Calcium passivation and properties of Al/Ca composite conductors

Charles Czahor
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Calculus passivation and properties of Al/Ca composite conductors

by

Charles Frederick Czahor

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Wind Energy, Science, Engineering, and Policy

Program of Study Committee:
Iver Anderson, Major Professor
Alan Russell
James McCalley
Frank Peters
John Jackman
Peter Collins

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2019

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ACKNOWLEDGMENTS

I would like to thank my major-professors Iver Anderson and Alan Russell, who not only helped along the way in performing the research that went into preparing this dissertation, but also provided me with the opportunity to come to Iowa State and work on this interesting project. In addition, I would like to thank the other members of my committee, Jim McCalley, Frank Peters, John Jackman, and Peter Collins for all of their help.

The assistance of Trevor Riedemann was vitally important to the success of this project and is greatly appreciated. I would also like to acknowledge all of those at Ames Laboratory who contributed to this work over the past several years. In addition, I would like to acknowledge the contributions of Dustin Hickman who performed numerous experiments for this project.

I would like to acknowledge the financial support that I have received from the National Science Foundation (NSF) Integrative Graduate Education and Research Traineeship (IGERT) Fellowship through the Wind Energy, Science, Engineering, and Policy (WESEP) program. This research was supported by the U.S. Department of Energy Office of Electricity and performed at Ames Laboratory under contract no. DE-AC02-07CH11358.
Light, strong, high-conductivity materials are desirable for overhead power transmission and distribution conductors. An aluminum/calcium composite with nano-filamentary reinforcement was produced by powder metallurgy and deformation processing to fine wires. Upon achieving the desired dimension, the wires were heat treated to convert the calcium to Al$_2$Ca intermetallic reinforcement filaments. Extended heat treatments were used to evaluate the upper operating temperature of the material. The processing steps, microstructure, conductivity, and tensile strength of Al/Ca composites were evaluated. The measured properties indicate that the number of support towers required for a HVDC transmission line can be reduced by more than 23% when using Al/Ca composite conductors. The properties of this material can be tailored to specific applications by modifying parameters during production.

The lack of availability of fine calcium powder necessary to produce Al/Ca composites of sufficient strength is a barrier to their development. A method for protecting Ca surfaces from moisture in the environment was studied to enable its safe production. Preliminary experiments identified a fluorine containing compound that could be introduced in a gaseous stream and passivate Ca. This compound was implemented into a gas atomizer to protect Ca during production and limit exposure of bare metal to atmospheric conditions. Atomization parameters were evaluated, and powder was characterized for size distribution, surface chemistry, and flammability indicating that passivation treatments were successful.
GENERAL INTRODUCTION

Deformation-processed metal-metal composites (DMMCs) provide an appealing approach for producing lightweight materials with high strength and high conductivity. DMMCs can be produced by powder metallurgy and severe plastic deformation resulting in nano-filamentary reinforcement. Al/Ca composites with monolithic construction have shown promise as next-generation overhead transmission conductors. Previous research has shown that these materials tend to form various intermetallic species when exposed to elevated temperatures resulting in the degradation of properties. This study examines the effect of using a reduced loading of Ca and intentionally converting the reinforcement to an intermetallic species to produce a material with enhanced high-temperature stability while retaining superior performance properties. Al/Ca (11.5 vol.%) composites were produced and converted to Al/Al₂Ca (18 vol.%) by heat-treatment at 260°C. In addition to the effect of reinforcement material, the influence of filament spacing was studied. The transformation to Al₂Ca was analyzed by differential-scanning calorimetry and scanning electron microscopy. Tensile strength and electrical conductivity were investigated for unconverted and converted materials as well as samples that had undergone extended heat treatment. Two alternative deformation methods were compared to identify the importance of the processing method on final material performance. The measured material properties were used in line sizing calculations to determine the benefits of using these composites for high-voltage direct-current transmission.

Due to the lack of availability of fine calcium powder needed to produce Al/Ca composites, a safe production method was sought. Preliminary gas-phase passivation experiments were performed to identify an appropriate gas composition capable of protecting
Ca from excessive oxidation, making it safe to produce and handle. These findings were utilized to design an in-situ method of protecting Ca during the process of gas atomization to minimize the exposure time of bare metal surfaces to the environment. The calcium from both of these experiments was analyzed to help guide decisions about scaling the production to the level necessary to generate the amount of powder necessary to produce full size Al/Ca conductors.
PART 1: PROPERTIES OF Al/Ca COMPOSITE CONDUCTORS AFTER CONVERSION TO INTERMETALLIC REINFORCEMENT
CHAPTER 1. INTRODUCTION

A 48% increase in worldwide energy demand is expected by 2040, which will require expansion of electrical power transmission infrastructure [1, 2]. Expanded long-distance transmission grids in China, the United States, and elsewhere are expected to make greater use of high-voltage direct current (HVDC) transmission, the preferred technology for long distances [3]. Conventional aluminum-conductor steel-reinforced (ACSR) conductors are not well suited for HVDC transmission due to the presence of the heavy, poorly conducting steel core needed for strength and sag-resistance. Al/Ca composite conductors with monolithic construction produced by powder metallurgy and deformation processing have shown promise as a possible next-generation conductor for this application.

Deformation-processed metal-metal composites (DMMCs) provide an appealing approach for producing lightweight materials with high strength and high conductivity. DMMCs can be produced by powder metallurgy and severe plastic deformation resulting in nano-filamentary reinforcement. Extensive study of this class of materials has shown that they exhibit strength that increases exponentially with true strain while maintaining conductivity close to the rule-of-mixtures prediction [4]. Both materials in the composite must be highly ductile in order to withstand the extensive deformation processing without fracturing. The proposed conductor material utilizes Al as the primary phase and Ca as the secondary reinforcement phase, both starting as elemental powders. They are blended and deformed into sub-micron-thickness filaments with extremely high aspect ratio during wire drawing, resulting in interface strengthening. Al and Ca are ductile fcc metals with high conductivities, similar mechanical properties, and low densities.
The first-generation of Al/Ca conductors proved the strengthening mechanism of the material but was limited by the coarse Ca powder size used [5]. The second-generation material, Al/Ca (20 vol. %), was made with high-purity powders with smaller powder particle sizes, enabling strengths superior to existing conductor technologies [6]. One key finding from these studies was the identification of a transformation of the reinforcing Ca phase to Al$_2$Ca intermetallic at temperatures as low as 175°C, a temperature sometimes reached by transmission conductors during periods of heavy electrical demand [5, 6].

Part 1 of this study examines the effect of intentionally converting the reinforcement phase to an intermetallic species to produce a material with high-temperature stability while retaining the superior performance properties that have been shown in the prior generation materials. The goal of this section is to determine whether the selected processing route can result in a material that could be used in place of existing overhead power transmission conductors. A reduced initial volume loading of Ca was necessary to compensate for volume expansion during transformation and an expected increase in resistivity. A formulation with 11.5 vol.% Ca was chosen with the aim of producing a composite with 18 vol.% Al$_2$Ca, found in previous research to be a desirable DMMC reinforcement fraction [7]. Microstructure, temperature stability, conductivity, and mechanical properties were investigated in both Al/Ca and Al/Al$_2$Ca composite samples produced by two different deformation methods. The first method reduced the extrudate to fine wires by a combination of swaging and drawing performed at Ames Laboratory. The second method only used drawing to reduce the wire diameter in an effort to avoid greatly altering the filament shape. The design criteria and performance of these materials as overhead conductors were also studied.
CHAPTER 2. BACKGROUND INFORMATION

This chapter will provide relevant background information that has motivated the research that will be presented. A brief history of previous studies of DMMCs will be given in addition to an overview of Al/Ca research progress to date. Additionally, the options for overhead power transmission will be discussed along with some of the existing conductor technologies available.

2.1 Early DMMC Research

Composite materials consist of two or more different phases in order to achieve a combination of properties that cannot be attained from either phase by itself. The primary phase is referred to as the matrix, which surrounds the second dispersed phase. The matrix can be a metal, ceramic, or polymer with three different possible reinforcement types including particle, fiber, or structural. [8]. Deformation metal-metal composites consist of ductile metals as both the matrix and dispersed phase with fiber reinforcement being created by mechanical working. DMMCs can be prepared by either powder metallurgy or co-melting two metals that are miscible as liquids but immiscible as solids then deformation by extrusion, swaging, and drawing to produce wire or rolling to make sheet. The final microstructure is typically sub-micron thick phases due to the large amount of deformation imparted on the material [7].

Typically, metal matrix composites exhibit strengths that are linearly dependent on the volume fraction of the reinforcement phase. The earliest Cu-Nb DMMCs produced by Bevk et al. showed that extensive deformation of reinforcements could lead to an exponential increase in strength that greatly exceeded rule of mixture predictions. These materials also
displayed good retention of electrical and thermal conductivity when using 18 to 20 vol.% Nb reinforcement [4]. The ability to achieve both high strength and high conductivity simultaneously is the main appeal of using this type of material.

Most studied DMMCs use a face-centered cubic (fcc) matrix (Al, Cu) with the earliest using body centered cubic (bcc) metals as the second phase. This combination results in a convoluted ribbon shaped morphology of the second phase embedded in the matrix [4, 9, 10]. In the early 1990’s, Ames Laboratory produced various DMMCs with Ti, Mg, Al, Sc, and Au as the matrix phase [7]. Much attention has been placed on Al matrix DMMCs with Nb, Ti, Mg, Sn, and Fe second phases being studied. These materials also showed exponential strengthening with high electrical conductivity [11, 12, 13, 14]. Despite the fact that all of these materials exhibited good material properties, aluminum/calcium DMMCs have been developed specifically for the intended application of overhead power transmission. The ultra-low density of this Al/Ca composite provides a major advantage over other heavier systems in suspension.

2.2 Previous Al/Ca research progress

Aluminum is almost universally accepted as the best material for overhead conductors because of its high conductivity and low density. The selection of calcium as the reinforcement phase for DMMC conductors was based on the combination of high conductivity, low cost, and extremely low density. In addition, aluminum and calcium have similar strengths and are highly ductile enabling them to withstand the extensive deformation required to achieve sub-micron filaments. A more detailed discussion of the selection of the combination of Al and Ca is provided by [15] and [6].
Study of the first generation of Al/Ca (9 vol.%) composite showed the strengthening effect typical of DMMCs but was limited by the large size (1.2 mm) of the Ca granules that did not allow filaments to reach the sub-micron level [5]. Second generation Al/Ca (20 vol.%) composites exhibited an ultimate tensile strength (UTS) of 476 MPa, exceeding the strength of all current commercial stranded conductors. This was enabled by a smaller Ca powder size (<200µm) and a relatively high reinforcement fraction [6]. Both formulations showed a ribbon shaped second phase despite the fact that a cylindrical filament morphology was expected for a fcc metal (Ca) in a fcc matrix (Al). This can be explained by a possible temporary phase transformation of Ca filaments from fcc to bcc during processing [15, 16].

The elevated temperature performance of Al/Ca (20 vol.%) composites was studied, and it was found that Al_{6}Ca intermetallics are formed at temperatures as low as 177°C. Two different exothermic events occur upon heating correlating to the formation of Al_{4}Ca and Al_{2}Ca [6]. The two phases are delineated in the Al/Ca binary phase diagram (Figure 1) [17].

![Figure 1. Al/Ca binary phase diagram.](image-url)
Al\textsubscript{2}Ca was found to be the final phase after high-temperature exposure, and its formation resulted in growth of the reinforcement filaments and an increase in electrical resistivity. In order to enhance the high-temperature performance of Al/Ca DMMCs, the Ca filaments could be transformed to Al\textsubscript{2}Ca after all deformation processing was completed. Further study of the deformation processing and heat treatment sequence is necessary to identify optimum final properties.

### 2.3 Current overhead power transmission conductor technologies

As the makeup of global energy production shifts from predominantly fossil fuels to a complex blend of sources, more efficient long-distance power transmission will be necessary. High-voltage direct-current transmission (HVDC) becomes preferred to alternating-current (HVAC) technology when transmission line length exceeds a certain break-even distance as shown by Figure 2 [18].

![Figure 2. HVDC break even distance.](image-url)
Intermittent sources such as wind and solar are typically located in remote areas far away from population centers and will likely make greater use of HVDC transmission in the future [19]. HVDC is often limited by the high cost of conversion equipment and difficulties in breaking elevated DC current [20]. HVDC does, however, offer several benefits compared to HVAC, including: greater power carrying capacity [20, 21], higher stability and reliability [20, 21, 22], freedom from compensation for inductance and reactive power [20], fewer conducting wires and towers [20, 23], and the absence of skin effects that result in localized surface heating [20]. The skin effect enables conductors with poorly conducting core materials such as conventional aluminum-conductor steel-reinforced (ACSR) to perform well for AC because current is concentrated in the outer (aluminum) portion of the conductor. ACSR as well as a selection of more recently developed overhead conductors are shown in Figure 3 and defined in Table 1 [24].

Figure 3. Selected overhead transmission conductor technologies.
Table 1. Commercial overhead transmission conductors.

<table>
<thead>
<tr>
<th>Conductor</th>
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<tr>
<td>ACSR</td>
<td>Aluminum Conductor Steel Reinforced</td>
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<td>ACCC</td>
<td>Aluminum Conductor Composite Core-CTC Global ©</td>
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<tr>
<td>ACCR</td>
<td>Aluminum Conductor Composite Reinforced -3M ©</td>
</tr>
<tr>
<td>ACAR</td>
<td>Aluminum Conductor Alloy Reinforced</td>
</tr>
<tr>
<td>AAAC</td>
<td>All Aluminum Alloy Conductor</td>
</tr>
</tbody>
</table>

ACSR is the most widely used conductor because of its ability to combine an acceptable level of strength and conductivity at a low cost. For DC current flow, however, the steel core acts as a “dead zone”, and the conductivity is reduced. Another disadvantage of ACSR is the large mismatch between the thermal expansion coefficients for Al and steel, which can result in bird-caging and thermal fatigue [25]. Newer materials have sought to replace the steel core with lighter and stronger materials in order to increase the thermal limit of the conductor and the current carrying capacity. ACAR uses Al alloy in the core but is not strong enough for long spans [26, 27, 28]. ACCR was invented by 3M and uses a core with 50 vol.% aluminum oxide fibers in an Al matrix. ACCR has very good sag resistance but is limited in its use by high cost and mediocre DC conductivity [26, 27, 29]. ACCC, invented by CTC Global, has a polymer matrix carbon and glass fiber reinforced composite core. AAAC is a conductor that has a single material for the entire cross-section made with precipitation hardened aluminum, but it is limited in strength and sag resistance [26, 27].

The issue with ACSR and the other materials that seek to replace it is that they are not specifically designed for DC. Al/Ca conductors can achieve high strength and high conductivity simultaneously without the need for a steel core making them extremely lightweight, but the development of the needed materials processing methods remains a barrier to realizing this predicted level of performance.
CHAPTER 3. EXPERIMENTAL PROCEDURE

This chapter will cover both the production steps necessary for sample preparation as well as the techniques used to gather results. Previously produced Al/Ca (20 vol.%) samples were analyzed in addition to the newest formulation. The newly produced samples were the primary focus of this work.

3.1 Samples preparation

An Al/Ca conductor sample was prepared starting from metal powders produced at Ames Laboratory. Al powder with 99.99% purity was produced by a gas atomization reaction synthesis (GARS) process with sizes 45-75 µm being used. Ca of 99.5% purity was made by centrifugal atomization with a rotating quench bath (CARQB), a system specifically designed for producing fine Ca powders. The first-generation material [5] used large commercial Ca granules (1.2mm), and the second [6] used Ames Lab Ca with $D_{50}=200\mu\text{m}$. A smaller starting Ca powder size allowed for filaments in this third-generation material to be smaller after deformation, so Ca of even smaller size (75-125 µm, $D_{50}=111$) was selected for the material used in this study. The formulation used to produce this sample included a reduced loading of calcium (11.5vol.%) with the remainder being aluminum (88.5vol.%). This reduction was made to allow for the volume expansion of Ca to intermetallic species resulting in a reinforcement fraction that was desirable based on previous findings as shown by Figure 4 [7].
Powders were weighed (155.45 g Al, 11.45 g Ca) in an inert atmosphere glovebox then blended with a Turbula multi-axis mixer for 30 minutes. The mixed powders were die compacted with a pressure of 61.2 MPa into cylindrical green bodies (diameter=72.1 mm) giving a compact density of 83.8% of the rule of mixtures (ROM) value. This value is in close agreement with the expected compressibility of Al powder as shown by Figure 5 [30]. The slightly higher density can likely be explained by the fact that relatively small powder sizes were used.

Figure 5. Compressibility of atomized aluminum powder as a function of pressure.
The compacted powder “pucks” were stacked in a pure Al (1100-H14 alloy) can with outer diameter 90.7 mm, inside diameter 78 mm and interior height 196.8 mm. The can was wrapped in heating tape to warm it to about 200°C as it outgassed under vacuum (10⁻⁶ Torr) to remove moisture adsorbed on the powder particles, and then it was sealed by electron-beam welding (Figure 6).

Figure 6. Extrusion can loaded with Al/Ca compacts sealed by E-beam welding.

3.2 Deformation processing

Indirect extrusion was performed at the TU Berlin Extrusion Research and Development Center with an exit die diameter of 21 mm, giving an effective extrusion ratio of 14.9 when accounting for the porosity and void space present in the billet. The billet was preheated to 285°C, and the die exit temperature was monitored in addition to other processing conditions. This temperature was high enough for dynamic recovery of both Al and Ca (0.4 Tₘ) but low enough to avoid the formation of Al/Ca intermetallic compounds in that time frame that could initiate cracks during extrusion. The deformation true strain can be
calculated according to Equation 1 where \( d_i \) and \( d_f \) are the initial and final wire diameters, respectively.

\[
\eta = \ln \frac{A_i}{A_f} = 2 \ln \frac{d_i}{d_f}
\]  

(1)

In order to account for the porosity in the billet and the space between the compacts and the can (Error! Reference source not found.), a correction was made to determine the effective starting diameter.

![Figure 7. Void space in extrusion can.](image)

Equation 2 shows how the deformation true strain is dependent on the different areas of the starting piece and the final extruded rod.

\[
\eta = \ln \left( \frac{A_{can} + A_{puck}}{A_{final}} \right)
\]  

(2)

where,

\[
A_{can} = \frac{\pi}{4} \left[ OD_{can}^2 - ID_{can}^2 \right]
\]  

(3)

\[
A_{puck} = \frac{\pi}{4} \left[ (OD_{puck}^2)(1 - porosity) \right]
\]  

(4)
By combining these three expressions, a true strain of 2.7 after extrusion was calculated by Equation 5. Given the size of the extrudate, this strain corresponds to an effective starting diameter of 81.1 mm.

$$\eta = \left( \frac{OD_{can}^2 - ID_{can}^2}{OD_{final}^2} + \left( \frac{OD_{puck}^2}{OD_{final}^2} \right) \left( 1 - \text{porosity} \right) \right)$$  (5)

A rod with a length of approximately 275 cm was returned to Ames Lab to undergo further deformation processing. Ultrasonic inspection of the tail section was utilized to identify the point at which there was no longer material from the extrusion can in the core of the rod. After removing this portion, the rod was sectioned into quarters, and the can material was machined from the rod’s exterior with a lathe. The final rod diameter after removal of the pure Al outer sleeve was 15.8 mm, which was used to adjust the effective starting diameter to 62.9 mm to account for the reduction in size by the lathe, which produced no additional plastic deformation of the Al/Ca portion of the specimen.

The rod was reduced at room temperature by swaging through a series of dies to 0.690 mm. At this point wire drawing was used to further reduce the material to a final diameter of 0.11 mm. The excellent ductility of the components in the composite allowed all deformation processing to be performed without any stress-release annealing. Various sample diameters were retained as deformation progressed to study the effect of strain on material properties. In addition to the swage and draw method performed at Ames Laboratory, the extrudate was also reduced to fine wire by drawing only by Fort Wayne Metals. Table 2 shows the different wire diameters used for this study along with the corresponding true strain values. The designations “SD” and “DO” indicate whether the sample size was
produced by the swage/draw method or drawing only. This nomenclature is utilized in figures and tables throughout Part 1. If the deformation processing technique is not specified, it can be assumed that the sample is SD.

Table 2. Wire sizes and strain levels for study of third generation Al/Ca wires.

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>η</th>
<th>SD</th>
<th>DO</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.97</td>
<td>6.11</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>2.16</td>
<td>6.74</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>0.94</td>
<td>8.41</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>0.50</td>
<td>9.67</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>0.40</td>
<td>10.1</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>0.31</td>
<td>10.6</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>0.20</td>
<td>11.5</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>0.11</td>
<td>12.7</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>0.09</td>
<td>13.12</td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

3.3 Conversion of filaments

The main goal of this study was to examine the effects of intentionally exposing Al/Ca DMMCs to elevated temperatures in order to observe how filaments were converted to intermetallic species and evaluate the performance of the resultant material. Both previous and current generation materials were studied in order to plan the appropriate method for processing these samples.

3.3.1 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) experiments were performed to study high-temperature events taking place in Al/Ca materials. A Netzsch STA449 F1 DSC system was used with heating rates ranging from 5-20°C/min for various samples of both Al/Ca (20vol.%) and Al/Ca (11.5 vol.%). Samples with various true strain values were examined to determine whether the heat treatment process required different exposure times for different size samples.
3.3.2 Conversion to Al/Al$_2$Ca

Using the results of DSC tests, it was determined that samples could be converted to Al$_2$Ca reinforcement with a short heat treatment. Short lengths of wire were sealed in Ar-filled quartz ampoules and heat-treated in a temperature-controlled tube furnace at 260°C for various times depending on size as shown in Table 3.

Table 3. Heat treatment time for samples conversion.

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>Time at 260°C (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>0.2</td>
<td>3</td>
</tr>
<tr>
<td>0.3</td>
<td>5</td>
</tr>
<tr>
<td>0.4</td>
<td>6</td>
</tr>
<tr>
<td>0.5</td>
<td>8</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
</tr>
</tbody>
</table>

DSC on these samples was run to confirm that the intermetallic transformation was complete. All further analysis was completed on both unconverted (Al/Ca) and converted (Al/Al$_2$Ca) samples at various levels of true strain.

3.4 Scanning Electron Microscopy

Microstructure was studied using a FEI Teneo LoVac Field–Emission Scanning Electron Microscope (FE-SEM). SEM images were taken before and after transformation to determine whether the heat treatment process had gone beyond simple conversion to the intermetallic and caused undesirable sinusoidal instabilities in the reinforcement filaments [31, 16]. Samples were prepared for examination by dry polishing to avoid the corrosive effects of water on the calcium filaments.
3.5 Four-point resistivity measurement

The electrical conductivity of wires at all strain levels included in Table 2 for both Ca and intermetallic reinforced samples was determined by the four-point probe measurement technique according to ASTM B193-16 [32]. A series of currents was applied with a Keithley 6220 Precision Current Source, and the voltage difference was measured with a Keithley 2182A nanovoltmeter. The accuracy of this measurement technique was confirmed with copper and stainless-steel standards of known conductivity. Measurements were taken at room temperature (20°C), which allows direct comparison to tabulated values of other conductors [24]. Given that the instruments used were very precise, the largest source of error came from the dimensions of the material, especially for small samples. The sample size was determined by measurement with calipers, microscope imaging, and weighing of wires.

3.6 Tensile Testing

Tensile testing was done with multiple instruments to accommodate the various wire sizes that were examined. For samples with $8 < \eta < 12$ the tensile strength was determined using a Zwick/Roell Z 2.5 instrument with an elongation rate of 2 mm/min. For the 0.11 mm diameter ($\eta = 12.7$) wire, tests were completed at Psylotech’s facility using their $\mu$TS under microscope universal test system allowing for precision measurements at low forces. For each technique, the average of at least three independent measurements of the ultimate tensile strength (UTS) was reported. UTS was used since it is more reproducible and reliable than yield strength for small specimens and is the strength value most often cited for transmission conductor materials [16].
3.7 High temperature aging

Wire samples were treated at elevated temperatures for extended periods of time to study the upper temperature limits of the material. Lengths of wire sufficient for conductivity measurements were placed in quartz tubes and sealed or left open to the atmosphere depending on the trial. The tubes were placed in a vacuum furnace for times ranging from 4 to 1000 hours beyond the initial conversion to intermetallic reinforcement. Thermocouples were used to monitor the temperature of the furnace shell and the inside of the chamber.
CHAPTER 4. RESULTS AND DISCUSSION

In addition to the properties that directly affect the performance of the material, several other characteristics have been investigated. Numerous considerations must be made in order to produce and operate with these materials. The results presented will explain how the desired material properties are influenced by processing conditions and intelligent design.

4.1 Extrusion

The extrusion of the Al/Ca (11.5 vol.%) billet both closed the porosity remaining from compaction and reduced the diameter of the sample. Figure 8 shows that the force required steadily increased as the ram was displaced until approximately 30 mm. At this point the void space in the can collapsed and the extrusion process continued with fully dense material.

![Figure 8. Extrusion temperature and force profile for Al/Ca (11.5 vol.%).](image)
The temperature at the die outlet starts off at the preheat temperature of 285°C and rises as a result of frictional force [33]. Elevated temperature was used in order to reduce flow stress and allow for dynamic recovery [34]. The extrusion ratio of 14.9 that was used was significantly higher than the extrusion ratio (i.e., 11) used in previous samples. This increase was made based on previous findings indicating that a reserve of ram force capacity was available to permit higher forces to be applied [5].

After extrusion, it was decided that the material from the extrusion can should be removed from the rod since it was desired to study only the properties of Al/Ca composite, not of pure-Al-clad Al/Ca composite. Prior to the removal of the outer aluminum “shell”, ultrasonic inspection was used in order to determine the point where there was no longer can material in the center of the extrusion. Figure 9 shows multiple cross-sections of the rod with the presence of the can material in the center being evident.

Figure 9. Cross-sectional view of tail section of extruded rod.
The can material in the tail section of the extrusion is introduced into the core of the rod due to the way in which the material flows during the extrusion process. Figure 10 shows the four different types of flow patterns that are generally observed during extrusion [33].

Figure 10. Schematic of the four different types of flow in extrusion.

Based on the fact that indirect extrusion was used with aluminum being the primary material, it was assumed that flow pattern A was present according to the study of other aluminum extrusions [33, 34]. In this case, the metal at the center of the billet moves faster than the metal at the periphery, leading to the presence of outer can material in the center of the rod near the end of the extrusion. Once the tail end of the rod and the outer shell had been removed, further deformation processing produced Al/Ca wires of various sizes that were used for the remainder of the study.

4.2 Differential scanning calorimetry on Al/Ca (11.5 vol.% and 20 vol.%) composites

Differential scanning calorimetry tests were performed on Al/Ca (20 vol.%) composite wires with $\eta=9.95$ at different heating rates to identify microstructure transformations at elevated temperatures. Figure 11 shows that for experiments run with heating rates of 5, 10, 15, and 20 K/min, there are two exothermic events taking place. Previously reported work confirmed these events to be the formation of Al₄Ca and Al₂Ca intermetallics by X-ray diffraction [5].
It can be seen that the use of a greater heating rate results in the peaks being shifted to higher temperatures. Using the results of these experiments, a time-temperature-transformation (TTT) diagram was constructed that shows how the formation of these two intermetallics takes place in succession and is dependent on heating rate (Figure 12).

Figure 11. DSC results for Al/Ca (20 vol.%) at various ramp rates.

Figure 12. Time-temperature-transformation diagram for Al/Ca (20 vol.%).
The findings from experiments on Al/Ca (20 vol.%) were used to help design experiments for the current-generation material and to help gain a better understanding of the transformation process. In addition, the determination that Al$_2$Ca was the more preferred phase guided the current formulation to allow for the use of an appropriate amount of reinforcement phase. Figure 12 showed that a temperature in excess of 250°C was needed to complete both transformation events for samples with 20 vol.% initial calcium loading.

The intent of this current study was to transform the reinforcement phase to Al$_2$Ca, so it was desired to identify the temperature of this particular event for the current formulation. Figure 13 shows the results of DSC experiments on three different wire samples that had not received any heat treatment prior to testing with a heating rate of 20 K/min since it was shown to provide adequate peak resolution on Al/Ca (20 vol.%).

![Figure 13. DSC curves of Al/Ca (11.5 vol.%)-SD wires with various true strain levels.](image-url)
The Al$_2$Ca phase has a high melting point (1075°C) with good creep resistance [35], and these characteristics are believed to stabilize the shape of reinforcement filaments against spheroidization and coarsening that can cause degradation of both strength and conductivity [16]. The Al$_4$Ca peak has a lower magnitude of enthalpy of formation (-43.9±4.2 kJ/mol) than Al$_2$Ca (-73.2±4.2 kJ/mol), contributing to the smaller exotherm of the former [17]. Table 4 shows that the temperature at which the Al$_2$Ca event peak occurs is lower for wires with greater strain likely because the smaller filament spacing creates a shorter diffusion path for the formation of the intermetallic compound and greater Gibbs-Thomson curvature effect [16]. A prominent peak for the formation of Al$_4$Ca is seen only in samples with high strain (η>9.5), since Al$_4$Ca can be formed quickly at clean interfaces resulting from mechanical working [36] before being consumed in the transformation to Al$_2$Ca. Wires with larger filament spacing do not inter-diffuse rapidly enough at the high heating rate used to form an isolated Al$_4$Ca intermetallic phase at the temperature seen for smaller wires (220°C), and the two event peaks begin to merge. Further study of the activation energy for diffusion of each atom type into the other is necessary to better understand the kinetics of the intermetallic phase formation.

Table 4. Al$_2$Ca DSC peak maximums for various deformation true strain levels.

<table>
<thead>
<tr>
<th>η</th>
<th>Max Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.5</td>
<td>264</td>
</tr>
<tr>
<td>9.67</td>
<td>269</td>
</tr>
<tr>
<td>8.41</td>
<td>269</td>
</tr>
</tbody>
</table>
Based on the results from Table 4, small pieces of select wires were sealed under argon and heat treated in a furnace at 260°C for the times specified in Table 3. The objective was to transform the Ca filaments to Al$_2$Ca but without excessive exposure to high temperature. Doing so could potentially lead to diffusion along the interface creating sinusoidal perturbations, giving a “string of pearls” morphology [7]. DSC tests were done on these wires that underwent a “flash” heat treatment to confirm the completion of reinforcement phase transformation seen in the suppression of the exothermic peaks as shown by Figure 14.

![DSC graph](image)

**Figure 14.** DSC of Al/Ca-SD wire after heat treatment with comparison to as-drawn wire.

Based on these results it appears that the smaller wires were fully transformed, while the largest sample still had trace amounts of pure Ca in the reinforcement filaments. After transformation to intermetallic reinforcement, the wire microstructure becomes more stable, making it resilient (highly resistant to Joule heating effects), even during emergency
overloading. These DSC results were used in conjunction with microstructural analysis to determine an appropriate heat treatment schedule for the array of wires to be used for further testing. DSC experiments were also conducted on “DO” samples processed by FWM with very similar results that have been omitted for clarity.

4.3 Microstructural analysis of Al/Ca (11.5 vol.%) and Al/Al\(_2\)Ca (18 vol.%) composites.

The microstructures of DMMCs have been studied in great detail in the past several decades [4, 7, 37] and in recent years for the Al/Ca composite system [5, 6, 23]. This section is broken into two parts that further study the microstructure of these materials. The first examines the microstructure of Al/Ca composites in their as-drawn state and the effect of converting the filaments with short heat treatments previously described. The second part looks at the microstructure after prolonged exposure to elevated temperatures. The term “as-drawn” is used to identify samples that received no heat treatment and does not designate between the two processing methods. Unless otherwise mentioned, the results shown are for samples produced by a combination of swaging and drawing (SD). Comparisons will also be made between the SD and DO processing routes for heat treated samples.

4.3.1 Microstructure: As-drawn and converted Al/Ca composites

Figure 15 shows the “swirled” ribbon-shaped morphology seen in the prior generation of Al/Ca composite at lower strain levels, but it is altered by extensive mechanical working.

The resultant morphology is in contrast to the expectations of classic composite morphology theory that predicts cylindrical filaments due to axi-symmetrical deformation for a fcc secondary phase in a fcc matrix. A possible explanation is a temporary crystal structure transformation in Ca from fcc to bcc during extrusion that leads to plane-strain deformation.
giving rise to the ribbon-like shape [5, 6, 7], but this has not been further explored in this study. With conversion of Ca filaments to Al$_2$Ca, the microstructure undergoes changes that have a direct impact on the performance properties of the material. Figure 16 shows a transverse view of wires at different magnifications that underwent filament transformation.

Figure 15. Backscattered electron micrographs of Al/Ca (11.5 vol.%) composite transverse cross section with pure Ca filaments: (a) $\eta=6.74$, (b) $\eta=9.67$.

Figure 16. Backscattered electron micrographs of Al/Ca (18 vol.%) composite transverse cross section with converted filaments at two magnifications: (a/c) $\eta=6.74$, (b/d) $\eta=9.67$. 
In comparing Figures 15 and 16, it is difficult to see the effects of the filament transformation process. By looking at the longitudinal cross-section instead this change becomes more apparent. Figure 17 shows evidence of change in the reinforcement filaments in the longitudinal direction.

![Figure 17](image)

Figure 17. Backscattered electron micrographs of Al/Ca (11.5 vol.%) composite longitudinal cross section at $\eta=9.67$: (a) pure Ca filaments, (b) Al2Ca reinforcement after heat treatment.

The Ca second phase displays a long continuous morphology with nearly uniform thickness. During swaging or drawing, the filament size decreases exponentially by a factor directly related to the reduction in the overall wire cross section according to Equation 1. Filaments are able to deform with a consistent thickness since Al and Ca have nearly equal flow stresses, avoiding problems with a softer phase flowing around a harder second phase [7, 38]. Filament size and spacing are critical parameters that affect the performance of DMMCs and allow comparison of small, lab-scale specimens to potential full-size extrusions on the basis of true strain.

The conversion process results in Al$_2$Ca filaments that appear brighter in the micrographs shown. One critical concern with the heat treatment process is spheroidization that can lead to breaking of filaments that degrades mechanical and electrical properties.
Based on micrographs at various strain levels, it appears that this did not occur to a significant extent during the heat treatment period, and the filaments remained intact. Longer term exposure to elevated temperatures is a matter of interest and will be discussed further.

One of the intended consequences of transformation was the growth of the secondary phase from 11.5 vol.% Ca to 18 vol.% Al$_2$Ca. The micrographs in Figure 17 clearly show a change in the filament size (dia.) with a measured increase in thickness from 0.9µm to 1.5µm for the selected strain level. This difference is very close to what is expected indicating that the transformation to Al$_2$Ca is essentially complete, as confirmed by DSC and XRD [5, 6]. Figure 18 shows additional longitudinal cross-sections at a lower strain level for comparison. At the two levels of magnification shown, it appears as if the transformation is complete and the filaments are relatively straight.

Figure 18. Backscattered electron micrographs of Al/Ca (11.5 vol.%) composite longitudinal cross section at η=6.74: (a/c) pure Ca filaments, (b/d) Al$_2$Ca reinforcement after heat treatment.
As reported here, DSC and SEM confirmed that the transformation was completed but not excessive, enabling the study of modified performance properties. The next part will discuss changes to the microstructure that occur as a result of extended heat treatments.

4.3.2 Microstructure: Extended heat treatments

Concerns about the long-term stability of Al/Ca composites drove the decision to intentionally convert the reinforcement material to Al$_2$Ca. Therefore, it is important to study how the microstructure and properties of the material evolve as a result of prolonged exposure to elevated temperatures. The samples that were already converted were further heated in a vacuum furnace at 150 and 200°C for periods ranging from 4 hours to 1 week. The corresponding micrographs for wires with moderate deformation treated at 200°C are shown in Figure 19.

It is clear that after extended periods, the long and continuous filaments begin to break up and develop a more complex morphology. This spheroidization and coarsening was expected based on previous research [7, 15, 31], but the effect that it has on Al/Ca composite properties has not yet been well studied.

Several micrographs were gathered on smaller wires processed by drawing only to examine differences in the filament shape upon completion of extended heat treatments. Figure 20 shows that even after 1000 hours of exposure to 200°C, wires with η=9.67 still maintained long and continuous filaments indicating a noticeable difference from those that were initially processed by swaging.
Figure 19. Backscattered electron micrographs of Al/Al$_2$Ca (18 vol.%) at 6.74 after heat treatment at 200°C for: (a) 0 hours, (b) 4 hours, (c) 45 hours.

Figure 20. Backscattered electron micrograph of Al/Al$_2$Ca (18 vol.%) at 9.67 after heat treatment at 200°C for 1000 hours (draw only).
The following sections will discuss the electrical conductivity and tensile strength of these materials, both of which are extremely important for the intended application. The effects that converting filaments to an intermetallic species and extended heat treatments have on these properties were also investigated. Samples from the alternative processing route are also studied to determine whether the differences in filament morphology lead to modified performance properties.

### 4.4 Electrical conductivity of Al/Ca (11.5 vol.%) and Al/Al\(_2\)Ca (18 vol.%) composites

Given that the intended application of Al/Ca composites is high-voltage power transmission, conductivity is a critical property in evaluating the commercial viability of such conductors. The primary advantage of this material is the absence of a highly resistive steel core needed for strength in conventional conductors (ACSR). This monolithic construction allows for high conductivity across the entire cross section of the conductor with the direction of current flow being parallel to the filaments. The conductivity will be examined in as-drawn, converted, and wires with long exposure time to high temperature.

#### 4.4.1 Electrical conductivity: As-drawn and converted Al/Ca composites

Figure 21 shows results for conductivity measurements on both unconverted wires and those that have been transformed at various strain levels after the completion of all deformation processing (swaging and drawing).
Figure 21. Electrical conductivity of third-generation Al/Ca (11.5 vol.%)-SD composite before and after transformation of filaments to Al$_2$Ca intermetallic at various strain levels.

At low strain levels the conductivity is very close to the rule of mixtures prediction for the given formulation since current flows across the entire cross section and the filament size is significantly larger than the mean free path of electrons. Tian et al have studied the numerous scattering mechanisms in DMMCs and shown that by reducing the filament thickness and spacing, there is an increase in interface and grain boundary scattering that reduces the conductivity of the material [39]. These mechanisms have been shown to exist in previous generations of Al/Ca composite [6] and are clearly present here.

The effect on conductivity of the transformation of the filaments to Al$_2$Ca is evident, i.e., a diminished value, but the diminution was found to be small. For the wires subjected to the greatest level of deformation in this study ($\eta=12.7$), the measured drop in conductivity is less than 1%. Al/Ca (20 vol.%$)$ showed similar behavior as the material in this study for unconverted wires but displayed severe degradation after heat treatment [6]. This drop off in
conductivity can be attributed to a large fraction (32 vol.%) of the cross section being occupied by Al$_2$Ca after transformation. With the reduced loading of Ca in Al/Ca (11.5 vol.%), the transformation has a less substantial impact on the increase in interfacial area, and therefore the influence of interface scattering is not greatly affected. Even with this consideration, the very slight reduction that does not agree with (is well above) the ROM expectation for Al/Al$_2$Ca (18 vol.%) is a pleasant surprise. This minimal decrease in conductivity seems a worthwhile sacrifice in exchange for the high-temperature stability that the intermetallic phase could potentially provide. With complete transformation to Al$_2$Ca, the composite conductor material could have an increased upper use temperature, making it resilient even during emergency overloading situations [16].

4.4.2 Electrical conductivity: Extended heat treatment

As shown in the previous section, the microstructure undergoes significant change after heat treatment at 200°C. The filaments break up causing an increase in interfacial area between the Al$_2$Ca filaments and the aluminum matrix. This increase in area is in excess of what is caused by the initial conversion of the reinforcement to an intermetallic and is more difficult to quantify. Figure 21 showed that the modest increase in filament size had a small effect on the electrical conductivity since the filaments still remained straight and continuous. Figure 22 shows the electrical conductivity of samples that were exposed for various combinations of time, temperature, and atmosphere (air or vacuum) and includes the results from Figure 21 for comparison. The highest strain levels are not reported due to the inability to test finer wires that were more brittle than before aging.
Figure 22. Electrical conductivity of third-generation Al/Ca (11.5 vol.%) composite before and after transformation of filaments to Al$_2$Ca intermetallic at various strain levels with extended heat treatment samples.

It is clear that the electrical conductivity of converted wires is reduced as a result of all of the different heat treatment conditions used. There are several things that can be inferred from these results including the fact that it did not make a significant difference whether wires were heated in the presence of air or not. This indicates that the mechanism of degradation is not due to oxidation along the filaments. Additionally, from the small number of conditions tested, it appears that the conductivity will reach a minimum independent of the temperature at which the wires are aged. The implication of this finding is that this is a time dependent process that can be designed for or controlled.
4.4.3 Electrical conductivity: Alternative processing method

Figure 22 clearly showed that subjecting Al/Ca (or Al/Al$_2$Ca) wires to high temperatures for extended periods reduced the electrical conductivity of the material. The effects of eliminating the swaging step in producing fine wire on the electrical conductivity are shown in Figure 23.

![Figure 23. Electrical conductivity of Al/Al$_2$Ca composite wires produced by swaging and drawing (SD) and drawing only (DO).](image)

Figure 23 shows that unconverted wires without any heat treatment had a greater electrical conductivity when only using wire drawing to reduce the cross section. By maintaining a cylindrical filament shape as compared to increasing the aspect ratio, previously shown in Figure 15, the interfacial area for electron scattering is not as great. Selected exposure times at 150°C show that the draw-only samples also see a decrease in conductivity, but to a lesser extent than those that undergo swaging. Conductivity
measurements for the SD samples were only available for one wire size due to the limited amount of material that was produced.

Knowing that the material will reach an endpoint in terms of conductivity, the amount of initial calcium loading and the amount of strain imparted on the sample can be managed to give the properties that are desired. Given that the electrical conductivity is a function of at least these two parameters, it is also important to examine how changing them affects other properties of the material such as the tensile strength.

4.5 Tensile strength of Al/Ca (11.5 vol.%) and Al/Al<sub>2</sub>Ca (18 vol.%) composites

While decreasing the filament size by mechanical working lowers the conductivity of the composite, the primary motivation for doing this is to benefit from the unique strengthening mechanism of DMMCs. The Al/Ca (11.5 vol.%) composite had a reduced loading of Ca to facilitate the volume expansion of filaments upon transformation to Al<sub>2</sub>Ca but, it has been shown that there is an additional increase in interfacial area beyond this expansion after prolonged heat treatment. The tensile strength has been investigated for various strain levels because the strength increases exponentially as a function of reduced filament spacing in these materials [4, 7, 15]. The effect of converting filaments to Al<sub>2</sub>Ca reinforcement and thermal aging of wires has again been studied along with the elimination of swaging.

4.5.1 Tensile strength: As-drawn and converted Al/Ca composites

Figure 24 shows representative stress-strain curves for Al/Ca (11.5 vol.%) and converted Al/Al<sub>2</sub>Ca (18 vol.%) composites from tensile testing of 0.2 mm wires (η=11.5).
It is evident from the tensile test curves in Figure 24 that samples with intermetallic reinforcement fibers have superior strength to unconverted wires for this given level of deformation true strain. These trends are representative of other wires sizes that showed very similar behavior with increasing strength and apparent retention of ductility. Figure 25 shows the fracture surfaces corresponding to the wires that underwent tensile testing depicted in Figure 24.

Figure 24. Stress-strain curves for 0.2mm (η=11.5) Al/Ca (11.5 vol.%) and Al/Al₂Ca (18 vol.%).

Figure 25. Fracture surfaces of 0.2mm (η=11.5) tensile specimen: (a) pure Ca filaments, (b) Al₂Ca reinforcement after heat treatment.
The fracture surfaces seen in Figure 25 exhibit classic dimples in the Al matrix typical of fibrous ductile fracture [15]. Surprisingly, the composite still demonstrates ductile behavior after conversion to intermetallic reinforcement, even while achieving increased ultimate tensile strength. This could be very beneficial during both operation and winding of the conductor. The overall necking and area reduction in the unconverted sample are greater and indicates that macroscale defects dominate. The converted sample has greater strain-to-failure and less area reduction indicating that local micro defects are more dominant. Further analysis of the fracture surfaces of tensile specimen is necessary to fully characterize the ductility upon transformation to Al$_2$Ca reinforcement. The wires with the highest level of deformation true strain ($\eta=12.7$) were independently tested by Psylotech with the results shown in Figure 26.

![Figure 26: Stress-strain curve for ten 0.1mm ($\eta=12.7$) wires (a) five of which were unconverted, and (b) five of which had been converted.](image)

Again, it is shown that converting the reinforcement phase results in a higher strength. In addition to the results shown in Figures 24 and 26, various other size wires were tested to determine their ultimate tensile strength. Figure 27 shows the exponential relationship between deformation true strain and UTS for as-drawn and converted wire
samples at various strain levels with comparison to other conductors that would be suitable for HVDC transmission. The existing commercial wires used for comparison are shown in Table 1.

![Graph](image)

Figure 27. Tensile strength of Al/Ca (11.5 vol.%) and Al/Al₂Ca (18 vol.%) with Hall-Petch model fitting.

The influence of filament size and fractional loading suggests that interfacial area plays a major role in strengthening the composite. Study of early DMMCs had shown that interphase boundaries act as barriers to dislocation glide leading to interface strengthening [4]. This effect causes strength to increase sharply at high strains, which has been successfully modeled by a modified Hall-Petch barrier model for previous Al/Ca composites [5, 6, 23]. Based on measurements of filament thickness, the dependence on true strain was assumed to be ideal following the relationship of Equation 6 where \( d_0 \) is the starting Ca size.
\[ t = d_0 e^{-\frac{t}{z}} \]  

(6)

Using the calculated thickness from Equation 6 and the measurements of UTS, Hall-Petch relationships were determined for both as-drawn and transformed wires shown by Equations 7 and 8, respectively.

\[
UTS = -10.7 + \frac{148.0}{\sqrt{t}}
\]  

(7)

\[
UTS = 32.3 + \frac{146.8}{\sqrt{t}}
\]  

(8)

The evident strengthening effect from conversion of the reinforcement phase to intermetallic was expected due to the increase in interfacial area upon volume expansion of the filaments. It has been shown that both the material and composition of the reinforcement phase in aluminum matrix DMMCs influence the ultimate tensile strength of the composite \[5, 13, 12\]. When compared to Al/Ca (20 vol.%) and Al/Ca (11.5 vol.%), it appears that the filaments being comprised of Al\(_2\)Ca rather than Ca has little effect, and the volume of reinforcement is the dominant factor. The curves for these wires have a very similar shape and differ by an offset for most strain levels. This direct comparison of as-drawn and transformed wires however, fails to account for the impact of volume expansion on the effective true strain, but the heat-treatments are likely to reduce dislocation densities to low values. Measurements of the wire cross-section from SEM micrographs for various wire sizes indicate that the expansion of filaments does not appreciably change the overall dimension. The consequence of this finding is that the filament thickness calculated by Equation 6 needs to be adjusted by a factor related to the volume expansion of the filaments. By implementing this change, the effective true strain is reduced, and the measured strength values are shifted to the left as shown in Figure 28.
Figure 28. Tensile strength of Al/Ca (11.5 vol.%) and Al/Al₂Ca (18 vol.%) modified strain.

The major takeaway from analyzing the tensile strength with this adjustment is that Al₂Ca is a more effective reinforcement material than pure Ca. At high effective true strain levels (η>11), Al₂Ca-reinforced composite is expected to be stronger than Al/Ca wires containing a greater reinforcement fraction (higher than Al/Ca (20 vol.%)). Further study of the material properties of the Al₂Ca compound is necessary in order to utilize more advanced modeling techniques that incorporate the individual contributions from each phase to predict the strength [40]. From a practical standpoint, comparing unconverted and transformed wires on the basis of effective true strain is not ideal, as this would necessitate a larger starting extrusion billet size for converted wires that are of the same size.
4.5.2 Tensile strength: Extended heat treatment

Just as the microstructural changes resulting from thermal aging affect the electrical conductivity, they also affect the strength of converted Al/Al$_2$Ca composites. Figure 29 shows the strength measured at room temperature of wires that were aged for 45 hours at 200°C and various times at 150°C. Only samples that were aged in vacuum conditions are shown since it was found that they were not significantly different from those heated in air. Also, the highest strain ($\eta=12.7$) samples were not tested due to resource limitations.

![Figure 29. Tensile strength of Al/Al$_2$Ca after extended heat treatments.](image)

It is apparent that strength is reduced by long term exposure to elevated temperature. Similar to the results for electrical conductivity, differences in aging temperature and time did not have a significant effect on the results. Although the strength of these samples was reduced, it was still greater than that of the unconverted wire for all strain levels. Similar to
the modification of the deformation true strain that was made in the previous section to account for the volume expansion upon conversion of filaments, the strength values could be shifted based on their increased interfacial area from the break-up and coarsening of filaments. This is difficult to quantify in a definitive manner due to the irregular shape of the reinforcement after aging but, it could help guide future formulations since the curves would again be shifted further to the left as in Figure 28.

4.5.3 Tensile strength: Alternative processing method

In addition to the primary series of tensile tests conducted for Al/Ca composite wires deformed by a combination of swaging and drawing, selected samples that were drawn from the original extrudate by FWM were also tested. Figure 30 shows a comparison between these two methods for samples that were unconverted and those that were heat treated for an extended period.

At lower levels of true strain, the DO samples exhibit a lower ultimate tensile strength than those that were swaged. The lower values for this portion of this data series suggest that the more uniform filament deformation shown by SEM results in less interfacial area, a major contributor to the strengthening of DMMCs. This difference was also observed in the higher conductivity as compared to unconverted-SD samples. Beyond true strain values of 12 this difference in processing method becomes insignificant and the strength is similar. The strain gradient effect allows for the strength to greatly exceed rule-of-mixtures predictions.
Samples that were heat treated at 200°C for 45 hours also experience an increase in strength due to the conversion to Al<sub>2</sub>Ca reinforcement and the corresponding increase in interfacial area between the matrix and the filaments. An UTS of 515 MPa is observed for heat treated-DO wires drawn to a true strain of 13.12, the greatest measured strength of all samples in this study. It should be noted that the DO samples with a strain greater than 12 were measured with a Zwick/Roell Z 2.5 instrument at less than 10% of the load cell capacity. It is therefore necessary to independently confirm these data points with Psylotech. Despite this, it is still encouraging that high strength is observed and that the material is not becoming extremely brittle as was the case with Al/Ca (20 vol.%) after conversion to intermetallic reinforcement. It is therefore likely that the initial loading of calcium in this
composite is near the ideal level as high strength is achieved without degradation after prolonged exposures to high temperature. With this given composition, the strain level can be managed in order to achieve the properties necessary for a given application.

4.6 Summary of properties of Al/Ca (11.5 vol.%) and Al/Al₂Ca (18 vol.%) composites

For composites including two ductile phases such as the Al/Ca system, strains as high as 16 can be reached without fracturing, but in doing so, one must be mindful of the need to balance the tradeoff between strength and conductivity. Figure 31 shows the relationship between strength and conductivity for converted wires of the swage-draw series tested in this study. Existing commercial conductor technologies are included for comparison in addition to the 200°C-45 hr.-draw only Al/Ca sample that exhibited very high strength. This figure uses specific strength to highlight the benefit of reduced weight in Al/Ca composites.

Figure 31. Summary of specific strength and electrical conductivity of Al/Al₂Ca composites and commercial conductor technologies.
The very high strength of the result delineated with a star in Figure 31 highlights the fact that a wide range of properties can be achieved with a single formulation. Having lower weight is advantageous for overhead conductors since it enables larger conductors or increased tower spacing. In addition to these considerations, the highest attainable strain level seems to be dictated mainly by the starting billet size and ram force of the commercial extrusion capabilities that are available. Moving towards higher strain levels should be investigated as the potential benefits could be substantial. One potential option to be explored is sectioning and bundling of the extrudate then extruding a second time in order to achieve smaller filament spacing.
CHAPTER 5. Al/Ca COMPOSITE PERFORMANCE CASE STUDY

The effects of the reinforcement fraction and level of deformation on strength and conductivity have been discussed, and the tradeoff between the two is evident. This chapter will explore how the properties determined in CHAPTER 4. would provide benefits relative to conventional aluminum-conductor steel-reinforced (ACSR) materials. This analysis will use properties of converted Al/Al₂Ca (18 vol.%) composites with η=12.7, but the framework presented could be applied to other formulations and strain levels. Comments will be made about the previously discussed 200°C-45 hr.-draw only sample due to the high strength, but it has been excluded from the primary analysis since these results warrant further verification.

5.1 Case study design criteria

As discussed in CHAPTER 2. Al/Ca composite materials show promise for commercial adoption as overhead conductors. Therefore, it was decided to study the Pacific DC Intertie (Path 65), an existing HVDC transmission line in the western United States shown in Figure 32 [41].

Figure 32. Pacific DC Intertie map.
Using this existing system with the properties summarized in Table 5 [42], Al/Ca materials’ performance can be compared to conventional ACSR conductors’ performance. The comparison of the two was completed for two different cases including reconductoring on existing towers and a new installation with varied tower spacing. The conditions that were kept constant and varied in order to make this comparison are shown in Table 6.

Table 5. Pacific DC Intertie conditions specification.

<table>
<thead>
<tr>
<th></th>
<th>Total Distance</th>
<th>846 miles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductor Cross Section</td>
<td>1171 mm$^2$ (Bluebird)</td>
<td></td>
</tr>
<tr>
<td>Voltage</td>
<td>±500 kV</td>
<td></td>
</tr>
<tr>
<td>Rated Power</td>
<td>3100 MW</td>
<td></td>
</tr>
<tr>
<td>Number of Towers</td>
<td>4200</td>
<td></td>
</tr>
<tr>
<td>Current</td>
<td>3100 A</td>
<td></td>
</tr>
</tbody>
</table>

Table 6. Scenarios for case study.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Constant with base case</th>
<th>Varied</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACSR</td>
<td>As built</td>
<td>As built</td>
</tr>
<tr>
<td>Case 1</td>
<td>Tower spacing and weight per tower</td>
<td>Conductor Size</td>
</tr>
<tr>
<td>Case 2</td>
<td>Losses and weight per tower</td>
<td>Tower spacing and Conductor Size</td>
</tr>
</tbody>
</table>

In order to evaluate the size, installation conditions, and performance of Al/Ca composite conductors, several properties needed to be determined. The temperature of the conductor as a function of the current is important because conductors have upper operating limits [43, 44, 45]. Determination of this relationship was done according to the IEEE-738 standard and allowed for specification of the ampacity [43]. Another critical parameter for designing overhead transmission lines is the sag resulting from thermal expansion or added loading. This was determined by the numerical sag method (NSM) for initial stranding, high
temperature, and wind and ice conditions as specified by the National Electrical Safety Council (NESC) [44, 45].

5.2 Case 1 results

Case 1 considers a direct replacement of the transmission line using the same towers and assumes equal spacing for the ruling span. Additionally, it is assumed that the tower will only support the same conductor weight per tower. Figure 33 shows the relationship between current and temperature for the Al/Al\textsubscript{2}Ca and ACSR conductors. The conditions used as inputs for IEEE-738 to determine this relationship are shown in Appendix.

![Figure 33](image)

It is clear that under the assumed conditions Al/Al\textsubscript{2}Ca conductors would operate at a slightly lower temperature for a given current. This is mainly due to the fact that the cross-sectional area is larger, which is enabled by Al/Ca’s lower density. From an operational standpoint, using a different material that has a similar ampacity would not result in any
significant change. The primary difference comes in the vertical sag of the conductor as shown by Figure 34.

![Figure 34. Case 1 sag compared to ACSR.](image)

The sag of Al/Al$_2$Ca is lower because of a combination of higher strength and lower density. The upper temperature limit of a traditional conductor is typically limited by the thermal sag [44] so being able to achieve both of these properties simultaneously is advantageous. The NESC heavy condition for wind and ice loading was used to design the conductor for this case study. Table 7 shows the sag at these conditions in addition to the size of the conductor and other related results.

<table>
<thead>
<tr>
<th></th>
<th>ACSR</th>
<th>Case 1</th>
</tr>
</thead>
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<tr>
<td>Conductor diameter</td>
<td>mm</td>
<td>44.8</td>
</tr>
<tr>
<td>Conductor Area</td>
<td>mm$^2$</td>
<td>1181</td>
</tr>
<tr>
<td>Temperature at Max Amps</td>
<td>ºC</td>
<td>79</td>
</tr>
<tr>
<td>Sag at Peak Amps</td>
<td>m</td>
<td>9.22</td>
</tr>
<tr>
<td>Wind/Ice Total Sag</td>
<td>m</td>
<td>7.25</td>
</tr>
<tr>
<td>Wind/Ice %Rated Tensile Strength</td>
<td>%</td>
<td>42.7</td>
</tr>
</tbody>
</table>
One important parameter to point out is that a maximum rated temperature of 120°C was assumed for the design of this conductor. This was not of great significance in this case since the conductor size used would operate well below that point, and sag does not appear to be a major concern for the existing tower spacing. Since the use of larger conductors is enabled by high strength and low density, the benefit of Al/Al₂Ca for this case is a reduction in electrical losses from Joule heating as shown by Figure 35.

Figure 35. Case 1 electrical losses compared to ACSR.

Over the long span that is used in this case, and is typical of HVDC transmission lines, this reduction in electrical losses is very substantial. Even though the performance is improved for this case, the conditions are not ideal because the conductor is limited by size rather than sag or ampacity.

5.3 Case 2 results

The results from Case 1 showed that replacing an existing line with Al/Ca composite conductors can provide significant benefits, even though the system was not specifically
designed for their use. This case will show the benefits of using these materials with the tower spacing and conductor size being optimized for use on support towers that can hold the same load as the ACSR base case. Again, the ampacity was determined from the conditions summarized in Appendix and compared to that of ACSR as shown in Figure 36.

![Figure 36. Case 2 ampacity compared to ACSR.](image)

As with Case 1, the temperature of the conductor would be slightly lower for a given current, but the difference is less pronounced. The major difference is that the tower spacing was optimized so that at the maximum allowable temperature value specified, the sag of the conductor was equal to a maximum value. Figure 37 shows the relationship between temperature and sag for this case and compared to ACSR. The sag has a linear relationship with temperature since the conductor is constructed with a single material. ACSR also appears to be linear due to the fact that the maximum rated operating temperature is below the knee point of the conductor [44]. The accuracy of the conductor design in this case would be improved by further study of the upper operating temperature of Al/Ca conductors. Table 8 shows the conductor dimensions in addition to the sag values at the limiting conditions.
Figure 37. Case 2 sag compared to ACSR.

Table 8. Case 2 conductor properties.

<table>
<thead>
<tr>
<th></th>
<th>Conductor diameter</th>
<th>Conductor Area</th>
<th>Weight per unit length</th>
<th>Temperature at Max Amps</th>
<th>Sag at Peak Amps</th>
<th>Max Temperature</th>
<th>Sag at Max Temperature</th>
<th>Wind/Ice Total Sag</th>
<th>Wind/Ice %RTS</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>mm</td>
<td>mm²</td>
<td>lb/ft</td>
<td>°C</td>
<td>m</td>
<td>°C</td>
<td>m</td>
<td>m</td>
<td>%</td>
</tr>
<tr>
<td>ACSR</td>
<td>44.8</td>
<td>1181</td>
<td>3736</td>
<td>79</td>
<td>9.22</td>
<td>100</td>
<td>10</td>
<td>7.25</td>
<td>42.7</td>
</tr>
<tr>
<td>Case 2 Al/Al₂Ca</td>
<td>46.1</td>
<td>1253</td>
<td>3320</td>
<td>75.2</td>
<td>8.1</td>
<td>120</td>
<td>10.0</td>
<td>5.4</td>
<td>40.7</td>
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</tbody>
</table>

Table 8 shows that the conductor used for this case is slightly larger than the existing ACSR material. Even with a larger diameter, the support towers are able to be spread farther apart because of the higher strength and lower density that Al/Al₂Ca possesses. Figure 38 shows that the number of towers required is reduced while achieving equivalent electrical losses to the existing material.
Spacing towers further apart would likely not be done for an existing line, but new installations could benefit from the advantage that this provides. Towers and their associated engineering, installation, and right-of-way costs can contribute a significant amount (as much as 50%) to the total cost of a transmission project so eliminating towers would be a great benefit. Performing the same analysis as above for the 200°C-45 hr.-draw-only sample shows an example of even greater savings that may be achievable from reaching higher strengths, indicated in Figure 39. By increasing the spacing and using these very high strength wires, made possible by extensive deformation and heat treatment, a savings of nearly 1000 towers can be achieved for the given example. The exact spacing and size of the conductor may very slightly, depending on the application based on the necessary ampacity, tower support limits, and other factors.
It has been shown that using Al/Al₂Ca composite conductors in place of conventional ACSR steel-core conductors can provide benefits in terms of both initial investment and long-term costs. The properties of these materials can be tailored through intelligent formulation and processing to meet the needs of a specific application. The calculations presented in this chapter can easily be applied to other formulations and different existing conductors in order to quantify the benefits of using a certain material. The tradeoffs between strength and conductivity can be optimized in order to realize the full potential of this composite material.

Figure 39. Towers required for Case 2 using 200°C-45 hr.-draw-only conductor.
CHAPTER 6. CONCLUSIONS

- An Al/Ca (11.5 vol.%) composite with nanofilamentary reinforcement was produced by powder metallurgy and deformation processing to a maximum true strain of 12.7 by a combination of swaging and drawing.
- Differential scanning calorimetry identified the temperature at which Al$_4$Ca and Al$_2$Ca intermetallic compounds are formed and the dependence on true strain for these events.
- SEM micrographs showed similar ribbon-shaped filaments seen in prior generations of Al/Ca composite and the development of a complex morphology after extensive deformation processing. This modification of the filament distribution upon deformation was altered by the elimination of the swaging step during processing.
- After transformation of the reinforcement phase, volume expansion occurred producing Al/Al$_2$Ca (18vol.%) composite. Longitudinal micrographs revealed no significant filament coarsening or spheroidization after initial conversion.
- The electrical conductivity decreased with reduced filament spacing at high true strains. The transformation of filaments to Al$_2$Ca caused the conductivity to drop by less than 5% for wires subjected to the greatest level of deformation in this study (\(\eta=12.7\)).
- The ultimate tensile strength of as-drawn Al/Ca (11.5vol.%) composite increased with deformation true strain due to the strong influence of interface strengthening, which is well described by a modified Hall-Petch barrier model. The UTS increased upon transformation of the secondary phase due to
the increase in interfacial area and presence of a stronger reinforcement phase, but retention of a remarkable ductility also was found, even in the strongest wires.

- Extended thermal aging of wires resulted in the breakup of filaments and a modified microstructure. These changes led to a decrease in electrical conductivity and an effect on the tensile strength that does not appear to be significant.

- The alternative method of deformation processing explored without the inclusion of drawing showed improved conductivity for as-drawn wires as well as greater strength and conductivity at very high strain levels.

- Preliminary line sizing calculations indicate that the use of Al/Al$_2$Ca conductors in place of ACSR could reduce electrical losses by 12.4% for existing tower spacing or reduce the number of towers by 11.1% for the same losses. This reduction in the number of towers can be improved to a 23.5% reduction by using wires with the highest strain level studied.

- Al/Al$_2$Ca composite wires show promise to exhibit strength superior to current conductor technologies combined with high electrical conductivity, low density, and high temperature performance making them excellent candidates for use as HVDC transmission conductors.
CHAPTER 7. RECOMMENDATIONS FOR FUTURE WORK

- Laboratory samples were produced with high-purity aluminum powder supplied by Ames Laboratory. In order to ensure the same “clean” microstructure in commercial-scale production, Al with low oxide content must be used. This will require working with a corporate partner to improve their practices in producing Al of pigment quality in the appropriate size.

- Now that the concept of intentionally converting the reinforcement phase to Al₂Ca intermetallic has been proven, further confirmation of test results is necessary from industrial conductor companies. In addition, a full industrial prototype extrusion billet should be produced in order to provide enough wire for a complete conductor of sufficient length to test at Oak Ridge National Laboratory’s (ORNL) Powerline Conductor Accelerated Testing (PCAT) facility.

- In addition to the tasks described that will enable commercialization of Al/Ca conductors, further study of the transformation of Ca filaments to Al₂Ca is required. The effects of long-term heat treatments need to be better understood in order to assess the upper temperature limit of the material. Also, these studies will help guide the decision of the appropriate amount of calcium and deformation level in the production of future samples.
## APPENDIX. AMPACITY AND SAG CALCULATION PARAMETERS

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<th>Condition</th>
<th>Condition</th>
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<tr>
<td>Lat</td>
<td>Degrees of latitude</td>
<td>degrees</td>
</tr>
<tr>
<td>N</td>
<td>Date (M/DD/YY)</td>
<td>—</td>
</tr>
<tr>
<td>$T_a$</td>
<td>Ambient air temperature</td>
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</tr>
<tr>
<td>$V_w$</td>
<td>Speed of air stream at conductor</td>
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<tr>
<td>ZI</td>
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<tr>
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<td>Solar absorptivity (0.23 to 0.91)</td>
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<tr>
<td>$\varepsilon$</td>
<td>Emissivity (0.23 to 0.91)</td>
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<tr>
<td>$\varphi$</td>
<td>Angle between wind and axis of conductor</td>
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<tr>
<td>$\omega$</td>
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<td>Ice Density</td>
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<table>
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<tr>
<th>Case 1</th>
<th>Case 2</th>
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<tbody>
<tr>
<td>Conductor Type</td>
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</tr>
<tr>
<td>Tc</td>
<td>Minimum Temperature</td>
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<tr>
<td></td>
<td>Maximum Operating Temperature</td>
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<td>Conductor diameter</td>
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<td>$T_{low}$</td>
<td>Minimum temp dc resistance is specified</td>
</tr>
<tr>
<td>$T_{high}$</td>
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<td>Plastic Deformation</td>
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<tr>
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<td>---------------------</td>
</tr>
<tr>
<td>Strength</td>
<td>Rated Strength</td>
</tr>
<tr>
<td>%RBS</td>
<td>% Rated Break Strength at installation</td>
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<tr>
<td>weight/tower</td>
<td></td>
</tr>
<tr>
<td>Area</td>
<td></td>
</tr>
<tr>
<td>number of towers</td>
<td></td>
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<tr>
<td>total span</td>
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</tr>
<tr>
<td>total weight</td>
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**Initial Sag/Tension at Stringing Temperature**

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<tr>
<td>Total Initial Tension at Stringing Temp</td>
<td>lbs</td>
<td>28697.7</td>
<td>25505.3</td>
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<tr>
<td>Sag at Initial Stringing Temperature</td>
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**Sag at Peak Operating Amps**

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<th>75.16</th>
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<td>18010.3</td>
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<tr>
<td>Sag at Peak Amps</td>
<td>m</td>
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<td>6.75</td>
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**Sag at Max Operating Temperature**

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<th>120</th>
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<td>12173.2</td>
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<tr>
<td>Sag at Max Temperature</td>
<td>m</td>
<td>8.54</td>
<td>9.99</td>
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**Temperature/Ampacity at Max Sag**

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<td>12158.0</td>
</tr>
<tr>
<td>Sag</td>
<td>m</td>
<td>10.00</td>
<td>10.00</td>
</tr>
<tr>
<td>Ampacity at Max Sag</td>
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<td>2942.8</td>
<td>2305.3</td>
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**Wind/Ice or Cold Temperature Sag**

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<th>lbs</th>
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<tbody>
<tr>
<td>Total Sag</td>
<td>m</td>
<td>4.16</td>
<td>5.36</td>
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<tr>
<td>Vertical Sag</td>
<td>m</td>
<td>3.77</td>
<td>4.81</td>
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<tr>
<td>%RTS</td>
<td>%</td>
<td>40.01</td>
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PART 2: IN-SITU GAS-PHASE PASSIVATION OF MOLTEN CALCIUM SURFACES TO ENABLE DEVELOPMENT OF ATOMIZATION METHOD FOR GENERATING CALCIUM POWDER
CHAPTER 8. INTRODUCTION

Deformation processed aluminum/calcium composites are lighter, stronger, and more conductive than conventional overhead power transmission conductors, which gives them the potential to reduce electrical losses, lower costs, and enhance grid reliability. A principal barrier to full strengthening of Al/Ca composites is availability of fine Ca metal powder for co-extrusion with commercial Al powder, as it is not currently produced commercially. Fine Ca powder (<200µm) enables Al/Ca composites to achieve high strength by Hall-Petch hardening after the composite has been deformed to produce sub-micron-diameter filaments. Calcium powder does not form a protective oxide layer on its surface and must be passivated to ensure safe production and handling. A centrifugal atomization method for producing fine Ca powder at the laboratory-scale by has been developed that produces high yields of spherical powders in the desired size range [46]. This system utilizes an oil quench bath that cools and passivates the Ca powder coming off the rotating disc. In order to scale this process to larger atomizers (either gas or centrifugal), it would be advantageous to passivate the Ca powder surface during production through the use of a reactive cover gas rather than with an oil bath, which requires additional cleaning processes.

Experiments using an Induction Melting Passivation (IMPass) apparatus developed earlier and used to successfully passivate Mg powder were used to identify appropriate gas mixture and processing conditions for passivating Ca metal. The use of reactive cover gases is common in the Mg die-casting industry where the metal remains molten for timescales ranging from minutes to hours. Steinmetz used the IMPass system where shorter time scales of Mg exposure to reactive cover gases could be studied. These trials led to the eventual utilization of a cover gas during the gas atomization of Mg where the exposure time is even
shorter [47]. This work established a general method for the safe production of metal powders that do not form protective oxide layers [48]. Although gas passivation of Mg is practiced commercially, the exact protection mechanism is not completely understood. A similar strategy has been employed to develop conditions for an in-situ passivation technique during the atomization of Ca. Early attempts at achieving passivation of Ca with this system were done with a 1% SF₆ stream in Ar that had been successfully employed to create a protective layer on Mg surfaces. Various concentrations and exposure temperatures were investigated to determine conditions that could be used during atomization. An alternative passivating agent 3M™ Novec™ 612 Magnesium Protection Fluid (dodecafluoro-2-methyl-3-pentanone) was also studied [49].

The results of the different passivation trials were used to determine inputs to calculations that modeled the gas atomization of Ca powder. The atomizer was setup to inject a combination of gas streams to safely produce a very small batch of powder. The powder produced was analyzed to determine the success of the treatment. The preliminary production run can be used to inform decision about scaling to larger experimental trials and eventual commercial production.
CHAPTER 9. BACKGROUND INFORMATION

This chapter will explore the need to passivate calcium and methods previously used to protect reactive metals. The different compounds tested and the prospect of applying the findings of preliminary experiments to an atomization is discussed. Calculations necessary for implementing in situ passivation during atomization are performed.

9.1 Calcium oxidation

Like Mg, Ca does not form a protective oxide layer on its surface, which leaves it unprotected from its surroundings. The oxide that does form is permeable, allowing Ca vapor to escape and oxidize further. Pilling and Bedworth proposed a rule for determining whether the native oxide coating formed is protective as described by Equation 9, where \( n \) is number of metal atoms per oxide molecule and \( V_{\text{oxide}} \) and \( V_{\text{metal}} \) are the volumes of the elementary cell of the oxide and metal, respectively [50]. This ratio can also be expressed in terms of the molecular weight (MW) and density (\( \rho \)) of the metal and the corresponding oxide.

\[
R_{PB} = \frac{V_{\text{oxide}}}{V_{\text{metal}}} = \frac{MW_{\text{oxide}} \rho_{\text{metal}}}{n MW_{\text{metal}} \rho_{\text{oxide}}} \quad (9)
\]

When this ratio is less than 1, the oxide layer is porous or cracked, leaving the base metal exposed to continued oxidation. Ideally \( 1 < R_{PB} < 2 \), indicating that the layer is passivating. Table 9 shows the P-B ratio for a selection of metals.

Table 9. Pilling-Bedworth ratio for selected metals.

<table>
<thead>
<tr>
<th>Metal</th>
<th>P-B Ratio</th>
<th>Metal</th>
<th>P-B Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>1.28</td>
<td>Iron</td>
<td>2.06</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.65</td>
<td>Magnesium</td>
<td>0.84</td>
</tr>
<tr>
<td>Copper</td>
<td>1.70</td>
<td>Nickel</td>
<td>1.68</td>
</tr>
</tbody>
</table>
When Ca is left unprotected it will react with water or moisture in the air, forming flammable hydrogen gas. This is a significant safety concern; thus, it would be of great benefit to protect the exposed surface of molten Ca during production.

### 9.2 Calcium passivation reactions

Various studies on the passivating characteristics of Mg and other metals have found that fluorine-containing gases such as SF₆ are effective at modifying the native oxide layer and forming a protective coating [51, 52]. Metals react with fluorine until an adherent and protective film is formed that inhibits further reaction. Figure 40 shows a free-energy diagram for various relevant reactions with Ca [53].

![Figure 40. Ellingham diagram for various reactions with calcium.](image-url)
The formation of calcium fluoride is thermodynamically favorable and results in a more compatible surface layer. The oxide surface becomes cracked and susceptible to reaction to moisture in the environment without being treated. Given the similarity of Ca’s and Mg’s native oxide layer formation and oxidation and fluorination potentials, SF$_6$ cover gas was used for Ca passivation experiments following the established technique used for passivating Mg.

SF$_6$ is the standard in the Mg die-casting industry and was used to prove the feasibility of passivating Ca powder during atomization. This study investigates the passivation of Ca with SF$_6$ utilizing a modified version of the IMPass system originally constructed by Steinmetz [47]. The apparatus used by Steinmetz was adopted from earlier work by Cashion et al. that investigated the passivation of small molten puddles of Mg using fluorine containing gases [52]. This work led to the submission of Patent US 2017/0305808 that established a method for safely producing oxygen-reactive metals by gas atomization [48].

### 9.3 Alternative Passivating agent

In addition to the use of SF$_6$ as a passivating agent, other fluorine containing compounds were considered for utilization with calcium. One of these compounds was 3M™ Novec™ 612 Magnesium Protection Fluid (dodecafluoro-2-methyl-3-pentanone), a fluid that was developed to replace ozone depleting substances and materials with high global warming potential such as SF$_6$ (23,900 times that of CO$_2$ [54]) [6]. Novec™ 612 is a liquid at room temperature, so the gas delivery system utilized in these experiments was modified to incorporate a bubbling device allowing the F-containing compound to be transported by an Ar carrier gas that could be further diluted to a final concentration at a mixing point. The
concentration was calculated by assuming vapor-liquid equilibrium and from knowing the flowrate of the carrier and diluting stream, as well as the temperature and pressure of the bubbler [7]. In general, a much lower concentration of Novec™ should be required because it is a much less stable molecule than SF₆ [8].

9.4 Atomizer particle trajectory calculations

In order to scale the gas-phase passivation of calcium to an atomization trial, it was decided to use gas atomization rather than centrifugal. This allowed for easier control of the atmosphere, particle size distribution, and process monitoring. The location of where the reactive gas mixture was injected was calculated based on the target particle temperature determined by IMPass experiments. These calculations used the momentum and heat transfer framework outlined by Singh et al. to determine the velocity, temperature, and axial position of the droplet as a function of time [55]. Figure 41 shows the velocity of the particle as a function of distance, with the function of the form A/x representing the gas velocity.

![Figure 41. Atomization particle velocity profile.](image-url)
This plot shows that the velocity of the particle increases until the point where gas is moving slower at which point the acceleration becomes negative. The momentum results are coupled with the heat transfer of the particle which is primarily cooled by convection. Figure 42 shows a summary of these calculations and highlights the significant effect of particle size, which is primarily influenced by atomization pressure with this atomization gas die design [56].

Figure 42. Calculated particle temperature as a function of axial distance downstream, with origin at gas die.

The plateaus in Figure 42 represent the point at which the superheat is removed, and latent heat is being released. The time, and thus distance, over which this occurs is greater for larger particles due to a slower cooling rate and increased mass. The atomization pressure was controlled in order to achieve a desired particle size and the amount of gas delivered dictated the amount of reactive gas to be used. Further details about the concentrations of gas streams injected into the chamber will be discussed in the following chapter.
CHAPTER 10. EXPERIMENTAL PROCEDURE

This chapter will highlight the equipment and procedures used to study the passivation and atomization of calcium. The analytical techniques used to gather results from the materials produced are also discussed.

10.1 IMPass apparatus

An Induction Melting Passivation (IMPass) reactor was designed in order to study the passivation characteristics of Ca with brief exposure times similar to those that would be experienced during atomization. A schematic of the main components of the system is shown in Figure 43 [47].

Figure 43. Induction Melting Passivation (IMPass) schematic.
The IMPass system includes a quartz tube reaction chamber with 304 stainless steel flanges and is held in place by O-ring seals. Feed-through ports on the upper cap allow two rods to be moved vertically within the chamber during operation. The sample holder is threaded to the bottom of the center rod with an R-type thermocouple fixed to the vertical arm of the holder. The base of the sample holder is a removable rectangular stainless-steel piece with a cavity of approximately 0.2 cm$^3$ allowing for the sample to quickly be transferred to an inert glovebox after production. The use of the removable sample holder was required because, unlike Mg, Ca wets the stainless-steel surface due to its lower surface tension [57]. A water-chilled copper mold is located at the base of the chamber allowing for the sample to be rapidly cooled if needed. The second rod has a flat edged wiper blade allowing the surface of the sample to be cleared of floating impurities. Two Ta susceptor elements hang from the center rod allowing for sacrificial gettering of residual oxygen and heating of the sample. An induction coil surrounding a portion of the chamber is able to be moved vertically to switch between gettering and melting of the sample. The system has the ability to draw vacuum down to 10$^{-6}$ Torr and backfill the chamber with inert gas. The oxygen level is monitored with an Illinois Instruments 810 oxygen monitor, which can be isolated from the chamber before the introduction of reaction gases.

A gas mixing and delivery system allows for the reaction gas to be diluted with inert, ultra-high-purity (UHP) argon and routed either the sample chamber to or the exhaust system. When the gas is directed to the chamber, it passes through a crook-shaped tube positioned to spray directly at the sample. Sierra SmartTrak 2 Series 100 mass flow controllers are used to meter gas flows before the mixing point. Outflow gases from the
chamber are passed through a chemical scrubber containing a solution of Ca hydroxide to neutralize any potentially hazardous reaction products.

In order to introduce Novec into the reaction chamber it was necessary to bubble the liquid with a carrier stream. An assumption of Raoult’s Law allows for the concentration in the vapor space of the bubbler to be calculated when at equilibrium. The same setup used for IMPass experiments was utilized when injecting Novec into the atomizer. Three-way valves on both sides of the bubbler were used in order to allow flow to be diverted to the exhaust system or the reaction chamber prior to the initiation of flow through the bubbler.

### 10.2 IMPass samples/procedure

For each IMPass sample produced, approximately 0.3g of 99.99%+ purity Ca from the Ames Laboratory Materials Preparation Center was loaded into the removable portion of the stainless steel (SAE304) sample holder and affixed to the rod assembly. The cap and other components were then set atop the reaction chamber and tightened so that the atmosphere could be evacuated and exchanged. After several backfills, the system was left slightly over-pressured at approximately 14 kPa, which allowed the oxygen monitor to be utilized. After ensuring that the oxygen level was less than 200ppm, the induction coil was positioned for gettering, and power was supplied in steps until the reading was 0ppm. The sample holder was then aligned with the crook, and the induction coil was moved into the melting position. The melting point of Ca (842°C) was approached incrementally to ensure that the sample was heated uniformly and fully molten before the power was turned off. Once the Ca was fully molten and a clean surface was verified visually, the power was either shut off or reduced depending on the trial. Table 10 shows the different samples that were produced.
Table 10. Calcium IMPass samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Baseline-no gas</td>
</tr>
<tr>
<td>A2</td>
<td>SF₆ spray when molten</td>
</tr>
<tr>
<td>A3</td>
<td>SF₆ spray after cool to 550°C-long heat</td>
</tr>
<tr>
<td>A4</td>
<td>SF₆ spray after cool to 550°C-short heat</td>
</tr>
<tr>
<td>B1</td>
<td>Novec-0%</td>
</tr>
<tr>
<td>B2</td>
<td>Novec-0%</td>
</tr>
<tr>
<td>B3</td>
<td>Novec-0.34%</td>
</tr>
<tr>
<td>B4</td>
<td>Novec-1.0%</td>
</tr>
</tbody>
</table>

The reaction gas mixture used in the “A#” series of experiments was 1% SF₆ in Ar carrier gas with a total flowrate of 1500 scm³/m. The gas spray was initiated according to the descriptions shown in Table 10. The “B#” set of samples were allowed to solidify and cool to 400°C before initiating a gas (Ar) flow of 1500 sccm total flowrate with varied concentrations of Novec. Only the sample top surface was exposed with a surface area of approximately 0.6 cm². When molten, the calcium metal wet the surfaces of the sample holder resulting in a slightly concave surface that was sufficiently flat for analysis by auger electron spectroscopy (AES).

The flow was first established and routed to the vent so that it could quickly be switched to the sample chamber. Once the sample reached the desired temperature, the gas was allowed to flow for 10 seconds before being shut off, and the sample being quenched by the water-cooled Cu mold.

10.3 Calcium atomization

Preliminary experiments indicated that a Novec concentration of less than 0.3% mass was sufficient to passivate Ca surfaces, even at low flowrates (1500 sccm) [58]. It has been
demonstrated that lower concentrations can be used at greater flowrates because of the high F-content of the molecule [59]. An overall concentration of 0.1\% mass Novec was targeted for the initial Ar gas atomization experiment with molten Ca, where this concentration calculation included atomization gas, carrier gas, and other diluting gas streams. Oxygen containing Ar gas was injected into the atomization chamber prior to the Novec to achieve 2000 ppmv in order to prevent unwanted byproducts that could form upon breakup of the F-containing Novec molecule [59].

The locations and concentrations of the gases injected into the atomization chamber were calculated (Figure 44) to achieve the described overall concentrations. An atomization die with 30 discrete circular jets, each with a diameter of 2.08mm (0.082 inches) and a jet apex angle of 14 degrees was used. An atomization pressure of 100 psia was used to ensure suction and promote Ca flow. Immediately around the die, a “mini-halo” of Ar supplemental gas was utilized to contain the spray and to prevent early contact with the chamber walls. A pressure of 65 psia was used for the mini-halo flow to balance the total amount of gas in the chamber. Mass flow correlations were conducted for the die (10.9 kg/min), mini gas halo (0.8 kg/min) and oxygen injection halo (1.3 kg/min) so that they could be controlled based on pressure. The reaction gas halo was controlled with rotameters since the desired mass flowrate was much lower (0.085 kg/min) and Novec had to be bubbled with a carrier stream. Argon was used for the carrier stream, atomization gas, mini gas halo, and to dilute the carrier stream. The oxygen stream was from a premixed tank containing 2\% vol. O\textsubscript{2} in Ar. The relative locations of the various gas streams within the atomization spray chamber are depicted in Figure 44.
The reaction gas halo supply was comprised of a Novec bubbler stream and a separate Ar diluting stream since the concentration of the bubbler stream is governed by vapor pressure, gas pressure, and temperature with a vapor-liquid equilibrium assumption being made [60]. The overall concentration of Novec delivered through the halo was 19.1% mass. The reaction gas halo was made of stainless steel, previously shown not to react with Novec, and placed downstream of the gas die between main spray chamber sections with an outside diameter of 30cm (1.7 in.). The other 30cm (11.7 in.) O.D. oxygen halo and 15.24cm (6 in) O.D. mini gas halo were constructed from 9.53mm (3/8 in.) copper tubing and inserted inside of the chamber walls. The halos contained 0.737mm (0.029 in) diameter holes around the circumference oriented as shown in Figure 44.

Passivation experiments indicated that spraying a “fresh” calcium surface after melting, solidification, and cooling to 400°C resulted in a protective layer [58]. Momentum and heat transfer calculations were performed to determine the location where the droplets
would reach this temperature [55]. Based on these calculations, the reaction gas halo was located slightly beyond 1 meter downstream of the die to ensure that large particles were solid at this point, even though a d50 of less than 100 µm was expected. The oxygen halo was placed 0.3 m above the Novec halo so that oxygen was present in the chamber atmosphere at the time the Novec was introduced.

An initial atomization attempt was made but was unsuccessful because the desired superheat temperature of 950°C (MP=842°C) was not reached and the Ca froze out when the stopper rod was pulled (Figure 45).

Figure 45. Freeze-out of Ca atomization without sufficient superheat.

This deviation from the plan was made because the high vaporization rate of Ca made it appear as if the charge was completely molten for an extended period. System modifications were made that improved visual monitoring of the crucible and mitigated the negative impacts of rapid vaporization. The melt system consisted of a crucible, stopper rod, and pour tube that were all constructed of mild steel. Yttria paint was used to coat the stopper rod and pour tube to ensure that the melt was not discharged prior to pulling the stopper rod and to prevent bonding of the steel/steel interface. A charge of 600 g of Ca pellets was used
with a targeted atomization time of less than 5 seconds. This short second experiment was designed to generate a minor Ca powder sample for testing, but to minimize risks associated with a Ca droplet spray or Ca powder since calcium had not been gas atomized previously.

### 10.4 Analysis techniques

IMPass samples were analyzed using a FEI Teneo LoVac Field–Emission Scanning Electron Microscope (FE-SEM) and Auger Electron Microscopy (AES) for surface characterization. Samples were immediately transferred from the reaction chamber to an inert glovebox and sealed to minimize exposure to air. The “B” samples described in Table 10 were tested to identify their response to exposure to atmospheric conditions.

The small amount of powder produced (<3 g) was collected and analyzed for size distribution with a Microtrac S3500 laser diffraction particle size analyzer. Energy dispersive X-ray spectroscopy (EDS) provided an early determination of whether fluorine was present and to identify any undesired materials in the powder sample. AES was used for further surface characterization and depth profiling of powder samples. Spark testing with a Tesla coil in air provided an early indication of the ignition behavior of the powder. Further analysis of the ambient atmosphere ignition behavior was completed by heating powder samples in a small crucible in air with a type K thermocouple in a furnace with a temperature ramp programmed at a rate of 15°C/min. While crude, this method has successfully been employed for both Mg and Ca powders and gives a clear picture of the ignition temperature. Thermal gravimetric analysis (TGA) was also utilized to observe the ignition temperature and, together, these results were compared to previously produced powders and those from different size ranges. The results of this experiment provide an indication of whether Ca powder can be safely gas atomized and if the product is safe to handle.
CHAPTER 11. RESULTS AND DISCUSSION

This chapter is divided into three main topics. The first two discuss the results from IMPass experiments with SF$_6$ and Novec cover gases. The third shows the results of the atomization trial that was conducted with in situ passivation.

11.1 IMPass experiments with SF$_6$

Sulfur hexafluoride (SF$_6$) was investigated first due to the previous reported success in the passivation of magnesium. The intention of this experiment was to use a low concentration of SF$_6$ that would provide fluorine for reaction with bare metal surfaces.

11.1.1 Temperature profiles of SF$_6$ IMPass trials

To establish a baseline, Sample A1 was produced by simply melting the Ca sample and quenching it without any gas flow to the reaction chamber. Sample A2 introduced the reaction gas stream just as the power to the induction coil was shut off when the Ca was fully molten. Figure 46 shows the temperature profile for the production of Sample A2.

![Temperature profile](image)

Figure 46. Temperature profile with 1%SF$_6$ sprayed when molten, Sample A2.
Figure 46 shows that the melting point was approached incrementally. This was done because the thermocouple was positioned on the arm of the sample holder, so brief holds allowed the Ca sample to heat through and ensure uniform temperature. In addition, the power adjustment to the induction coil was controlled manually, so reaching the melting point in stages allowed for greater precision. By turning the power off and cooling the sample on the water-chilled copper mold, the temperature dropped by more than 600°C within five minutes. The still frame images in Figure 47 from video taken of the IMPass unit for Sample A2 show the progression of events.

Figure 47. Sample A2 still frame images. a) Before melting, b) Fully molten, c) Gas spray on and power off, d) Solidification.
In Figure 47a, the Ca has not yet melted, and power is still being supplied to the induction coil. The next image shows the sample once fully molten with the presence of a clean, mirror-like surface. The Ca liquid spills over the edge of the cavity due to the large volume expansion upon transition to the liquid state (1.55 to 1.38 g/cm$^3$) [61] and wets the surface of the sample holder. At this point vaporization of calcium is visually evident, but no significant loss of mass was observed over the brief exposure to elevated temperature. Figure 47c shows the simultaneous shut off of power and initiation of the gas flow. Due to the close proximity of the crook to the sample surface, the gas velocity disrupted the melt pool at the lower left corner during the spray prior to solidification. The sample’s incandescence indicates that the gas stream is reacting exothermically with the molten Ca surface. The disruption of the molten Ca surface and excessive reaction prompted tests on Samples A3 and A4 where the sample was solidified prior to initiation the gas flow. Sample A3 and A4 were both produced after cooling to 550°C with the same gas velocity and composition as Sample A2. The only difference between these two samples was the amount of time that they were held at high temperature prior to the completion of melting. Figure 48 shows the temperature profile for both of these runs with the time scale adjusted so that the point where the heat was reduced to begin solidification lines up. The axes of this figure are restricted to give greater detail in the area of interest.
Figure 48. Temperature profile with 1% SF₆ sprayed after cooling to 550°C, Sample A3 and A4.

Figure 48 shows that Sample A3 was held at the highest power setting that led to complete melting for approximately eight minutes in contrast to Sample A4, which was held at this setting for only three minutes. By holding the sample at a temperature of over 425°C for a longer time, the Ca is able to oxidize to a greater extent due to the onset of “breakaway” where the rate of oxidation increases dramatically [62]. Although the chamber was evacuated and gettered prior to operation, there are still trace amounts of oxygen with which the Ca can react. Figure 49 shows the various stages of production in the IMPass system for Sample A4 which had the shorter heat-up time.
Figure 49. Sample A4 still frame images. a) Before melting, b) Fully molten, c) Solidification, d) Gas spray.

Similar to Figure 47, Figures 49a and 49b show the sample before and after melting, respectively. In this case the power was reduced to a lower setting rather than completely turned off since it was desired to reach a temperature of 550°C. Figure 49c shows that shortly after the power is reduced the sample solidifies and appears to be relatively flat and uniform. Once the target temperature was reached, the heat was turned off completely, and the gas spray was started. Figure 49d shows a significant decrease in sample specularity. In the case of Sample A3 the color change was not as significant, possibly due to the fact that a base oxide layer formed preventing the Ca from reacting as forcefully with the fluorinated reaction gas. Figure 50 shows images of the three different samples that were exposed to SF$_6$ after removal from the IMPass unit.
Figure 50 clearly shows that the three samples produced appear to be very different as a result of their processing conditions. Sample A2 has a pinkish color with the lower left corner appearing different from the remainder of the sample due to the high gas velocity in that area. Sample A3 looks similar to bare calcium with areas that appear porous arising from shrinkage during solidification. Sample A4 is similar to Sample A3, but the color is much darker. The correlation between the different processing conditions and the physical appearance of the samples was explored further by using SEM to examine the surface at higher resolution and AES to determine the composition at various depths of the sample.

### 11.1.2 Microstructural analysis of calcium produced by IMPass reacted with SF$_6$

Prior to etching during Auger spectroscopy, scanning electron microscopy was used to identify scan locations and reveal differences in topography. Figure 51 shows micrographs of Sample A1 that was not exposed to any reaction gas at two different magnifications.
Figure 51. Sample A1 baseline calcium microstructure with no gas spray.

The poor $R_{PB}$ of the oxide layer is evident with cracks seen across the sample. In subsequent samples it was desired to modify this layer during production to eliminate cracking and protect the base metal. As previously described, Sample A2 was the first attempt at passivating the surface of Ca; with the SF$_6$ gas spray being initiated when the sample was still molten. As shown in Figure 47 and Figure 50, the gas appeared to react excessively with the molten Ca. Figure 52 shows micrographs of Sample A2 and confirms that this reaction was excessive because charging occurred.

Figure 52. Sample A2 microstructure with 1% SF$_6$ sprayed when molten.

The sample surface looks significantly different than Ca metal without reaction gas because there are no cracks. The fact that charging was an issue and the sample appeared pinkish indicate that there is little base metal and the reaction proceeded further than the
intended goal of producing a thin reaction layer. Sample A3 was produced with the gas being sprayed after solidification and cooling to 550°C in an attempt to decrease the extent of the reaction. Figure 53 shows micrographs of Sample A3 where there appears to be limited cracking.

![Micrograph of Sample A3](image)

Figure 53. Sample A3 microstructure with 1% SF₆ sprayed after cooling to 550°C-long heat.

Instead of cracks, there appears to be wrinkles on the sample surface, which is consistent with the protective films formed in the passivation of Mg [47]. This layer is likely more ductile and adherent than that formed on pure Ca and can possibly act as a barrier to diffusion. Sample A4, which was processed at the same conditions as Sample A3 other than the amount of time to heat to the melting point, has a similar appearance as shown by Figure 54.

![Micrograph of Sample A4](image)

Figure 54. Sample A4 microstructure with 1% SF₆ sprayed after cooling to 550°C-short heat.
Although there appears to be a modification of the sample surface from spraying it with SF₆, micrographs do not give any indication of the film composition. Further analysis with Auger electron spectroscopy was conducted on locations identified with SEM.

11.1.3 Auger Electron Spectroscopy analysis of calcium produced by IMPass reacted with SF₆

Auger electron spectroscopy (AES) was utilized for surface characterization of Ca samples produced in the IMPass unit. AES was performed at different depths after etching with an ion beam gun that was calibrated using a silica-on-silicon standard to an etching rate of 10 nm/min. Sample A1 was analyzed to establish a baseline for the analysis to get a sense of how thick the native oxide layer was after being exposed to air during transfer to storage and the analysis chamber. Figure 55 shows the relative intensity of the AES signal (counts per second) against the etching depth.

![Figure 55. Sample A1 baseline calcium AES with no gas spray.](image-url)
The thickness of the oxide layer was estimated to be 40 nm by identifying the position of half the height of the peak as delineated by the dashed line on Figure 55. One thing to note is that the oxide thickness is not necessarily a product of the reaction conditions because oxidation continues through the film that does not prohibit diffusion. Care was taken to quickly disassemble the apparatus and transfer the removable portion of the sample holder to an inert glovebox. Samples were transferred from the glovebox to the AES unit just prior to analysis to limit air exposure. This same procedure was followed for all subsequent samples to ensure consistency. An attempt was made to analyze Sample A2, but excessive charging caused issues with the AES spectral signal. In addition, both S and F still appeared to exist in high concentrations after sputtering for a total of 150 minutes indicating that the layer formed was extremely thick. The AES results for Sample A3 where the film formed is not excessively thick are shown by Figure 56.

Figure 56. Sample A3 AES with 1% SF$_6$ sprayed after cooling to 550°C-long heat.
The results in Figure 56 are surprising because there appears to be no fluorine present at any depth since the signal does not rise above the baseline value. This is inconsistent with the thermodynamic predictions of Figure 40, which indicated favorable fluorination under the experimental conditions. Instead, sulfur was found to be present after an initial layer of oxide at a very shallow depth of less than 5 nm. The presence of oxide was most likely due to the oxygen entrainment during sample transfer because it is on top of sulfur which is present to a depth of about 18 nm. Sample A4 gave also showed no significant fluorine signal and a layer of sulfur was present before reaching the base metal (Figure 57).

![Graph](image_url)

**Figure 57.** Sample A4 AES with 1% SF₆ sprayed after cooling to 550°C-short heat.

In this case oxygen is present to a depth of about 5 nm, while sulfur remains at 30 nm based on the position of the half height of the peaks. The film in Sample A4 being thicker
than Sample A3 is consistent with what was observed visually during production where the reaction appeared more extensive and a greater degree of color change was seen. Still the fact that sulfur reacts with Ca instead of fluorine is surprising and undesirable. The various experiments on the passivation of magnesium found that fluorine reacted with the metal surface and little to no sulfur was present [47, 51, 52]. Given that Mg and Ca have similar thermodynamic properties in the reaction environment, a similar result was expected in these Ca passivation trials.

SF₆ is known to decompose to a certain extent at elevated temperatures where fluoride ions are released and free to react with other substances. The unexpected absence of fluorine indicates that that the SF₆ molecule is decomposing or reacting with other surfaces in such a way that sulfide ions become available to react with Ca. The Ta elements in the chamber were sampled and analyzed by SEM and Energy Dispersive X-Ray Spectroscopy (EDS) to see if the fluorine was preferentially reacting with that material, which operates at a higher temperature, but no significant amount of F was found on the Ta. The stainless-steel spray tube in the reaction chamber was also sampled and found to contain more than 3.6% wt. fluorine by EDS. Figure 58 shows SEM images of a clean stainless-steel tube and the reacted piece taken from the IMPass chamber.

Figure 58. SEM of a) clean and b) reacted and oxidized stainless-steel tube.
One difference from the Mg experiments was that the temperature at which the gas spray initiated for Samples A3 and A4 was 550°C instead of 400°C. This value was selected to match the ratio of absolute temperature to the melting point that had been successfully utilized in the passivation of Mg. It is possible that the decomposition path of SF₆ is different at this higher temperature in leading to the results that have been observed. Since the gas was found to react with the tube, possibly even before being delivered to the sample surface, a Monel tube that is more susceptible to reaction with fluorine was used instead. Additional tests using SF₆ revealed that there was still no fluorine on the surface. Since the SF₆ reaction resulted in an undesired sulfide product being deposited selectively on the Ca surface, alternative F-containing compounds were sought.

11.2 IMPass experiments with Novec 612

Given that Ca surfaces were found to contain high concentrations of sulfur upon reaction with SF₆, Novec 612 was investigated because it contains no sulfur. The decomposition of the fluorinated ketone happens more readily than with SF₆, a very steady molecule, thus a lower concentration is required [49].

11.2.1 Temperature profile of Novec 612 IMPass trials

The temperature profiles and sample appearance during production of Novec samples were very similar to those when SF₆ was used. Figure 59 shows the temperature profile for sample B3, the first sample that contained any reactive material.
Figure 59. Temperature profile of IMPass experiment B3 with 0.34% wt. Novec spray.

The temperature was allowed to drop down to a target temperature of 400°C and gas flow was directed at the sample surface. Prior to reaching this temperature, the argon carrier gas was started with the valve arrangement of the bubbler system set so that it was vented to the exhaust. This enabled the stream to be established and quickly run through the bubbler for the short time desired. After initiation of the reactive gas flow a change in the shade of the sample is evident as indicated by Figure 60.
Figure 60. Sample B3 still frame images. a) Before melting, b) Fully molten, c) Solidification, d) Gas spray.

After the reactive gas flow was terminated by bypassing the bubbler, the sample was lowered to the chilled copper block. In the case of reaction with SF$_6$ it was initially believed that a change in the sample appearance would correspond to successful passivation with fluorine. With Novec, the absence of sulfur again suggests that this may be the case.

11.2.2 Microstructural and Auger Electron Spectroscopy analysis of calcium produced by IMPass reacted with Novec 612

The sample surface was analyzed by SEM and found to be more adherent than the native oxide of untreated Ca surfaces as shown by Figure 61. As was evident from the previous section, the fact that the sample surface appears to have been modified does not
necessarily correspond to fluorination. AES is a more appropriate indicator so scan locations were identified as shown by Figure 62.

Figure 61. Sample B3 microstructure with 0.34% wt. Novec spray at 400°C

Figure 62. Calcium with 0.34% Novec™ spray AES scan locations SEM.
The sample showed crystallites on the sample surface in addition to large charging artifacts. Figure 63 shows results of AES depth profiling for sample B3 treated with 0.34% wt./0.04% vol. Novec™ 612 in two different locations on the surface delineated in Figure 62.

![Auger depth profile](image)

**Figure 63.** Auger depth profile in two different locations (a) Location 1 (light). (b) Location 2 (dark).

Figure 63a shows that the lighter shaded region in Figure 62 contained a significantly enhanced fluorine concentration for at least the first 5 nm of milling. While such a thin surface layer is desirable, it must inhibit excessive air oxidation by penetration of the base metal. Figure 63b shows that there was no F-enhancement in the darker shaded region, represented by scan location 2. This could be due to incomplete coverage with the passivating agent or, more likely, preferential fluorination of existing cracks in the oxide layer formed upon solidification and cooling.
The presence of fluorine only in existing cracks supports the postulate that CaF$_2$ is being formed by reaction with the base metal. Steinmetz reported the formation of a magnesium oxy-fluoride as a result of passivation treatments and these compounds have also been utilized for other coating applications [4,9]. However, calcium oxy-fluorides are not known to exist and studies on reactions of perfluorocarbon (PFC) gases with calcium oxide have shown no stable calcium oxy-fluoride products [10]. The implication of this is that reacting Ca metal with F-containing gases will not result in a continuous layer if there is an existing oxide on the surface. If there is already some CaO layer, as is the case in Figure 62, the passivating gas appears to fill in the exposed oxide-free surface cracks that result from Ca having a Pilling-Bedworth ratio of 0.65 [2]. With this ratio far less than 1, CaO acquires a cracked and spalled structure on cooling that is weak and not effective in preventing further reaction by oxidizing gases, unless over-coated with a passivating layer [11]. The discontinuous CaO layer is subject to further cracking as the material cools and layer adhesion, plasticity, residual stress, and differences in thermal expansion interact.

After demonstrating the ability to deposit a F-enhanced surface layer on Ca, oxidation weight gain experiments in ambient air were used to evaluate the effectiveness of passivation treatments. Apel and Svec studied the kinetics of the reaction between calcium and water vapor and determined that weight gain followed a logarithmic rate law [12]. A parabolic oxidation rate law is used to describe most metals that form a compact and protective film while a linear relationship is indicative of a porous coating. These data trends were used for comparison in determining whether successful passivation had occurred. The “B#” series in Table 10 listed the different samples that were produced for these trials according to the same procedure used for samples analyzed by AES.
These samples were produced and kept under inert conditions until cooling to room temperature. At this point each sample was removed and immediately placed on a high-precision balance and mass gain data was logged using 5 second intervals, over 22 hours. The experiment for Sample B1 was conducted in a controlled atmosphere with the relative humidity maintained at less than 5% using cylinders of dry air. No measurable weight gain was observed so it was determined that the effect of water vapor in the air was the dominant contribution to oxidation of the metal. All of the remaining trials were conducted under ambient conditions with the humidity being monitored but not controlled. Variations over time fell within the interval of 48\textless RH \textless 53 for all of these trials and were considered to be insignificant to the observed results. Figure 64 shows the results of the various oxidation weight gain experiments.

![Figure 64](image)

Figure 64. Oxidation weight gain for various passivation treatments with Novec™ 612.
The oxygen uptake displayed by Sample B2 follows the logarithmic profile that was anticipated for bare Ca metal that does not form a protective native oxide layer. By introducing 0.34% wt. Novec™ after melting and cooling to 400°C, as was done with the AES sample shown, the initial oxidation rate was greatly reduced providing a passivation delay. However, after a period of approximately 5 hours a sudden increase in the oxidation rate occurred. This undesirable increase can likely be attributed to blistering of the surface where cracks admit oxygen and fresh metal surface are exposed resulting in the resumption of logarithmic oxidation behavior [12]. It has been shown with SF₆ passivation of Mg that a higher concentration of the passivating compound results in a film with a greater fluorine content and that longer exposure times can lead to thicker films [13]. Sample B3 utilized a higher concentration (1% wt. Novec™) to determine whether a layer that is not susceptible to cracking could be formed. Figure 64 shows that this change instead resulted in a higher initial oxidation rate and a similar breakaway oxidation event occurring after a similar number of hours.

Given that this two-staged behavior still existed for higher concentrations, it has been considered that the cause of the increased diffusion of oxygen stems from the excellent wetting of liquid Ca with the stainless-steel sample holder and the large solidification shrinkage that occurs. The samples produced are essentially small castings, and with good adhesion to the edges, the part is restrained resulting in residual stresses. Increased hinderance of a feature has been shown to result in greater tensile forces in castings and can lead to cracking [14]. Since the cast Ca part is unable to be removed from the mold before cooling to room temperature, this effect is significant, and the large solidification volume decrease of 11.1% is accommodated (Figure 65) by residual tension on the surface and
cracking [15]. Fortunately, this situation does not accurately reflect atomization conditions where droplets are not in contact with other surfaces during solidification. Attempts have been made to coat the sample holder with various “release” compounds but wetting still occurred.

Attempts were made to use a levitation melting approach where the sample holder is eliminated completely. This electromagnetic levitation (EML) technique can exert a force on a sample such that gravity is opposed while melting and solidification can be performed without the use of a container [16]. This method has been used for levitating metals in both the solid and liquid state with the coupling of levitation and heating being an important feature [17]. Elimination of the sample holder would allow for Ca sample processing that is more representative of atomization where the metal droplets are not constrained. By solidifying and cooling in the sample holder, the Ca sample is in tension leading to the formation of cracks in the surface as shown in Figure 65.

![Figure 65. Cracks on surface of Ca passivation sample.](image)

These cracks in the surface are not necessarily a product of poor passivation, but rather may be related to the casting technique and large solidification shrinkage. Removing
the container and repeating the oxidation weight gain experiments discussed above would result in a better understanding of the influence of the passivation treatments.

Ultimately, these passivation experiments should produce a thin, F-containing layer on the surface of Ca that results in an oxidation rate that slows over time. This would indicate that the layer is compact and protective and could be aided by the surface layer under compressive strain resulting from solidification while not being hindered by the sample holder walls. This method was not pursued further due to an inability to maintain stable levitation of the sample, likely caused by the very low density. The results of IMPass experiments and preliminary EML tests provide insight on how a lab-scale atomization trial with in-situ passivation could be performed.

11.3 Calcium gas-atomization trial

Given the safety concerns associated with the production of calcium with a high surface area to volume ratio, several precautions were taken to ensure that risks were minimized. The first attempt at atomization was unsuccessful with freeze out occurring immediately after the stopper rod was lifted. The second attempt was successful after raising the amount of superheat delivered to the charge in the crucible. Since such a small quantity of powder was produced, the number of tests that could be run was limited to those that require little material. Emphasis was placed on visualization of the atomization, non-destructive analysis techniques, and those requiring small amounts of material.

11.3.1 Calcium powder production overview

High-speed video of the atomization at the die was captured for the short duration of the experiment with a still image from this video shown in Figure 66.
Figure 66. Still frame of established atomization spray from high-speed (7360 fps) video.

The flow of liquid metal was terminated by unintended freeze-off after only 0.22 seconds, apparently the increased superheat (~50°C more) was still only marginally sufficient. A larger Ca crucible charge amount was chosen to provide metallostatic head pressure to ensure that the liquid metal would flow, even though it was intended to produce a much smaller amount of powder. A total of 2.4 grams of powder was collected and used for analysis with the particle size distribution shown in Figure 67.

Figure 67. Calcium atomization particle size distribution.
The average particle diameter was determined to be 85\(\mu\)m, which was anticipated from similar experimental knowledge based on the selected atomization pressure and gas die. A smaller powder size could be achieved to give a finer final filament size in Al/Ca composites for enhanced strengthening by modifying the parameters of the atomization. For this initial attempt at atomization, it was more desirable to maintain a smaller surface area to volume ratio to mitigate the inherent safety risks of producing clean metal surfaces. Although 2.4 grams of powder is seemingly very little, the low density of calcium makes this appear to be a significant amount as shown by the photograph in Figure 68.

![Figure 68. Photograph of collected gas atomized calcium powder.](image)

The collected powder was screened to define the particle size ranges used for analysis. Prior to this, a top cut was made that removed the small amount of material that was greater than 250\(\mu\)m and a random sample was taken to study the microstructure of the powder produced.
11.3.2 Microstructural analysis of gas-atomized calcium powder

The low magnification micrograph of the powder sample shown in Figure 69 indicates that the atomization was successful in producing generally spherical Ca powder particles. Given the short duration of this run and the fact that this was the first time Ca was gas atomized, it is not surprising that the size distribution is wide and that there are satellites on many particles.

![Wide field micrograph of -250μm Ca powder.](image)

Figure 69. Wide field micrograph of -250μm Ca powder.

There are many irregularly shaped particles and some occurrences of internal porosity are evident. Higher magnification micrographs were captured to further study the surface topography of the powder sample and the various surface features exhibited. Figure 70a shows the entrance to internal porosity displayed in a single particle and, in Figure 70b, the presence of apparent oxide flakes/patches (~6 μm) that seem to cover the surface of a particle.
The porosity shown is a result of the entrainment of a significant amount of gas within the particle. Although porosity is seen in several particles, it could likely be reduced by fine tuning of the atomization parameters including the gas-to-metal ratio. The oxide particles present on the surface are mostly calcium oxide, but there is also some yttrium oxide present that can be traced back to the paint used to coat the surfaces of melt system components. Oxygen levels in the system were intentionally high in order to mitigate any risk associated with the decomposition of the Novec compound. Future atomization experiments could reduce oxygen levels by confirming that there are no dangerous byproducts resulting from the exposure of Novec to high temperatures.

The intent of this gas-phase reaction experiment was to create a thin passivation layer on the surface of the particles that would protect the base metal and inhibit excessive oxidation upon exposure to atmospheric air with typical humidity levels. Prior experiments have indicated that a ductile and adherent surface film, often exhibiting wrinkles rather than cracks, is critical to such protection [47, 58]. Some of the smaller powders shown in Figure 71 appear to have a wrinkled surface layer, despite the presence of oxide particles.
A continuous film is not present on all particles and there is likely high variability in the thickness of the oxide layer and the amount of fluorine that is present. The transient nature of the experiment and differences in exposure time to the reactive gas atmosphere are significant contributors to the oxide coating characteristics. A longer atomization trial where the reactive gas spray has an established steady-state should allow for uniform coating of the powder.

11.3.3 Auger and EDS of gas-atomized calcium powder

The powder was analyzed further by energy dispersive X-ray spectroscopy (EDS) to identify the surface composition of the material. A powder particle that was spherical with relatively little porosity and satellites was chosen with the analyzed area depicted in Figure 72.
The area bounded by the circle labeled as “Map Data 3” was analyzed to generate the composition maps shown in Figure 73 and the red, single line spectrum in Figure 74, which is a sum of all of the counts from the mapped area and represents the average composition. In addition, a smaller area within this larger region was selected in order to exclude the edges and focus on where fluorine appeared to be most abundant.
From the spectra gathered, it is evident that the surface of the powder particle contains some measurable amount of fluorine. This result is important because it demonstrates that the reactive gas was successfully injected into the atomization chamber and that a reaction occurred with the powder as it was being produced. Table 11 shows the measured relative abundance of the various elements identified with the fluorine content being greater than 3 at%.

Table 11. EDS spectrum elemental composition.

<table>
<thead>
<tr>
<th>Spectrum Label</th>
<th>C (at%)</th>
<th>O (at%)</th>
<th>F (at%)</th>
<th>Al (at%)</th>
<th>Si (at%)</th>
<th>Cl (at%)</th>
<th>Ca (at%)</th>
<th>Y (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Map Sum Spectrum</td>
<td>12.16</td>
<td>32.07</td>
<td>3.16</td>
<td>0.26</td>
<td>0.43</td>
<td>0.91</td>
<td>50.65</td>
<td>0.37</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>8.96</td>
<td>34.96</td>
<td>3.55</td>
<td>-</td>
<td>0.41</td>
<td>0.86</td>
<td>51.26</td>
<td>-</td>
</tr>
</tbody>
</table>

While the EDS result gives very useful and encouraging information about the success of the targeted passivation treatment, it does not provide any insight to the depth of
the film on the powder surface. Auger Electron Spectroscopy (AES) and sputter depth profiling were used to analyze the composition as the particle surface was removed in 1.25 nm (12.5 Å) steps. Figure 75 shows the area that was probed and the resulting depth profile.

![Figure 75. a) AES scan location, b) AES depth profile.](image)

This result is significantly different than expected when only considering the previous EDS results as very little F is identified (<1 at%). There are several possible reasons that no fluorine appears on the surface according to this analysis technique. First, these samples were analyzed by an outside laboratory that did not maintain the strictest atmosphere control for the sample prior to the measurement, in contrast to our in-house instrument scientist, since they had not worked with this material previously. Passivation experiments on Ca surfaces that were completed prior to this atomization trial were also analyzed by AES with in-house capability, but it took multiple samples in order to narrow in the appropriate parameters to successfully identify F which only appeared in the first 10 nm. In addition, it has been shown...
that the reaction with Novec gas does not form a continuous uniform layer, but instead results in an outer CaO shell where F reacts solely with the base metal. This is because Ca oxy-fluoride formation is not thermodynamically favorable and CaF$_2$ is seen in areas where a crack might otherwise exist [58]. Given that the presence of F is highly dependent in the exact location analyzed, it is not surprising to find no fluorine in certain locations with the small probe size used in AES. When considering the EDS results that are averaged over the entire particle and this more focused region with no F present, it is possible to conclude that particles that contain F have high concentrations in localized areas for relatively small thicknesses. This is consistent with previous passivation experiments on larger Ca samples where only select areas contained a measurable concentration of F on the surface. A more comprehensive Auger analysis where numerous areas are analyzed is planned to help further verify this to be true for this powder sample.

### 11.3.4 Thermal analysis of gas-atomized calcium powder

The presence of fluorine alone is only a sign of a modified surface and does not guarantee improved resistance to excessive oxidation or ignition at elevated temperatures. The oxidation kinetics of treated Ca surfaces upon exposure to environmental conditions were previously studied to identify growth rate changes that can be used as indicators of successful passivation. Given the small quantity of powder produced, it was not possible to use this kind of experiment for this batch of material as accuracy would have been sacrificed.

However, thermal gravimetric analysis (TGA) was used in order to verify the surface passivation of the gas atomized Ca powders produced with Novec gas injected into the atomization chamber. -80/+100 mesh (149-177 µm) atomized powder and fragmented pieces
of Ames Lab distilled high purity Ca of the same size were analyzed to compare the ignition
temperature of both forms of the Ca particulate material. Each material was tested with a
combined gas flow of 40 mL/min of dry air (RH<1%) and 20 mL/min N₂. An isothermal
hold at 100°C was conducted for 10 minutes before increasing the temperature at a rate of
20°C/min for 40 minutes followed by cooling at the same rate. The results of the TGA
experiments are shown in Figure 76 with the TG of both atomized powder and bulk Ca
shown as a function of time and the temperature profile indicated.

![Figure 76. TGA of atomized and bulk calcium.](image)

The atomized powder remained passivated until 772°C at which point the protective
layer on the surface broke leading to exposure and rapid oxidation of the pure base metal.
The bulk Ca pieces had an ignition temperature of 786°C with the difference possibly
resulting from less pre-existing stress in the material compared to atomized powder,
requiring more energy to break the surface oxide. Another possible reason for this slightly
higher value is a difference in the surface area of the sample, despite the fact that the same size range was used.

Tian measured the ignition temperature of bulk Ca to be 835°C and that of centrifugally atomized powder to be 825°C in the same size range [16]. The difference in ignition temperature between atomized and bulk Ca from these experiments was similar to those measured by Tian (~10°C) and the absolute ignition temperatures for each type of material were approximately 50°C less in each case. The reason for this significant difference is a result of the isothermal hold used at the beginning of the heating cycle. The desorption of water molecules from the surface takes place during this additional time at 100°C prior to the ramp up leading to an earlier onset of ignition. Despite these values being slightly lower in comparison, the results of this thermal gravimetric analysis indicate that the powder is passivated and is sufficiently safe to handle.
CHAPTER 12. CONCLUSIONS

- An Induction Melting Passivation (IMPass) system was constructed to enable the study of the passivation of calcium and other metals that do not form a protective oxide layer.

- A Ca sample was produced without a reactive cover gas spray to establish a baseline for comparison of other samples.

- A sample was produced with the 1% SF\textsubscript{6} reaction gas being sprayed when molten resulting in an excessive reaction. AES results showed that the layer was very thick, and the base metal was not reached by the analysis.

- Samples were produced after solidification and cooling to 550°C with two different heating sequences in order to slow the reaction. Both samples showed that Ca reacted with sulfur rather than fluorine despite the fact that fluorination is thermodynamically favorable.

- Although no fluorine was found on the surface, there appeared to be a reduction in cracking. A possible explanation for the absence of fluorine is a reaction with the stainless-steel spray tube or other hot metal surface in the reaction chamber.

- Novec 612 was used as an alternative cover gas in place of SF\textsubscript{6} which, has strongly deleterious greenhouse gas behavior once released to the atmosphere. The use of Novec was found to result in fluorine reacting with the sample surface, primarily in existing cracks in the oxide.

- Oxidation kinetics experiments showed that passivation with Novec resulted in a slowed reaction rate. Complete protection was still not achieved due to the design of the sample holder.
• Calcium powder with an average particle size of 85 µm was produced by gas atomization. The atomization was recorded with high-speed imaging for the short duration of the run that yielded 2.4 g of powder.

• Argon was used as the atomization gas and also as a diluting gas in streams of oxygen and fluorine-containing Novec gas in an attempt to passivate the powders by a gas-phase reaction.

• SEM micrographs revealed that spherical powder was produced with some porosity and satellites present.

• EDS showed that fluorine was present on the surface of the powder. Auger depth profiling did not observe a significant concentration of fluorine.

• TGA in dry air of 149-177 µm atomized powder and bulk calcium determined the ignition temperatures without humidity to be 772°C and 786°C, respectively.
CHAPTER 13. RECOMMENDATIONS FOR FUTURE WORK

- The above results indicate that calcium can be gas atomized and that fluorine is present in a measurable amount on the surface. Further study is necessary to tune the parameters for controlling the particle size distribution, suppressing porosity and satellites, and achieving the optimal oxygen and fluorine concentrations.

- A longer atomization run yielding more powder would allow for a more detailed analysis of oxidation kinetics, including the study of ignition in ambient air with a typical humidity level, which is known to rapidly degrade CaO protective coverage. Expanded utilization of auger electron spectroscopy could help understand the passivation mechanism that takes place in the atomization chamber.

- After completing a longer atomization trial and expanded analysis, scaling to a larger atomization chamber could be pursued. Up-scaling of the Ca powder production process is required to enable further evaluation of the Ca powders and the Al/Ca composite material. In fact, being able to produce fine Ca powder is important for achieving high strength in Al/Ca composite conductors. With the 85 µm powder produced, a stranded conductor with a uniform construction of 2mm composite wires could be produced with an ultimate tensile strength in excess of 285 MPa when starting with a commercial size extrusion. The strength can be increased further by reducing the Ca powder size to maintain a practical final wire diameter of 1-3 mm.
GENERAL CONCLUSION

Aluminum/calcium composite conductors provide a unique approach to achieving high strength and eliminate the need for structural reinforcement with a steel core. The very low density of both aluminum and calcium allow for long spans and a specific strength of more than double existing power transmission conductors. The concept of reducing the loading of the reinforcement phase and intentionally converting Ca filaments to an intermetallic species was successfully demonstrated. Enhanced performance properties were observed under certain conditions and were maintained after extended heat treatments. One key advantage to Al/Ca composites is the ability to modify the properties while using a single material in a stranded conductor.

A method for the passivation and production of calcium powder was exhibited that can further the development of Al/Ca composite conductors. Calcium with a slowed oxidation rate and high resistance to flammability was produced by treatment with a fluorine containing compound. Passivating Ca during atomization with this in-situ technique allows for the safe production of a material that is inherently dangerous. The findings of these experiments can be utilized to scale this process further and produce powder in a quantity sufficient for testing of a larger Al/Ca extrusion. Future work will further verify the findings that have been presented and continue towards the overall goal of commercializing the technology.
REFERENCES


