.22mg/cm² of water was desiccated after water immersion and its corrosion layer had fewer fully formed crystals than others in the group. The greatest water removal occurred on a sample with a significantly longer immersion period of 112 days compared to ~30 days. SEM revealed cracking across the corrosion layer similar to those on the room temperature samples but no delamination occurred. Again, the cracking was seemingly random pointing toward water escaping from the lower layers as the culprit. Very small crystallites were found within the cracks in the upper crystalline layer that somewhat resembled those found
within cracks of the intermediate layer of room temperature surrogates. Aside from the cracking across the surface, the microstructure of crystals on the outermost layer once again did not seem to change significantly after drying.

_100 °C Immersion Surrogates_

Surrogates immersed in 100°C water experienced a mass loss between 0.18 and 0.35mg/cm² during their heating programs in the TGA. There was one exception to this range which lost 0.76mg/cm². This is attributed to the fact that it spent 28 days in room temperature water after its heated immersion which led to the development of a formless hydroxide layer rather than the needle-like boehmite layer typical of other samples immersed at 100°C. This same sample also showed an increase in mass loss at 220°C which closely resembles the one seen in experiments on room temperature samples. This similarity may prove that most of the water removed from all of these samples was originally housed within the amorphous corrosion layer below the crystalline outer layer. This along with the high decomposition temperature for boehmite seen in powder analyses suggests the well-formed crystals are not decomposing concurrently but even if they are, the amount of water released in that reaction may be very small relative to the total mass loss. XRD before and after the TGA for these types of samples started out with only boehmite peaks but after drying, only aluminum was detected despite SEM showing the needle-like structures remained.

_ATR Boehmited Plate_

The ATR endbox sample that was heated to 500°C released 0.2mg/cm², much lower than that which was seen in 20 and 50°C immersed surrogates but comparable to the lower end of the 100°C surrogates. This result was expected because this type of
corrosion layer is known to be rather stable at least compared to the others. XRD of the ATR endbox sample indicated boehmite dominance with some very weak peaks for bayerite. After drying however, only alumina was detected and not boehmite.

**Full-Scale Drying**

The intent of this research was to contribute to the ongoing work of the DOE Spent Fuel Group to better understand the drying process for ASNF on a microscopic scale and in turn use the information gathered to guide full-scale drying experiments. The drying processes that have been attempted in the past indicated drying of the simulated corrosion product used to mimic that which is found on ASNF in spent fuel pools using a cyclic vacuuming and heating process [30]. This procedure involved vacuuming down to 5 Torr to remove bulk water, backfilling with air, heating to 220°C for 35 to 45 minutes depending on the stage, and repeating for four cycles. Although the simulated corrosion product was believed to be dry, TGA of the material after being scraped off indicated that a significant amount of water remained which shows the chemically bound water was not removed. In that series of tests, the simulated corrosion product consisted of clays and pseudo-boehmite, so it is unsurprising that such a low temperature did not decompose it.

**Suggested Drying Parameters**

Based on what was found in previous drying experiments and the findings described in this paper, the maximum temperature of 220°C might sufficiently remove water from any gelatinous hydroxides present. Crystalline gibbsite and bayerite may also decompose but that is less certain. A slightly higher temperature of 240°C would expedite the process saving time and therefore money for those responsible for the work. However, water trapped within the crystal structure of boehmite regardless of
microstructure will almost definitely remain so long as the drying temperature remains below the 250°C suggested limit and therefore never approaches the dehydroxylation range of 440-520°C.

**Future Work**

Although this particular project has concluded, the overall effort continues as spent fuel pools reach capacity for ASNF driving the need to dry it in preparation for interim and long-term storage. Upon completing a research endeavor, it’s important to reflect on difficulties encountered and opportunities for improvement in future work.

The variability in bulk sample treatment provided a valuable perspective on the different oxyhydroxide structures to expect on ASNF if the fuel element history is known or can be estimated. However, future experimentation might find it useful to conduct analyses on surrogate samples with more consistent treatment or with one parameter altered. This would help solidify the findings documented here and allow for a statistical analysis of the results to reduce speculation on the causes of certain observations. X-Ray Photoelectron Spectroscopy (XPS) would be useful in future work for mapping a depth profile of the sample surface structures using the Secondary Ion Mass Spectrometry (SIMS) method. This would provide a quantitative analysis of the composition of the adherent hydroxide layers down to the metal substrate. Additional analysis of XRD data already gathered may be helpful in determining the typical particle sizes present at different stages of the drying process and for identification of the poorly formed aluminas.

Thermal analyses of oxyhydroxide powders were conducted on a significant number of samples but the temperature profiles varied along with the heating rate so
future work employing a consistent heating rate and temperature profiles would make statistical analyses of the results more straightforward and telling. Low-temperature thermal analyses below 250°C will be necessary for further explaining bulk drying results. For the same reason, further XRD of dehydroxylated powders could support the reevaluation of surface XRD data from aluminum surrogates dried in the TGA.

An obvious shortcoming of the drying experiments on bulk samples by TGA is the number of experiments that were run. This testing is actively ongoing to round out the data and to improve upon the certainty of the results presented. In addition to simply conducting more experiments, the parameters of the new experiments are key. Most of the drying tests were conducted at 260°C or 500°C but the recommended temperature limit for ASNF during drying is 250°C. Therefore, conducting the experiments at temperatures below 250°C will be most useful for making estimates of the effectiveness of the drying methods employed currently. Also, stepwise heating profiles may be better suited for quantifying liberated water mass at different temperatures.
REFERENCES


