**Michigan
Technological
University**

Michigan Technological University
Digital Commons @ Michigan Tech

Dissertations, Master's Theses and Master's Reports

2020

EFFECT OF CERIUM AND MAGNESIUM ADDITIONS ON THE STRENGTH AND MORPHOLOGY OF THE INTERMETALLIC COMPOUND LAYERS IN ALUMINUM-STEEL DISSIMILAR CASTINGS

Matt Thomas

Michigan Technological University, matthoma@mtu.edu

Copyright 2020 Matt Thomas

Recommended Citation

Thomas, Matt, "EFFECT OF CERIUM AND MAGNESIUM ADDITIONS ON THE STRENGTH AND MORPHOLOGY OF THE INTERMETALLIC COMPOUND LAYERS IN ALUMINUM-STEEL DISSIMILAR CASTINGS", Open Access Master's Thesis, Michigan Technological University, 2020.
<https://doi.org/10.37099/mtu.dc.etr/1040>

Follow this and additional works at: <https://digitalcommons.mtu.edu/etr>

Part of the [Metallurgy Commons](#)

EFFECT OF CERIUM AND MAGNESIUM ADDITIONS ON THE STRENGTH AND
MORPHOLOGY OF THE INTERMETALLIC COMPOUND LAYERS IN
ALUMINUM-STEEL DISSIMILAR CASTINGS

By

Matthew J. Thomas

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Materials Science and Engineering

MICHIGAN TECHNOLOGICAL UNIVERSITY

2020

This thesis has been approved in partial fulfillment of the requirements for the Degree of
MASTER OF SCIENCE in Materials Science and Engineering.

Department of Materials Science and Engineering

Thesis Advisor: *Dr. Paul Sanders*

Committee Member: *Dr. Douglas Swenson*

Committee Member: *Dr. Stephen Kampe*

Department Chair: *Dr. Stephen Kampe*

Table of Contents

LIST OF FIGURES	V
LIST OF TABLES	VII
ACKNOWLEDGEMENTS	VIII
ABSTRACT	IX
1 INTRODUCTION	1
1.1 MOTIVATION FOR ALUMINUM-STEEL DISSIMILAR CASTINGS	1
1.2 BONDING IN DISSIMILAR CASTINGS	1
1.2.1 Mechanical Bonding	1
1.2.2 Metallurgical Bonding	2
1.3 MICROSTRUCTURE OF PURE ALUMINUM/IRON INTERFACE	3
1.4 STRUCTURE OF THE Fe_2Al_5 UNIT CELL	5
1.5 EFFECT OF ALLOYING ELEMENTS	5
1.6 GROWTH RATE OF IMC LAYERS	7
1.7 ALUMINUM-CERIUM ALLOYS	7
1.7.1 Binary Aluminum-Cerium alloys	7
1.7.2 Ternary Aluminum-Cerium-Magnesium Alloys	9
1.8 HYPOTHESES	11
2 EXPERIMENTAL METHODS	12
2.1 IMMERSION EXPERIMENT	12
2.1.1 Specimen Preparation	12
2.1.2 Immersion Process	13
2.1.3 Aluminized Rod Preparation	14
2.2 MICROSTRUCTURAL ANALYSIS	15
2.2.1 Scanning Electron Microscopy	15
2.2.2 Image Analysis	15
2.3 PIN-PULL EXPERIMENT	16
2.3.1 Sample Preparation	16
2.3.2 Casting Simulation	17
2.3.3 Casting Process	17
2.3.4 Mechanical Testing	18

3	TRIPLE IMC LAYER PHASE GROWTH MODEL.....	19
4	RESULTS	23
4.1	IMC LAYER GROWTH.....	23
4.1.1	<i>Total IMC Layer Thickness.....</i>	<i>23</i>
4.1.2	<i>Phase Identification</i>	<i>25</i>
4.1.3	<i>IMC Layer Component Thickness.....</i>	<i>27</i>
4.1.4	<i>IMC Layer Morphology.....</i>	<i>28</i>
4.2	PREDICTED LAYER GROWTH.....	29
4.3	MECHANICAL BEHAVIOR.....	31
4.3.1	<i>Experimental Cooling Curves.....</i>	<i>31</i>
4.3.2	<i>Pin Casting Extraction Force.....</i>	<i>31</i>
5	DISCUSSION.....	33
5.1	IMC LAYER DEVELOPMENT	33
5.2	MULTI-LAYER GROWTH MODEL.....	35
5.3	EFFECT OF ALLOY ADDITIONS ON MECHANICAL STRENGTH	37
5.4	HYPOTHESES.....	40
6	CONCLUSION.....	41
7	APPENDIX A: TRIPLE LAYER GROWTH MODEL MATLAB CODE	45
8	APPENDIX B: IMC GROWTH MODEL INPUTS.....	48

List of Figures

Figure 1. Aluminum rich corner of the aluminum-iron binary phase diagram for the aluminum rich corner, generated through Thermo-Calc 2020a using the TCAL6 database.	2
Figure 2. The growth of the IMC layer between pure aluminum and pure iron for various dipping times [6].	4
Figure 3. Fe_2Al_5 unit cell showing partial occupancy of aluminum atoms along the c-axis.	5
Figure 4. Binary Al-Ce phase diagram modeled through Thermo-Calc 2020a utilizing the TCAL6 database.	8
Figure 5. Retained phase fraction of $\text{Al}_{11}\text{Ce}_3$ as a function of temperature modeled through Thermo-Calc 2020a for an Al-10wt%Ce alloy using the TCAL6 database.	9
Figure 6. Isopleth Al-10wt%Ce-Mg phase diagram modeled through Thermo-Calc 2020a using the TCAL6 database.	10
Figure 7. (a) Thermal stability of $\text{Al}_{11}\text{Ce}_3$ precipitates with varying Mg concentration and (b) Site fraction of Mg in the $\text{Al}_{11}\text{Ce}_3$ precipitates within varying Mg concentration, both simulated through Thermo-Calc 2020a using the TCAL6 database.	10
Figure 8. Immersion experiment furnace setup where the end of the sample holder (left) inserted into the furnace (right).	13
Figure 9. Processing for aluminized rods where red indicates boron nitride coating and gray is steel.	14
Figure 10. Prints for the four pins utilized in the study.	16
Figure 11. Interfacial shear test mold.	17
Figure 12. Chem-bond and pipe assembly set up for the pin-pull casting.	18
Figure 13. Setup for measuring the extraction force where the full sample assembly is shown in the red box.	19
Figure 14. Concentration profile of element A across the IMC layers in the hypothetical AB-C system.	20

Figure 15. Optical micrographs depicting the development of the IMC layer with time for the 99.99% Al samples.....	24
Figure 16. Total IMC layer Thickness for the five alloys investigated in the immersion study.	25
Figure 17. Al-6Ce and Al-10Ce BSE images showing the IMC layer components.....	26
Figure 18. Thickness of the constituent phases present in the IMC layer, where the first layer is either $\text{Fe}_4\text{Al}_{13}$ or $\text{Al}_{10}\text{CeFe}_2$ (a) and the second phase is Fe_2Al_5 (b) measured from BSE images.....	28
Figure 19. Al-4.4Mg optical micrographs showing indistinguishable IMC layers, (a) and (c), and distinct IMC layers, (b) and (d), found in the magnesium containing alloys.	29
Figure 20. Total IMC layer thickness predicted by the triple layer growth model compared with experimental data for the three cerium containing alloys.....	30
Figure 21. Experimental cooling curves for the three cerium containing alloys used in the pin-pull study.	31
Figure 22. Extraction force for all alloys used in the study.....	32
Figure 23. Ternary Al-Fe-Ce phase diagram at 750°C generated in Thermo-Calc 2020a using TCAL6 database.	34
Figure 24. Interval plot for the 95% confidence interval for the three alloys.	37
Figure 25. Extraction force for all alloys.	39
Figure 26. The combination of interfacial strength and contact pressure produce a better fit to the Al-10Ce-5Mg data.	40

List of Tables

Table 1. Purity and manufacturer of charge material used for the Al-4.4Mg alloy.....	12
Table 2. Composition of the electrogalvanized low carbon steel rods used in the study (wt%).	12
Table 3. Polishing procedure for samples investigated in this study [21].	15
Table 4. Phases present in the IMC layer for each alloy.	26
Table 5. Concentration of alloying additions in the aluminum coating analyzed through EDS.	27
Table 6. Compositional inputs for the IMC layer modeled at 750°C.	48

Acknowledgements

I would like to acknowledge Dr. Paul Sanders for his advisement throughout the duration of this work. His insight on experimental methodology, data analysis, and professional conduct will be invaluable for any of my future endeavors.

This project would not have been possible without the financial support given by the American Foundry Society Aluminum Division and the Ford Motor Company or the cerium containing alloys provided by David Weiss and Eck Industries

The scanning electron microscopy research was performed at the Applied Chemical and Morphological Analysis Laboratory at Michigan Technological University. The electron microscopy facility is supported by NSF MRI 1429232.

Thank you to the MSE staff: Dr. Dale Dewald, Russ Stein, and Tom Wood, for help with experimental design and endless trouble shooting. I greatly appreciate advice in regard to metallographic preparation from Dr. Dan Seguin.

I would like to thank Carl Soderhjelm for his assistance in designing the immersion experiment performed and metallographic preparation.

I would also like to thank the MSE family: Ale and Erin, for insightful discussions and for being great officemates. Phil, for being an amazing sounding board and for his insight on metallographic preparation.

Lastly, I would like to thank my family for all their support and encouragement.

Abstract

Dissimilar castings are under investigation due to their light-weighting opportunities within the automotive industry. In this case, dissimilar castings consist of a solid steel core and a poured aluminum component. The strength and integrity of the casting relies on the coherency of the bond between the two components; by optimizing the metallurgical component of the bonding phenomena, the weight and complexity of the insert can be reduced, further increasing the light-weighting opportunities. An interface comprised of intermetallics, generally $\text{Fe}_4\text{Al}_{13}$ and Fe_2Al_5 , forms between the two components with the latter forming nearest the steel. Cerium and magnesium additions to the aluminum component of the casting were investigated to increase the integrity of the metallurgical bond. Five alloys, 99.99wt%Al, Al-5Mg, Al-6Ce, Al-10Ce, and Al-10Ce-5Mg, were utilized to study the effect of cerium and magnesium on the intermetallic growth through an immersion experiment. Three alloys, Al-6Ce, Al-10Ce, and Al-10Ce-5Mg, were used to investigate the interfacial shear strength through a pin extraction experiment. The magnesium containing alloys showed a large decrease in total intermetallic compound layer thickness and an increase in the interfacial shear strength. A possible mechanism for the thickness reduction was magnesium reducing the lattice parameters of $\text{Fe}_4\text{Al}_{13}$ and Fe_2Al_5 reducing the diffusion of aluminum through the layer.

1 Introduction

1.1 Motivation for Aluminum-Steel Dissimilar Castings

Fuel efficiency and greenhouse gas emissions have come to the forefront for the automotive industry. Traditionally, these are improved by replacing ferrous components or castings with aluminum where possible. However, some parts, such as powertrain components, cannot be completely replaced with aluminum due to mechanical and thermal property limitations. One approach is to use a dissimilar casting, consisting of an aluminum and ferrous component, as a replacement for the pure ferrous casting.

The dissimilar casting would consist of a ferrous insert encased in cast aluminum, which offers weight reduction while maintaining the required mechanical properties, specifically stiffness, due to the insert. Currently, manufacturers are using ferrous ring inserts within cast aluminum diesel piston heads to assist with automotive light weighting [1].

1.2 Bonding in Dissimilar Castings

The integrity of a dissimilar material casting is directly dependent on the quality of the bond. If the bond lacks coherency or the intermetallic bonding layer becomes too thick, then the bearable load and toughness are greatly reduced. A coherent bond would consist of an interface free of voids and cracks. The bonding between two dissimilar materials is composed of two phenomena: mechanical bonding and metallurgical bonding.

1.2.1 Mechanical Bonding

The mechanical bonding phenomena occurs due to the aluminum shrinking around the ferrous insert during solidification and holds the ferrous insert in place. This bonding method requires complex insert geometries and rougher surface finishes for the aluminum to shrink into.

1.2.2 Metallurgical Bonding

Metallurgical bonding focuses on the intermetallic compound (IMC) layer that forms between the two metals upon reacting. The IMC layer initially forms upon the reaction between the molten aluminum and solid ferrous insert and then grows through diffusion at elevated temperatures. Due to the low solubility of iron in aluminum (Figure 1) a layer of brittle IMCs form at the interface between the aluminum and ferrous insert.

Figure 1. Aluminum rich corner of the aluminum-iron binary phase diagram for the aluminum rich corner, generated through Thermo-Calc 2020a using the TCAL6 database.

The optimization of the metallurgical bonding phenomena allows a simplification and weight reduction of the ferrous insert. Viala et al. was able to reduce the weight of the insert by 36% while maintaining mechanical properties [2]. This was done by performing a hot-dip aluminizing (Al-Fin) process on the ferrous insert prior to casting. The Al-Fin process helps to increase the bond coherency by increasing the wettability between the insert and aluminum melt.

The coherency of the metallurgical bond is affected by surface quality, reaction temperature, and insert coating. Soderhjelm found for an A356 alloy, the activation energy for diffusion increased when the steel surface was ground to finer grits using SiC paper [3]. Through immersion experiments, Bouché et. al. was able to show that the average Fe_2Al_5 layer thickness increased with temperature for both short and long immersion times [4]. Aguado et al. investigated the effect of numerous surface conditions on the formation of a metallurgical bond and found that pickling or coating [the ferrous component] with aluminum or zinc did not greatly alter the shear strength; however, an insert that was only shot blasted and cleaned with acetone greatly increased the shear strength [5]. They also noted that all conditions produced debonding at the corners of the rectangular inserts [5]. Zhe et al. used a zinc coating produced by hot-dip galvanizing to achieve a metallurgical bond between the insert and aluminum through an increase in wetting of the insert. The authors suggest that the zinc does not appear in the IMC layer due to its high diffusivity in the aluminum melt [6]. The ferrous insert should lack sharp features to reduce the chance of debonding due to stress concentrations and possess a thin uniform layer of zinc or aluminum to help increase the wettability of the insert surface.

1.3 Microstructure of Pure Aluminum/Iron interface

The IMC layer found between pure aluminum and steel is mainly composed of Fe_2Al_5 extending from the aluminum towards the steel and a small layer of $\text{Fe}_4\text{Al}_{13}$ along the aluminum (Figure 2).

Figure 2. The growth of the IMC layer between pure aluminum and pure iron for various dipping times [6].

The growth and morphology of the Fe_2Al_5 constituent has been proposed to be diffusion based and to be due to an applied stress field [7], [8]. Cheng and Wang suggest that the morphology of the Fe_2Al_5 phase is due to the high vacancy concentration in the c axis, [001] direction, that allows for the fast diffusion of aluminum [7]. Through the use of EBSD and TEM analysis, Takata et al. has proposed that the tongue like appearance of the Fe_2Al_5 phase is due to a stress field applied by the lattice mismatch between the cubic iron phase and the orthorhombic Fe_2Al_5 phase [8].

The rapid formation of the Fe_2Al_5 IMC can lead to Kirkendall voids that form on the aluminum side of the IMC layer [6], [9]. The voids are due to the unbalanced diffusion of aluminum atoms towards the insert during the growth of Fe_2Al_5 and are generally produced by thermal treatments. Through the inclusion of rare earths, Zhang found that the formation of Kirkendall voids was greatly reduced, which is attributed to rare earths diffusing into the steel and slowing the diffusion of aluminum [9]. The reduction of Kirkendall voids reduces the probability of crack initiation and propagation at the interface, further increasing the integrity of the bond.

1.4 Structure of the Fe_2Al_5 Unit Cell

The Fe_2Al_5 unit cell shows the orthogonal crystal structure, C24, that consists of one iron sublattice site and three aluminum sublattice sites with varying occupancy (Figure 3) [8]. The partial vacancies in the aluminum sublattice form channels that thread through the unit cell [10]. The partial occupancy has been predicted to be weakly unstable and decompose into a tetragonal structure [8], [10]. The large vacancy concentration along the c-axis of the unit cell greatly favors the rapid influx of aluminum atoms towards the growth front between the IMC layer and steel insert [11].

Figure 3. Fe_2Al_5 unit cell showing partial occupancy of aluminum atoms along the c-axis.

1.5 Effect of Alloying Elements

Rare earth additions to the aluminum substrate in dissimilar castings has been postulated to reduce the IMC layer thickness. Liu et al. investigated the effects of multiple alloying elements, including silicon, titanium, and lanthanum, in the aluminum substrate; they found that lanthanum had that largest impact on increasing the diffusion activation energy for aluminum atoms through the Fe_2Al_5 unit cell [12]. The increase in the diffusion barrier energy is due to an atom of the alloying element occupying a lattice site along the [001] direction. Increasing the diffusion barrier energy reduces the rate at which the

aluminum atoms diffuse through the unit cell; by increasing the alloying element content the probability of occupying a vacant lattice site in the [001] direction increases.

Rare earth additions have been shown to be an effective grain refiner for numerous alloy systems, but the influence on the IMC Fe_2Al_5 has yet to be investigated. Vijayn et al. investigated the effect of cerium additions to an aluminum-silicon alloy on the average α -Al grain size and found that the grain size decreased with increasing cerium content [13]. The grain refinement of the IMC layer in aluminum-iron components has been investigated through elemental additions to the aluminum. Through tungsten inert gas arc brazing, Furuya et al. analyzed the effects of nickel, chromium, manganese, and titanium on the relationship between the grain width of Fe_2Al_5 and tensile shear strength of the joint. They found that as the width of the Fe_2Al_5 phase decreased, the shear strength substantially increase [14]. Kyokuta et al. showed that refining the Fe_2Al_5 phase increased the crack interval and the increase in crack interval correlates to an increase in fracture toughness for the finer grained Fe_2Al_5 [15]. Grain refinement within the IMC layer is a large factor in increasing the tensile shear strength of the component. Cerium additions offer the possibility of refining the Fe_2Al_5 layer, increasing the integrity of the bond.

The addition of magnesium to aluminum has been shown to greatly reduce the thermal conductivity with increasing magnesium content [16]. The reduction in thermal conductivity would reduce the rate of heat transfer through the initial intermetallic layer, slowing further growth into the steel insert. In addition to reducing the thermal conductivity of the aluminum alloy, magnesium additions have been shown to refine the lattice parameters of the phases present in the IMC layer. Xie et al. hot-dip galvanized a Zn-Al-Mg on steel varying the magnesium content from 0 wt% to 5 wt% to analyze the impact of magnesium on the IMC layers. They identified the IMC layer components to be $\text{Fe}_4\text{Al}_{13}$ and $\text{Fe}_2\text{Al}_5\text{Zn}_{0.4}$ and that the thickness of the IMC layer decreased with increasing magnesium content [17]. The decrease in thickness was attributed to magnesium reducing

the lattice parameters of both the $\text{Fe}_4\text{Al}_{13}$ and $\text{Fe}_2\text{Al}_5\text{Zn}_{0.4}$ phases, restricting the diffusion of aluminum from the melt to the iron substrate [17]. The interdiffusion coefficient in fcc Al-Mg solid solution increases with increasing magnesium concentration [18]; however, because the rate limiting step is diffusion through the IMC layer, increasing the interdiffusion coefficient in the fcc solid solution has little effect on the IMC layer formation.

1.6 Growth Rate of IMC layers

The growth rate of the aluminum-iron IMC layer has been studied by numerous groups and has shown good agreement to a parabolic form, which depends on a parabolic coefficient, K , and reaction time, t :

$$l^2 = Kt \quad \text{Eq. 1}$$

and K has an Arrhenius type temperature dependence:

$$K = K_0 \exp \left[-\frac{Q}{RT} \right] \quad \text{Eq. 2}$$

where K_0 and R are constants and Q is the activation energy for layer growth [19], [20]. This parabolic relationship only accounts for the growth of the IMC layers and does not consider the dissolution of iron into the aluminum melt.

1.7 Aluminum-Cerium Alloys

1.7.1 Binary Aluminum-Cerium alloys

Aluminum-cerium alloys are under investigation for dissimilar castings due to their high castability and strengthening without the need of heat treatment. Recent research into both binary Al-Ce and ternary Al-Ce-Mg high cerium alloys has shown high castability in part due to the exothermic formation of the Al-Ce intermetallic phases increasing the melt fluidity; however, the castability is negatively affected when the cerium content exceeded 12 wt% [21], [22]. The increased castability of the alloy would allow for greater near-net shaped castings, potentially eliminating the post-production machining processes that could damage or break the bond.

The Thermo-Calc generated phase diagram for a binary Al-Ce alloy shows that there is essentially zero solubility of cerium in aluminum and a eutectic invariant point at roughly 10 wt%Ce at 640°C (Figure 4). The phase diagram shows that the binary alloys would be comprised of $\text{Al}_{11}\text{Ce}_3$ precipitates within an aluminum matrix for both hypo- and hyper-eutectic alloys.

Figure 4. Binary Al-Ce phase diagram modeled through Thermo-Calc 2020a utilizing the TCAL6 database.

It has been shown that heat treatment will not significantly affect the microstructure of a binary Al-Ce alloy. The $\text{Al}_{11}\text{Ce}_3$ strengthening phase is precipitated during solidification and the retained phase fraction does not change with heat treatment [21]. The formation of the $\text{Al}_{11}\text{Ce}_3$ phase without the need of a heat treatment process helps reduce the overall thickness of the IMC layer. The retained fraction of $\text{Al}_{11}\text{Ce}_3$ does not decrease until the solidus temperature is reached, allowing for use at elevated temperatures without decomposition of the strengthening phase (Figure 5). Another contribution to the stability of the $\text{Al}_{11}\text{Ce}_3$ intermetallic is a reduced vacancy mobility caused by a high binding energy between cerium atoms and vacancies [23]. This reduced mobility hinders vacancy diffusion mechanism of solute atoms through the aluminum matrix [23].

Figure 5. Retained phase fraction of $\text{Al}_{11}\text{Ce}_3$ as a function of temperature modeled through Thermo-Calc 2020a for an Al-10wt%Ce alloy using the TCAL6 database.

1.7.2 Ternary Aluminum-Cerium-Magnesium Alloys

The inclusion of magnesium in an Al-Ce alloy increases the strength of the matrix at elevated temperatures due to solid solution strengthening, precipitation strengthening through the formation of Al_3Mg_2 at lower temperatures with additions of at least 2.8wt% Mg and reduces the required casting temperature with increasing magnesium content (Figure 6).

Figure 6. Isopleth Al-10wt%Ce-Mg phase diagram modeled through Thermo-Calc 2020a using the TCAL6 database.

The thermal stability of the $\text{Al}_{11}\text{Ce}_3$ precipitates is reduced to 540°C when 5wt% Mg is added to the Al-10Ce alloy, which is due to the magnesium atoms occupying aluminum sites in the $\text{Al}_{11}\text{Ce}_3$ sublattice (Figure 7).

Figure 7. (a) Thermal stability of $\text{Al}_{11}\text{Ce}_3$ precipitates with varying Mg concentration and (b) Site fraction of Mg in the $\text{Al}_{11}\text{Ce}_3$ precipitates within varying Mg concentration, both simulated through Thermo-Calc 2020a using the TCAL6 database.

The castability and mechanical properties can be substantially altered by adding additional elements. Sims et al. found that adding 0.4wt% Mg did not negatively impact the castability of Al-Ce alloys and that the addition increased both the ultimate tensile strength and yield strength of the ternary alloy [22].

1.8 Hypotheses

Three hypotheses were developed for this project:

If magnesium is added to the aluminum component of the dissimilar casting, then the thickness of the IMC layer will be reduced, because the magnesium atoms will build up along the aluminum-IMC interface and serve as a barrier to aluminum atoms entering the IMC layer.

If cerium is added to the aluminum component of the dissimilar casting, then the thickness of the IMC layer will be reduced, because the stable $\text{Al}_{11}\text{Ce}_3$ precipitates form along aluminum-IMC interface tying up vacancies.

If magnesium is added to the aluminum component of the dissimilar casting, then the strength of the interface will be increased, because the magnesium additions reduces the lattice parameters of the intermetallics, making aluminum diffusion more difficult and reducing the thickness of the IMC layer.

2 Experimental Methods

2.1 Immersion Experiment

2.1.1 Specimen Preparation

Five alloys were investigated, four master alloys, provided by Eck Industries, and one aluminum-magnesium fabricated alloy. The four master alloys are: 99.99% pure aluminum, Al-6Ce, Al-10Ce, and Al-10Ce-5Mg, where all compositions for alloys presented in this study are in weight percent. The charge for the aluminum-magnesium alloy was generated from 99.99% pure aluminum and 99.80% pure magnesium (Table 1).

Table 1. Purity and manufacturer of charge material used for the Al-4.4Mg alloy.

Material	Purity (wt%)	Manufacturer
Aluminum Ingot	99.99	
Magnesium Ingot	99.80	US Magnesium LLC

Low carbon steel rods served as the ferrous insert for the immersion experiments. The electrogalvanized 1015 steel rods, 5/16-inch diameter, were cut into 4-inch-long samples (Table 2). The steel rods were ultrasonically cleaned in a mild commercial degreaser for 10 minutes, rinsed, and then ultrasonically cleaned in a 50% solution of ethanol in water for 5 minutes. The top 2.5 inches of the samples were coated in an aerosolized boron nitride coating (Momentive).

Table 2. Composition of the electrogalvanized low carbon steel rods used in the study (wt%).

Element	C	Mn	P	S	Si	Cu	Fe
Wt%	0.1600	0.7000	0.0050	0.0160	0.1800	0.1500	Bal

2.1.2 Immersion Process

Four pounds of the 99.99% aluminum and cerium containing master alloys were individually superheated to 750°C using a McEnglevan resistance furnace. The aluminum-magnesium alloy was produced by superheating 3.8 lbs of 99.99% pure aluminum to 750°C using a McEnglevan resistance furnace and then adding 0.2 lbs of 99.80% pure magnesium 10 minutes before the immersion experiment. An argon cover gas was used during the melting process and through the duration of the experiment.

The immersion rod holder was connected to the boron nitride coated end of the steel rod, inserted into the aluminum melt through the hole in the lid of the furnace, and placed on a ring stand to achieve a consistent depth (Figure 8). Three replicates, for a total of 12 samples per alloy, were immersed for 10s, 30s, 120s, and 300s, then quickly water quenched after removal to inhibit further reaction.

Figure 8. Immersion experiment furnace setup where the end of the sample holder (left) inserted into the furnace (right).

2.1.3 Aluminized Rod Preparation

Two pieces, 0.25 inches in height, were cross sectioned perpendicular to the rod axis from the uncoated section of the aluminized rod for IMC growth measurements for a total of 24 pieces per alloy, shown as surfaces A and B (Figure 9). The pieces were mounted in epoxy and let to set for at least 12 hours, then polished following the specified procedure (Table 3).

Figure 9. Processing for aluminized rods where red indicates boron nitride coating and gray is steel. Two pieces, 0.25 inches in height, were cut for IMC layer measurements denoted as surfaces A and B.

Table 3. Polishing procedure for samples investigated in this study [24].

<i>Step</i>	<i>Pad</i>	<i>Abrasive</i>	<i>Time</i>	<i>Pressure</i>
<i>1</i>	<i>Allied SiC paper</i>	<i>320 grit SiC, water wash</i>	<i>Until planar</i>	<i>Manual</i>
<i>2</i>	<i>Struers MD-Largo</i>	<i>Allied 15 micron diamond, glycol suspension</i>	<i>15 minutes</i>	<i>30 N</i>
<i>3</i>	<i>Struers MD-Mol</i>	<i>Allied 3 micron mono- crystalline diamond paste, Allied Red Lube</i>	<i>10 minutes</i>	<i>25 N</i>
<i>4</i>	<i>Allied Final P</i>	<i>Allied 0.05 micron silica suspension</i>	<i>2 minutes</i>	<i>15 N</i>
<i>5</i>	<i>Allied Final P</i>	<i>Water wash</i>	<i>2 minutes</i>	<i>15 N</i>

2.2 Microstructural Analysis

2.2.1 Scanning Electron Microscopy

Energy dispersive spectroscopy was completed on select cross sectioned samples to identify phases present in the IMC layer and aluminum coating. Additionally, backscatter electron images were acquired showing the individual IMC layers and morphology of the aluminum coating. A Phillips/FEI XL 40 environmental scanning electron microscope was used with a 15-kV accelerating voltage. The samples were carbon coated and directly connected to the sample stage with carbon tape.

2.2.2 Image Analysis

The total IMC layer thickness was measured using the ImageJ software. The magnification, 200x, was kept constant across all images and the scale was set prior to measuring each image. Two optical micrographs were taken per piece and five measurements were taken from each micrograph at varying IMC layer thickness to achieve a more representative average.

2.3 Pin-Pull Experiment

2.3.1 Sample Preparation

Four pins, 0.5 inches in diameter, with tapers varying from 0.5° to 25° and thermocouple channels through the center were machined from high strength 4340 steel (Figure 10). The depth of the thermocouple channels differed to achieve a consistent surface area to volume ratio directly above the thermocouple. The tapered portion of each pin was ground to a 600-grit finish using Emery paper on a lathe and cleaned with ethanol just prior to casting. A pipe and cap assembly comprised of a dual end threaded pipe 1.5 inches in diameter and 3.5 inches in length and a cap with a 0.5-inch diameter on center was placed over the pin (Figure 11).

Figure 10. Prints for the four pins utilized in the study. All measurements are in inches.

Figure 11. Interfacial shear test mold. All the measurements are in inches and four pin geometries were utilized. The start of the taper coincides with the base of the cap.

2.3.2 Casting Simulation

Casting solidification was simulated in Altair Inspire Cast 2019.4. The model was comprised of an un-tapered pin, cap, pipe, aluminum “casting”, (Figure 10) and no-bake sand mold. The pin, cap, and pipe were labeled as steel core components and the aluminum was classified as A206 due to lack of aluminum cerium data in the material selection database. The initial temperature was set to 750°C and the casting had a fill time of 5 seconds.

2.3.3 Casting Process

Three cerium containing master alloys, Al-6Ce, Al-10Ce, and Al-10Ce-5Mg, used in the study were provided by Eck Industries. For the Al-6Ce and Al-10Ce alloys, one taper, a total of 4 pins, were cast a time. The alloys were superheated in four-pound batches in a Thermolyne Type 46200 high temperature furnace to 756 +/- 2.4°C. All 16 pins were cast at the same time for the Al-10Ce-5Mg alloy. 21 pounds of the alloy was superheated to 750°C in a McEnglevan resistance furnace. Type K, brake style thermocouples (Temprel Inc.) were inserted into the base of the pins. The pin-thermocouple assembly were placed in the Chem-bond mold, careful not to touch the tapered surface, and the pipe assembly

was placed over the pin, making sure the lip of the cap was flush with the mold (Figure 12). The alloy was then poured off-center into the top of the vertically oriented pipe to avoid adding turbulence during the filling.

(a)

(b)

Figure 12. Chem-bond and pipe assembly set up for the pin-pull casting. First the Chem-bond drag was made and pins inserted (a). Then the pipes were inserted over the pins (b).

2.3.4 Mechanical Testing

Mechanical testing of the castings was done on an Instron 4206 with a 10kN load cell. A second cap with a threaded rod on center was threaded onto the pipe and the assembly was threaded into the tensile frame with the pin pointed to the top of the frame (Figure 13). The pin was pulled until failure to achieve a maximum force.

Figure 13. Setup for measuring the extraction force where the full sample assembly is shown in the red box.

3 Triple IMC Layer Phase Growth Model

Kajihara developed a kinetics model to calculate the thickness of a single IMC layer within a binary system [25]. The model assumes that the two substrates will act as semi-infinite boundaries due to the comparatively small thickness of the IMC layer. The model utilizes the interdiffusion coefficients for the three phases present, substrate A, IMC layer, and substrate B, and the atomic fraction of element B on each side of the moving interface. The Kajihara model assumes that the migration of the interface is controlled through volume diffusion [25].

The model was then expanded by Wang et al. to binary system comprised of two IMC layers. The initial results from the expanded model show an overestimation for the growth of both IMC layer. A correction to the interdiffusion coefficient is developed in the form of an effective diffusion coefficient that takes into account lattice and grain boundary diffusion. Through an analysis of the effects of lattice and grain boundary diffusion, Wang shows that growth of the columnar IMC layer is controlled by grain

boundary diffusion after a critical grain width is achieved and the relatively equiaxed IMC layer is controlled by lattice diffusion [26].

The approach is extended to a system containing three IMC layers by considering a hypothetical AB-C system of consisting of a binary AB alloy substrate and pure C substrate that forms three IMC phases: ACB (α -phase), AB (β -phase), and AB_2 (θ -phase). The composition profile of element A across the system is shown as a schematic (Figure 14). The AB and C phases have the initial compositions of C_{AB0} and C_{C0} . The addition of two IMC layers adds four boundary conditions when compared to the Kajihara model for one IMC layer.

Figure 14. Concentration profile of element A across the IMC layers in the hypothetical AB-C system.

The boundary conditions of each phase are taken as the composition of element A at both interfaces for the respective phase. The position of the AB/ α , α/β , β/θ , and θ/C interfaces are shown by $z_{AB\alpha}$, $z_{\alpha\beta}$, $z_{\beta\theta}$, and $z_{\theta C}$, respectively. The position of each interface is calculated through equations 3a through 3d described by Kajihara [25]:

$$z_{AB\alpha} = K_{AB\alpha}\sqrt{4D_{AB}t} = K_{\alpha AB}\sqrt{4D_{\alpha}t} \quad (3a)$$

$$z_{\alpha\beta} = K_{\alpha\beta}\sqrt{4D_{\alpha}t} = K_{\beta\alpha}\sqrt{4D_{\beta}t} \quad (3b)$$

$$z_{\beta\theta} = K_{\beta\theta}\sqrt{4D_{\beta}t} = K_{\theta\beta}\sqrt{4D_{\theta}t} \quad (3c)$$

$$z_{\theta C} = K_{\theta C}\sqrt{4D_{\theta}t} = K_{C\theta}\sqrt{4D_Ct} \quad (3d)$$

where D_{AB} , D_{α} , D_{β} , D_{θ} , and D_C are the interdiffusion coefficients for the AB substrate, α , β , and θ IMC layers, and C substrate, respectively. The $K_{AB\alpha}$, $K_{\alpha AB}$, $K_{\alpha\beta}$, $K_{\beta\alpha}$, $K_{\beta\theta}$, $K_{\theta\beta}$, $K_{\theta C}$, and $K_{C\theta}$ terms are dimensionless proportionality coefficients. Per the Kajihara model, the dimensionless proportionality coefficients are calculated based on their relationship to the boundary conditions through equations 4a through 4d [25]:

$$C_{AB\alpha} - C_{\alpha AB} = \frac{C_{\alpha\beta} - C_{\alpha AB}}{K_{\alpha AB}\sqrt{\pi}(\text{erf}(K_{\alpha\beta}) - \text{erf}(K_{\alpha AB}))} \exp(-(K_{\alpha AB})^2) + \frac{C_{AB\theta} - C_{AB\alpha}}{K_{AB\alpha}\sqrt{\pi}(1 + \text{erf}(K_{AB\alpha}))} \exp(-(K_{AB\alpha})^2) \quad (4a)$$

$$C_{\alpha\beta} - C_{\beta\alpha} = \frac{C_{\beta\theta} - C_{\beta\alpha}}{K_{\beta\alpha}\sqrt{\pi}(\text{erf}(K_{\beta\theta}) - \text{erf}(K_{\beta\alpha}))} \exp(-(K_{\beta\alpha})^2) + \frac{C_{\alpha AB} - C_{\alpha\beta}}{K_{\alpha\beta}\sqrt{\pi}(\text{erf}(K_{\alpha\beta}) - \text{erf}(K_{\alpha AB}))} \exp(-(K_{\alpha\beta})^2) \quad (4b)$$

$$C_{\beta\theta} - C_{\theta\beta} = \frac{C_{\theta C} - C_{\theta\beta}}{K_{\theta\beta}\sqrt{\pi}(\text{erf}(K_{\theta C}) - \text{erf}(K_{\theta\beta}))} \exp(-(K_{\theta\beta})^2) + \frac{C_{\beta\alpha} - C_{\beta\theta}}{K_{\beta\theta}\sqrt{\pi}(\text{erf}(K_{\beta\theta}) - \text{erf}(K_{\beta\alpha}))} \exp(-(K_{\beta\theta})^2) \quad (4c)$$

$$C_{\theta C} - C_{C\theta} = \frac{C_{C\theta} - C_{C\theta}}{K_{C\theta}\sqrt{\pi}(1 - \text{erf}(K_{C\theta}))} \exp(-(K_{C\theta})^2) + \frac{C_{\theta\beta} - C_{\theta C}}{K_{\theta C}\sqrt{\pi}(\text{erf}(K_{\theta C}) - (\text{erf } K_{\theta\beta}))} \exp(-(K_{\theta C})^2) \quad (4d)$$

where $C_{AB\alpha}$, $C_{\alpha AB}$, $C_{\alpha\beta}$, $C_{\beta\alpha}$, $C_{\beta\theta}$, $C_{\theta\beta}$, $C_{\theta C}$, and $C_{C\theta}$ are the concentrations of element A, in atomic percent, on one side of the respective interface.

The thickness of each IMC layer is calculated by equations 5a through 5c:

$$l_{\alpha} = z_{\alpha\beta} - z_{AB\alpha} \quad (5a)$$

$$l_{\beta} = z_{\beta\theta} - z_{\alpha\beta} \quad (5b)$$

$$l_{\theta} = z_{\theta C} - z_{\beta\theta} \quad (5c)$$

where l_{α} , l_{β} , and l_{θ} , is the thickness of the α , β , and θ phase.

When the hypothetical AB-C system is applied to the AlXCe-Fe system, where XCe is a set composition of cerium, the IMC layers are taken to be $Al_{10}CeFe_2$, Fe_4Al_{13} , and Fe_2Al_5 . The aluminum concentration on each side of each interface is obtained from the Thermo-Calc software package.

4 Results

4.1 IMC Layer Growth

4.1.1 Total IMC Layer Thickness

The Al-4.4Mg alloy showed the largest reduction in total IMC layer thickness when compared to the 99.99% Al data, while the Al-10Ce alloy increased the total thickness in relation to the 99.99% Al. The general growth behavior is shown for the 99.99% Al samples (Figure 15). The large error bars are due to the uneven growth of the intermetallic phases, causing layer thickness measurements to vary based on measurement location. All five alloys had a relatively similar thickness at the 10 and 30 second mark and began to differentiate at the 120 second mark (Figure 16).

(a) 10 seconds

(b) 30 seconds

(c) 120 seconds

(d) 300 seconds

Figure 15. Optical micrographs depicting the development of the IMC layer with time for the 99.99% Al samples.

Figure 16. Total IMC layer Thickness for the five alloys investigated in the immersion study. The lines are added to guide the eye. The error bars are the standard deviation of 60 measurements at each time duration.

4.1.2 Phase Identification

The phases present in the IMC layer were identified through EDS point analysis. A 30s and 300s sample was analyzed for each alloy. The 99.99% Al, Al-6Ce, and Al-4.4Mg samples showed two phases present, $\text{Fe}_4\text{Al}_{13}$ and Fe_2Al_5 . The IMC layer for the Al-10Ce and Al-10Ce-5Mg alloys consisted of the ternary phase $\text{Al}_{10}\text{CeFe}_2$ and Fe_2Al_5 (Figure 17). The aluminum coating produced by each alloy was analyzed through EDS and showed elevated levels of the alloying elements either in the aluminum matrix or the aluminum-cerium eutectic phase (Table 4).

Figure 17. Al-6Ce and Al-10Ce BSE images showing the IMC layer components. Al-6Ce BSE images show Fe, Fe_2Al_5 , $\text{Fe}_4\text{Al}_{13}$, and eutectic (a) and (b). The Al-10Ce BSE image shows Fe, Fe_2Al_5 , $\text{Al}_{10}\text{CeFe}_2$, and eutectic (c). EDS was used for phase identification.

Table 4. Phases present in the IMC layer for each alloy.

Alloy	Time	Phases
99.99 Al	30s	$\text{Fe}_4\text{Al}_{13}$, Fe_2Al_5
	300s	$\text{Fe}_4\text{Al}_{13}$, Fe_2Al_5
Al-4.4Mg	30s	$\text{Fe}_4\text{Al}_{13}$, Fe_2Al_5
	300s	$\text{Fe}_4\text{Al}_{13}$, Fe_2Al_5
Al-6Ce	30s	$\text{Fe}_4\text{Al}_{13}$, Fe_2Al_5
	300s	$\text{Fe}_4\text{Al}_{13}$, Fe_2Al_5
Al-10Ce	30s	$\text{Al}_{10}\text{CeFe}_2$, Fe_2Al_5
	300s	$\text{Al}_{10}\text{CeFe}_2$, Fe_2Al_5
Al-10Ce-5Mg	30s	$\text{Al}_{10}\text{CeFe}_2$, Fe_2Al_5
	300s	$\text{Al}_{10}\text{CeFe}_2$, Fe_2Al_5

Table 5. Concentration of alloying additions in the aluminum coating analyzed through EDS.

Alloy	Phase	Ce (wt%)	Mg (wt%)
Al-6Ce	Eutectic	12.3-13.1	N/A
Al-10Ce	Eutectic	20.6-22.3	N/A
Al-4.4Mg	Matrix	N/A	4.6-5.1
Al-10Ce-5Mg	Eutectic	14.6-19.0	2.9-6.1

4.1.3 IMC Layer Component Thickness

The thickness of each component of the IMC layer was measured through back scatter electron images for 99.99% Al and binary aluminum-cerium alloys. The magnesium containing alloys were not measured due to the lack of the distinct “tongue-like” Fe_2Al_5 morphology of the IMC layer. The ternary phase, $\text{Al}_{10}\text{CeFe}_2$, present in the Al-10Ce alloy samples shows a consistent thickness at both 30 and 300 second immersion times. The $\text{Fe}_4\text{Al}_{13}$ phase in the 99.99% Al and Al-6Ce alloy increases with immersion time to be relatively equal with the ternary phase at 300 seconds (Figure 18a). The Fe_2Al_5 phase shows an increase in thickness with time, where the Al-10Ce alloy sample showed the thickest and the 99.99% Al sample showed the thinnest layer (Figure 18b).

Figure 18. Thickness of the constituent phases present in the IMC layer, where the first layer is either $\text{Fe}_4\text{Al}_{13}$ or $\text{Al}_{10}\text{CeFe}_2$ (a) and the second phase is Fe_2Al_5 (b) measured from BSE images.

4.1.4 IMC Layer Morphology

Cerium additions did not alter the morphology of the IMC layers from pure aluminum. The tongue-like appearance of the Fe_2Al_5 is unaltered between the 99.99 Al, Al-6Ce, and Al-10Ce alloys. The magnesium containing alloys contain two morphologies, the blocky and indistinguishable IMC layer (Figure 19a & c) and the distinct “tongue-like” appearance of the Fe_2Al_5 IMC layer (Figure 19b & d). The samples made with the magnesium containing alloys showed alternating sections of the distinct and indistinguishable IMC layers and the distinct sections grew larger as the immersion time increased.

(a) 30s, indistinguishable IMC layers

(b) 30s, distinct IMC layers

(c) 120s, indistinguishable IMC layers

(d) 120s, distinct IMC layers

Figure 19. Al-4.4Mg optical micrographs showing indistinguishable IMC layers, (a) and (c), and distinct IMC layers, (b) and (d), found in the magnesium containing alloys.

4.2 Predicted Layer Growth

The model described above was implemented in MATLAB and the equilibrium composition of aluminum at the interface for each phase was determined through Thermo-Calc simulations (Appendix A). The initial Al composition for the aluminum alloy substrate was taken to be 0.9879, 0.9791, and 0.9192 for the Al-6wt%Ce, Al-10wt%Ce, and Al-10wt%Ce-5wt%Mg alloy, respectively, and 0 for iron substrate. The solubility of iron in aluminum is assumed to be unaffected by cerium and magnesium so that $C_{AB\alpha}$ is taken to be 0.9877, 0.9788, and 0.9189 for Al-6wt%Ce, Al-10wt%Ce, and Al-10wt%Ce-5wt%. The solubility of aluminum in iron is also assumed to be unaffected

by the alloying additions and that the additions will not diffuse into the iron so that the solubility of aluminum in the iron substrate is described by equation 6:

$$C_{C\theta} = 3.57 \times 10^{-1} - 4.11 \times 10^{-4}T + 3.00 \times 10^{-7}T^2 \quad \text{Eq. 6}$$

where T is the temperature in Kelvin [25].

The cerium containing alloys were used to validate the designed model using the composition inputs from Thermo-Calc 2020a, TCAL6 database (Appendix B, Table 6). The model under predicts the total thickness for all three alloys, but correctly predicts the thickness of the Al-6Ce and Al-10Ce samples will be similar and thicker than the Al-10Ce-5Mg samples (Figure 20).

Figure 20. Total IMC layer thickness predicted by the triple layer growth model compared with experimental data for the three cerium containing alloys. The error bars are the standard deviation of 60 measurements per condition.

4.3 Mechanical Behavior

4.3.1 Experimental Cooling Curves

The experimental cooling curves from the 0.5° taper pin-pull castings portray cooling rates in the range from 0.4 – 3.9°C/s (Figure 21). The Al-10Ce and Al-10Ce-5Mg thermocouple data presented is an average of four measurements, while the Al-6Ce data utilized three measurements for the average. The cooling curves for one Al-6Ce alloy sample had an erroneous reading. The Al-10Ce alloy samples had the highest peak temperature. The peak temperature for the Al-10Ce and Al-10Ce-5Mg alloy samples were consistent, however the Al-10Ce-5Mg samples demonstrated faster cooling rates.

Figure 21. Experimental cooling curves for the three cerium containing alloys used in the pin-pull study. The 0.5° pin geometry were used to gather the thermocouple data.

4.3.2 Pin Casting Extraction Force

The ternary alloy, Al-10Ce-5Mg, showed a large increase peak force compared to the two binary alloys, Al-6Ce and Al-10Ce at the lower draft angles (Figure 22). As the draft angle increased the extraction force for all three alloys decreased and tended towards the same values. The Al-10Ce-5Mg alloy only has two data points at 20° and three data points at 25° due to failure to adhere during casting.

Figure 22. Extraction force for all alloys used in the study. The Al-10Ce-5Mg alloy shows a large increase in extraction force at 0.5° and the difference between the alloys decreases as the draft angle increases.

5 Discussion

5.1 IMC Layer Development

The iron-aluminum intermetallics that form during immersion testing shows the well documented tongue-like morphology of the Fe_2Al_5 phase for all five alloys. The polycrystalline $\text{Fe}_4\text{Al}_{13}$ phase was present for the alloys containing 6% cerium or less. The alloys containing 10wt% cerium formed a ternary iron-aluminum-cerium phase, $\text{Al}_{10}\text{CeFe}_2$, in place of the $\text{Fe}_4\text{Al}_{13}$ phase. However, the formation of the ternary phase did not hinder the growth of the Fe_2Al_5 phase. Zinc, from the galvanized coating, was not found in any of the IMC layer components or in the aluminum coating. Therefore, the zinc likely dissolved and then diffused into the aluminum melt and/or was present at levels below the EDS detection limit.

The formation of the $\text{Al}_{10}\text{CeFe}_2$ phase in the alloys containing 10wt%Ce is attributed to the supersaturation of cerium in the aluminum immediately surrounding the steel rod. The supersaturation is caused by solidification outward from the steel rod where the initial boundary condition would be roughly 50wt% iron and 50wt% aluminum alloy; based off the iron-aluminum-cerium equilibrium phase diagram, the first phase formed would be Fe_2Al_5 . The formation of the $\text{Al}_{10}\text{CeFe}_2$ phase would be dependent on the dissolution of iron and diffusion of cerium into the nearby aluminum alloy. Through energy dispersive spectroscopy, there was no cerium detected in the Fe_2Al_5 phase, however, there was an increased concentration of cerium in the aluminum coating outside the IMC layer. In the iron and cerium poor corner of the iron-aluminum-cerium phase diagram at 750°C shows a region of $\text{Al}_{10}\text{CeFe}_2$ +liquid that would be achievable with ~14wt% cerium, shown in red (Figure 23). The cerium supersaturation measured in the Al-10Ce and Al-10Ce-5Mg alloys would allow for this phase formation. However, the lower level of supersaturation present in the Al-6Ce alloy would not permit the formation of the ternary phase, thus the $\text{Fe}_4\text{Al}_{13}$ phase forms.

Figure 23. Ternary Al-Fe-Ce phase diagram at 750°C generated in Thermo-Calc 2020a using TCAL6 database. An $\text{Al}_{10}\text{CeFe}_2$ phase field is present in the iron and cerium poor corner of the phase diagram that would be possible to achieve with enough cerium supersaturation.

The concentration of magnesium present in the aluminum matrix is well below the solubility limit, with a maximum of 9wt% at 490°C. The concentration of magnesium measured along the interface was found to be lower than the solubility limit, therefore, the magnesium will stay in solution along the interface and not form any magnesium containing phases (Table 5). The increase in magnesium concentration along the interface would cause a barrier to form that impedes transfer of aluminum into the IMC layer.

The magnesium additions also altered the morphology of the IMC layer from the typical tongue-like Fe_2Al_5 to a blocky layer of Fe_2Al_5 growths. In addition, the typically clear delineation between the intermetallic layers and the aluminum coating was obscured. This phenomenon reduced the accuracy of the relative thickness measurements, such that reliable measurements could not be obtained by optical microscopy. The interfaces showed crystals of either $\text{Fe}_4\text{Al}_{13}$, for the Al-4.4Mg alloy, or $\text{Al}_{10}\text{CeFe}_2$, for the Al-10Ce-5Mg alloy, floating in the aluminum coating. Observations made from optical

microscopy showed that there was a distinct IMC layer, similar to the layer seen in pure Al-Fe joints, and the indistinct IMC layer containing the mixture of disconnected crystals in the aluminum matrix and loss of the tongue-like morphology that would alternate as one moved radially around the sample. However, the frequency and breadth of the distinct IMC layer increased with immersion time. At the lower immersion times, the blocky Fe_2Al_5 layer was thicker than the “tongue-like” morphology, but with time the two morphologies grew to relatively similar thicknesses.

The cerium additions formed a eutectic microstructure, composed of $\text{Al}_{11}\text{Ce}_3$ and aluminum, surrounding areas of aluminum matrix (Figure 17). The majority of the interface between the aluminum coating and IMC layer is comprised of the aluminum matrix in direct contact with the IMC layer, while the $\text{Al}_{11}\text{Ce}_3$ phase formed further from the IMC layer. Additionally, the IMC layer thickness is not greatly reduced due to the addition of cerium alone. Therefore, hypothesis two is not supported.

5.2 Multi-Layer Growth Model

The alloys used to validate the model did not form the three layers required. However, the thicknesses predicted by the model follow the correct parabolic trend. This shows that the correct physics and kinetics are present and accounted for (Figure 19).

The model assumes a constant aluminum interdiffusion coefficient, however, it should either increase or decrease depending on the interdiffusion coefficient of aluminum through the phase or phases present between the aluminum melt and steel rod. Initially, the rate limiting step would be the diffusion of aluminum into steel until the first intermetallic layer forms, and then the diffusion through this layer becomes the rate limiting step. Diffusion through the intermetallic as the rate limiting step is supported through the observed parabolic growth rate (Figure 18). The rate limiting step will change with each additional layer that forms, if the diffusion of aluminum through the

new layer is slower than through the previously formed layer, then the new layer becomes the dominating factor.

The developed model assumes a steady state equilibrium, where each phase predicted on the phase diagram will form starting at 50 wt.% iron and moving towards the aluminum rich portion of the system. However, the samples produced to validate the model were produced in a non-steady state equilibrium system. Four major factors contribute to the non-steady state equilibrium system: initial temperature difference between the steel rod and aluminum melt, inconsistent temperature, immersion duration, and quenching. The steel rod is at room temperature directly prior to immersion and is not allowed to preheat before reacting with the aluminum melt. The large temperature gradient would cause a thin layer of aluminum to initially solidify around the steel rod and would need to remelt before more of the aluminum melt can react with the steel. The inconsistent temperature present during the immersion would alter the growth of the IMC layer, the temperature of the reaction area would initially drop up the steel rod entering the aluminum melt and then gradually increase with time. The short immersion times do not allow the aluminum melt and steel rod system to come to equilibrium and only allows the more stable and faster to nucleate phases to form and grow. The water quench immediately after removal from the aluminum melt inhibits any further reaction and halting any further progression of the system towards a steady state equilibrium.

The model could be applied to silicon containing alloys used in other dissimilar castings; these alloys produce three and sometimes four layers depending on the silicon content and immersion time [19]. The model would require experiments to determine appropriate aluminum diffusion coefficients through the respective phases in the IMC layer.

5.3 Effect of Alloy Additions on Mechanical Strength

The interfacial shear force can be determined from the pin-pull extraction force by applying a model that takes into account the draft angle and three unknown constants: interfacial shear force, contact force, and coefficient of friction, Equation 7 [27]:

$$F_e = A\sigma_{int} + A\sigma_{cp}(\mu \cos(\theta) - \sin(\theta)) \quad \text{Eq. 7}$$

where F_e is the extraction force, A is the lateral area, σ_{int} is the interfacial shear strength, σ_{cp} is the contact pressure, μ is the coefficient of friction, and θ is the draft angle. By holding the interfacial shear force to zero the contact force and coefficient of friction can be determined and by holding the friction force to zero the interfacial shear force can be determined.

A one-way ANOVA was performed on the data from the three alloys and showed that the 95% confidence intervals of the binary alloys overlapped but did not overlap with the 95% confidence interval of the ternary alloy (Figure 24). This analysis shows that the alloying additions did not affect the results of the test for the Al-6Ce and Al-10Ce alloys, therefore the data for these two alloys will be combined and then fitted to the equation presented above. The Al-10Ce-5Mg data will be fit to the model on its own.

Figure 24. Interval plot for the 95% confidence interval for the three alloys. The overlap between the Al-6Ce and Al-10Ce shows they are not statistically different and can be pooled before being analyzed.

The equation was fit to the data using the Microsoft Excel Solver add-in to minimize the sum of squares difference between the experimental data and the model. The area was taken to be only the drafted surface of the pin, the top of the pin was not considered due to the draft angle going to 90°. The best fit for the Al-6Ce and Al-10Ce alloys comes when the interfacial strength is set to zero, the contact pressure is 12.2 kPa, and the coefficient of friction is 0.71. The best fit for the Al-10Ce-5Mg alloy occurs when the interfacial strength is set to zero, contact pressure is 24.5 kPa, and coefficient of friction is 0.73, however the best fit greatly underestimates at the lowest draft angle. These best fit lines are plotted as “friction” (Figure 25). The interfacial strengths are also shown as “interfacial”. The inclusion of magnesium doubles both the interfacial shear strength and contact pressure, however it does not greatly impact the coefficient of friction. The increase in interfacial strength could be caused by the increased magnesium concentration at the interface increasing the solid solution strengthening directly around the pin. The three Al-10Ce-5Mg failed samples at higher draft angles could be due an increase in contact pressure forcibly expelling the pins while removing the casting from the molds. The increase in interfacial shear strength coincides with the thinnest IMC layer, thereby, the metallurgical bond between aluminum and steel is enhanced through magnesium additions. The addition of cerium did not have a substantial impact on the mechanical properties of the casting; the Al-10Ce and Al-6Ce produced statistically similar extraction forces.

Figure 25. Extraction force for all alloys. The friction only, shown as black lines, is the best fit of Equation 7 for the combined binary alloys and the ternary alloy.

The large under-estimation of the friction only line at the lowest taper, for the Al-10Ce-5Mg data, implies that the true best fit would be a combination of both interfacial strength and contact pressure. Equation 7 was fit using the Microsoft Excel Solver, however only the coefficient of friction was restricted to be between 0.4 and 0.9. The inclusion of both interfacial strength and contact pressure increased the R^2 value from 0.50, friction only, to 0.67. This increase in fit occurs when the interfacial strength, contact pressure, and coefficient of friction are 3.9 kPa, 33.1 kPa, and 0.53. The combination of interfacial strength and contact pressure is plotted as “Interfacial + Friction” (Figure 26).

Figure 26. The combination of interfacial strength and contact pressure produce a better fit to the Al-10Ce-5Mg data.

5.4 Hypotheses

The combination of the two proposed mechanisms for IMC layer thickness reduction due to magnesium additions, magnesium supersaturation forming a barrier to aluminum atoms entering the IMC layer and reduction in lattice parameter of the phases present in the IMC layer, was greater than the proposed mechanism due to cerium additions. The proposed lattice parameter refinement mechanism, would cause a reduction in aluminum diffusion down the c-axis, thereby reducing the IMC layer growth. The lattice parameters of the phases present between pure aluminum and steel and a binary aluminum-magnesium alloy and steel could be measured through x-ray diffraction. The effect of stable $\text{Al}_{11}\text{Ce}_3$ precipitates acting as an aluminum diffusion barrier was minimal due to the small volume fraction of the precipitate phase between the aluminum matrix and IMC layer.

6 Conclusion

The addition of magnesium was shown to greatly reduce the formation and growth of the intermetallic compound layer. This is attributed to magnesium reducing the lattice parameters of the components present within the IMC layer and reducing the thermal conductivity of the aluminum melt. Magnesium was not detected through EDS analysis in any of the IMC layer components, but in elevated levels within the aluminum coating outside the IMC layer.

The addition of cerium did not have a large effect on the growth of the IMC layer for the short and intermediate immersion times. However, at the longest immersion time, 300s, the Al-10Ce alloy produced a total layer thickness 23.3 microns thicker than the 99.99% Al samples. The Al-6Ce alloy IMC layer was 18.6 microns thinner than that of the 99.99% Al samples. The samples produced with the Al-10Ce and Al-10Ce-5Mg alloys formed $\text{Al}_{10}\text{CeFe}_2$ in the place of $\text{Fe}_4\text{Al}_{13}$. It is purposed this phase formed due to the supersaturation of cerium in the aluminum melt immediately around the rod. The supersaturation was caused by the initial reaction formation of Fe_2Al_5 , in which cerium was not detected through EDS.

Interfacial shear strength was increased from 12.2 kPa to 24.5 kPa due to the addition of magnesium. However, the coefficient of friction remains relatively constant, 0.71 for the pooled binary Al-Ce alloys and 0.73 for the Al-10Ce-5Mg alloy. The increase in interfacial shear force coincides with the decrease in overall thickness of the IMC layer. The combination of interfacial strength and contact pressure provided a better fit to the Al-10Ce-5Mg data, implying the magnesium additions increased the metallurgical bonding phenomenon.

Reference:

- [1] R. Scharp, "Piston for an internal combustion engine," US20060278180A1, Dec. 14, 2006.
- [2] J. C. Viala, M. Peronnet, F. Barbeau, F. Bosselet, and J. Bouix, "Interface chemistry in aluminium alloy castings reinforced with iron base inserts," *Composites Part A: Applied Science and Manufacturing*, vol. 33, no. 10, pp. 1417–1420, Oct. 2002, doi: 10.1016/S1359-835X(02)00158-6.
- [3] C. Soderhjelm, "Multi-Material Metal Casting: Metallurgically Bonding Aluminum to Ferrous Inserts," *Doctoral Dissertations (All Dissertations, All Years)*, Apr. 2017, [Online]. Available: <https://digitalcommons.wpi.edu/etd-dissertations/174>.
- [4] K. Bouche, F. Barbier, and A. Coulet, "Intermetallic compound layer growth between solid iron and molten aluminium," *Materials Science and Engineering: A*, vol. 249, no. 1–2, pp. 167–175, 1998.
- [5] E. Aguado, A. Baquedano, U. Uribe, A. I. Fernandez-Calvo, and A. Niklas, "Comparative Study of Different Interfaces of Steel Inserts in Aluminium Castings," *Materials Science Forum*, 2013. <https://www.scientific.net/MSF.765.711> (accessed Aug. 15, 2019).
- [6] M. Zhe, O. Dezellus, B. Gardiola, M. Braccini, and J. C. Viala, "Chemical Changes at the Interface Between Low Carbon Steel and an Al-Si Alloy During Solution Heat Treatment," *J. Phase Equilib. Diffus.*, vol. 32, no. 6, pp. 486–497, Dec. 2011, doi: 10.1007/s11669-011-9949-z.
- [7] W.-J. Cheng and C.-J. Wang, "Effect of silicon on the formation of intermetallic phases in aluminide coating on mild steel," *Intermetallics*, vol. 19, no. 10, pp. 1455–1460, Oct. 2011, doi: 10.1016/j.intermet.2011.05.013.
- [8] N. Takata, M. Nishimoto, S. Kobayashi, and M. Takeyama, "Crystallography of Fe₂Al₅ phase at the interface between solid Fe and liquid Al," *Intermetallics*, vol. 67, pp. 1–11, Dec. 2015, doi: 10.1016/j.intermet.2015.07.011.
- [9] W. Zhang, Z. Fan, P. Hu, Y. Long, H. Liu, and J. Wen, "Effect of Rare Earth on Void Band of Diffusion Layer and Properties of Aluminized Steel," *Journal of Iron and Steel Research, International*, vol. 13, no. 5, pp. 60–78, Sep. 2006, doi: 10.1016/S1006-706X(06)60096-4.
- [10] M. Mihalkovič and M. Widom, "Structure and stability of Al₂Fe and Al₅Fe₂: First-principles total energy and phonon calculations," *Phys. Rev. B*, vol. 85, no. 1, p. 014113, Jan. 2012, doi: 10.1103/PhysRevB.85.014113.
- [11] W. Deqing, S. Ziyuan, and Z. Longjiang, "A liquid aluminum corrosion resistance surface on steel substrate," *Applied Surface Science*, vol. 214, no. 1, pp. 304–311, May 2003, doi: 10.1016/S0169-4332(03)00505-1.
- [12] W. Liu *et al.*, "Inhibitory effect of Ti and La on Fe dissolution in Al–Zn–Si bath by in-situ SXRD, SXRF, TEM and DFT calculation," *Materials Characterization*, vol. 145, pp. 135–141, Nov. 2018, doi: 10.1016/j.matchar.2018.08.038.
- [13] V. Vijayan and K. N. Prabhu, "The effect of simultaneous refinement and modification by cerium on microstructure and mechanical properties of Al-8% Si

- alloy,” *International Journal of Cast Metals Research*, vol. 29, no. 6, pp. 345–349, Nov. 2016, doi: 10.1080/13640461.2016.1144698.
- [14] Furuya TakuNozomi, S. TakashiKatsu, H. Sato, H. Kokawa, and T. Yujiro, “Grain refinement and strengthening of Fe₂AlF using alloy elements in Al/Fe dissimilar metal joints,” *Welding Society National Convention Lecture Summary*, vol. 2017s, pp. 106–107, 2017, doi: 10.14920/jwstaikai.2017s.0_106.
- [15] N. Kyokuta, M. Koba, T. Araki, S. Nambu, J. Inoue, and T. Koseki, “Fracture Toughness Evaluation of Thin Fe–Al Intermetallic Compound Layer at Reactive Interface between Dissimilar Metals,” *Materials Transactions*, vol. 54, no. 6, pp. 994–1000, 2013, doi: 10.2320/matertrans.M2012425.
- [16] Y. Ho and M. W. Ackerman, “Thermal Conductivity of Ten Selected Binary Alloy Systems,” p. 239.
- [17] Y. Xie, A. Du, X. Zhao, R. Ma, Y. Fan, and X. Cao, “Effect of Mg on Fe–Al interface structure of hot-dip galvanized Zn–Al–Mg alloy coatings,” *Surface and Coatings Technology*, vol. 337, pp. 313–320, Mar. 2018, doi: 10.1016/j.surfcoat.2018.01.038.
- [18] K. N. Kulkarni and A. A. Luo, “Interdiffusion and Phase Growth Kinetics in Magnesium-Aluminum Binary System,” *J. Phase Equilib. Diffus.*, vol. 34, no. 2, pp. 104–115, Apr. 2013, doi: 10.1007/s11669-013-0189-2.
- [19] H. Springer, A. Kostka, E. J. Payton, D. Raabe, A. Kaysser-Pyzalla, and G. Eggeler, “On the formation and growth of intermetallic phases during interdiffusion between low-carbon steel and aluminum alloys,” *Acta Materialia*, vol. 59, no. 4, pp. 1586–1600, Feb. 2011, doi: 10.1016/j.actamat.2010.11.023.
- [20] S. Kobayashi and T. Yakou, “Control of intermetallic compound layers at interface between steel and aluminum by diffusion-treatment,” *Materials Science and Engineering: A*, vol. 338, no. 1, pp. 44–53, Dec. 2002, doi: 10.1016/S0921-5093(02)00053-9.
- [21] D. Weiss, “Castability and Characteristics of High Cerium Aluminum Alloys,” *Advanced Casting Technologies*, Dec. 2017, doi: 10.5772/intechopen.72830.
- [22] Z. C. Sims *et al.*, “Cerium-Based, Intermetallic-Strengthened Aluminum Casting Alloy: High-Volume Co-product Development,” *JOM*, vol. 68, no. 7, pp. 1940–1947, Jul. 2016, doi: 10.1007/s11837-016-1943-9.
- [23] Z. C. Sims *et al.*, “High performance aluminum–cerium alloys for high-temperature applications,” *Mater. Horiz.*, vol. 4, no. 6, pp. 1070–1078, Oct. 2017, doi: 10.1039/C7MH00391A.
- [24] P. D. Staublin, “Investigating Microalloying Elements to Accelerate Zirconium Trialuminide Precipitation in Aluminum Alloys,” p. 84.
- [25] M. Kajihara, “Quantitative Evaluation of Interdiffusion in Fe₂Al₅ during Reactive Diffusion in the Binary Fe–Al System,” *Materials Transactions*, vol. 47, no. 6, pp. 1480–1484, 2006, doi: 10.2320/matertrans.47.1480.
- [26] L. Wang, Y. Wang, P. Prangnell, and J. Robson, “Modeling of Intermetallic Compounds Growth Between Dissimilar Metals,” *Metall and Mat Trans A*, vol. 46, no. 9, pp. 4106–4114, Sep. 2015, doi: 10.1007/s11661-015-3037-7.

- [27] A. Monroe and P. Sanders, “Reducing Die Lubricant by Understanding the Importance of Draft Angle and Casting Alloy,” *North American Die Casting Congress, Cleveland OH, 2019*, vol. T19-083.

7 Appendix A: Triple Layer Growth Model MATLAB Code

```
%Three IMC layer Growth Kinetics
%Author: Matt Thomas
%Date:4/29/2020

%a=Al y=Al10CeFe2 b=Al13Fe4 g=Al5Fe2 c=Fe

R=8.314;
T=273+750; %temperature

%Diffusion Information from:

%Diffusion for Al
Qa=135000;
Dao=1.2e-5;
Da=Dao*exp(-Qa/(R*T));

%Diffusion for Al10CeFe2
Qy=276000;
Dyo=234;
Dy=Dyo*exp(-Qy/(R*T));

%Diffusion for Al13Fe4
Qb=276000;
Dbo=234;
Db=Dbo*exp(-Qb/(R*T));

%Diffusion for Al5Fe2
Qg=135000;
Dgo=7.04e-10;
Dg=Dgo*exp(-Qg/(R*T));

%Diffusion for Fe
Qc=246000;
Dco=5.2e-4;
Dc=Dco*exp(-Qc/(R*T));

%Atomic fraction of Aluminum in phase
Cao=0.9791;
Cay=0.9788;
Cya=0.9099;
Cyb=0.7449;
Cby=0.7613;
Cbg=0.7194;
Cgb=0.7449;
Cgc=0.6456;
Ccg=(3.57*10^-1)-(4.11*10^-4)*T+(3*10^-7)*T^2;
Cco=0;

%Equations for the expanded Kajihara model
syms Kay Kyb Kbg Kgc
```

```

Kya=Kay*( (Da/Dy)^(1/2));
Kby=Kyb*( (Dy/Db)^(1/2));
Kgb=Kbg*( (Db/Dg)^(1/2));
Kcg=Kgc*( (Dg/Dc)^(1/2));

a=Cao-Cay;
b=Kay*(pi)^(1/2)*(1+erf(Kay));
c=exp(-(Kay)^2);
d=Cyb-Cya;
f=Kay*(pi)^(1/2)*(erf(Kyb)-erf(Kya));
g=exp(-(Kya)^2);

eq1=((a/b)*c)+((d/f)*g);

a1=Cya-Cyb;
b1=Kyb*(pi)^(1/2)*(erf(Kyb)-erf(Kya));
c1=exp(-(Kyb)^2);
d1=Cbg-Cby;
f1=Kby*(pi)^(1/2)*(erf(Kbg)-erf(Kby));
g1=exp(-(Kby)^2);

eq2=((a1/b1)*c1)+((d1/f1)*g1);

a2=Cby-Cbg;
b2=Kbg*(pi)^(1/2)*(erf(Kbg)-erf(Kby));
c2=exp(-(Kbg)^2);
d2=Cgb-Cgc;
f2=Kgc*(pi)^(1/2)*(erf(Kgb)-erf(Kgc));
g2=exp(-(Kgc)^2);

eq3=((a2/b2)*c2)+((d2/f2)*g2);

a3=Cgb-Cgc;
b3=Kgc*(pi)^(1/2)*(erf(Kgc)-erf(Kgb));
c3=exp(-(Kgc)^2);
d3=Cco-Ccg;
f3=Kcg*(pi)^(1/2);
g3=exp(-(Kcg)^2);

eq4=((a3/b3)*c3)+((d3/f3)*g3);

s=vpasolve([eq1==(Cay-Cya),eq2==(Cyb-Cby),eq3==(Cbg-Cgb),eq4==(Cgc-Ccg)], [Kay,Kyb,Kbg,Kgc],[-1,1;-1,1;-1,1;-1,1]);

KAY=s.Kay;
KYB=s.Kyb;
KBG=s.Kbg;
KGC=s.Kgc;
KYA=KAY*( (Da/Dy)^(1/2));
KBY=KYB*( (Dy/Db)^(1/2));
KGB=KBG*( (Db/Dg)^(1/2));
KCG=KGC*( (Dg/Dc)^(1/2));

```

```

%Calculating layer thickness

t=[10,30,120,300];
ly=[];
lb=[];
lg=[];
ltotal=[];
for i=1:numel(t)
    zab=KAY*((4*Da*t(i))^(1/2))*(10^6);
    zbc=KYB*((4*Dy*t(i))^(1/2))*(10^6);
    zcd=KBG*((4*Db*t(i))^(1/2))*(10^6);
    zde=KCG*((4*Dc*t(i))^(1/2))*(10^6);
    ly(i)=abs(zbc-zab);
    lb(i)=abs(zcd-zbc);
    lg(i)=abs(zde-zcd);
    ltotal(i)=ly(i)+lb(i)+lg(i);
end

```

8 Appendix B: IMC Growth Model Inputs.

Table 6. Compositional inputs for the IMC layer modeled at 750°C.

Alloy	C_{AB0}	$C_{AB\alpha}$	$C_{\alpha AB}$	$C_{\alpha\beta}$	$C_{\beta\alpha}$	$C_{\beta\theta}$	$C_{\theta\beta}$	$C_{\theta C}$	$C_{C\theta}$	C_{C0}
Al-6Ce	0.9879	0.9877	0.8527	0.7497	0.7656	0.7166	0.7497	0.6632	Eq. 6	0
Al-10Ce	0.9791	0.9788	0.9099	0.7449	0.7613	0.7194	0.7449	0.6456	Eq. 6	0
Al-10Ce-5Mg	0.9192	0.9189	0.7985	0.7146	0.7146	0.6722	0.6979	0.6076	Eq. 6	0