Improvement in Toughness of Castings through Chemical Surface Modification

by

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ABSTRACT

Alloys with good toughness and elevated temperature properties like A201 are expensive and can be more difficult to process. This results in the use of heavier but less expensive alternatives in many applications where toughness is of concern, such as steels. Common alloys such as A356 and E357 are relatively cheap and easy to work with. However, these alloys have considerably lower toughness than premium alloys. This research aims to investigate surface modification treatments that could yield better toughness at a low cost in a common aluminum alloy. The process must show significant improvement in said properties, be cost effective, and easily adaptable in a common foundry. Diffusion of coating material into the substrate was investigated with a variety of coating metals. The diffusion process was facilitated in the solutionizing step for the given substrate aluminum in order to strengthen the sub-surface region of the parts. This research aims to provide a platform for further research into the practical effects of the coating and tempering on impact and toughness properties. These samples were characterized by optical and scanning electron microscopy, EDS, impact testing, and tensile testing.

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0 RESEARCH DETAILS

0.1 FOCUS GROUP

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0.2 PROBLEM STATEMENT

Alloys with good toughness and elevated temperature properties like A201 are expensive and can be more difficult to process. This results in the use of heavier but less expensive alternatives in many applications where toughness is of concern, such as steels. Common alloys such as A356 and E357 are relatively inexpensive and easy to work with. However, these alloys have considerably lower toughness than premium alloys. This research aims to investigate surface modification treatments that could yield better toughness at a low cost in a common aluminum alloy. The process must show significant improvement in said properties, be cost effective, and easily adaptable in a common foundry.

0.3 EXPECTED OUTCOMES

I) Develop a surface process for a common aluminum casting alloy
II) Characterize the microstructure of the subsurface region
III) Evaluate the change in toughness of a treated part
IV) Evaluate the change in impact strength of a treated part

0.4 APPROACH

I) Literature review
II) Develop appropriate methods for application of coatings
III) Evaluate toughness and impact strength of treated castings
IV) Improve process and optimize selected mechanical properties

0.5 TIMELINE

	2017		2018	
	Jan - Jun	Jul – Dec	Jan – Jun	Jul - Dec
Literature Review	I	I	I	I
Experimental Plan	II	II	II	
Experimental Work		III	III	III
Writing			IV	IV

0.6 PROJECT SCOPE

The scope of this project is to develop a method for chemically modifying the surface of castings that leads to improved toughness and impact strength. The process must be a cost effective and easily adaptable chemical method. In order to address the easily adaptable aspect, it is necessary to innovate processes already implemented for treating aluminum. Treatments of interest include coatings and age hardening.

Suggested base material for the substrate began as A356 but transitioned to A365 as the candidate alloy and A201 as the target alloy for mechanical properties. A356 is a commonly used alloy in the aluminum casting industry for air craft and automobiles whereas A201 is one of the premier alloys for its properties of excellent fracture and impact. Although A201 proves to be a useful alloy, the cost of using this type of material is the driving force for this research. Coatings to be investigated include common plating materials such as copper, nickel, and titanium. A365 is the most recent substrate due to small grains that form from high-pressure die castings and similar compositions to A356.

In moving forward with this research, alloy chemistry and diffusion are important considerations for the success of developing this new method. Another factor to consider is the method by which mechanical properties are evaluated. The properties that are intended to be improved only pertain to some depth through the surface and therefore shows no significant change compared to bulk properties. Impact strength and toughness may not be increased considerably enough in the bulk to show significant improvements due to the locality of change in the piece. Thus, methods for measuring improvements must be developed or taken from literature such as using nanoindentation to measure mechanical properties.

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1 INTRODUCTION

1.1 PROJECT NEEDS

Alarming climate change has driven the need for improved technology and materials across the world. A global effort on reducing emissions has reached nearly all industries, such as transportation and manufacturing sectors. In order to combat climate change, the Obama Administration finalized a mandate stating that all cars and light-duty trucks must be capable of reaching 54.5 miles per gallon of gas or better by 2025 [2]. For the automobile industry to achieve the feat, the development of a more efficient engine or a lighter vehicle are vital. According to the U.S. Department of energy, reducing the weight of a vehicle by 10% yields an improvement of 6% - 8% in fuel efficiency [3]. To this end, one may employ the use of high strength density metals such as aluminum. The use of aluminum would yield the high strengths of current materials and reduce the load of a vehicle.

In a similar vein, the aerospace industry currently employs about 80% by weight of aluminum in the typical construction of a commercial transport aircraft [4]. This aluminum is mainly in the wrought form, but a transition is being made towards cast aluminum for time reduction, material cost, and minimized post-processing. However, aerospace aluminum casting alloys are niche and require high standards due to safety concerns. Typically, high additions of copper or aluminum-lithium alloys are used for the excellent fracture and impact properties at a much higher cost. In contrast, the aluminum-silicon series are some of the easiest to process and cast while also being the most cost effective of all aluminum alloys.

This research is spurred by the need to employ more cost-effective materials in place of expensive niche alloys. A process to improve common casting alloys in the aerospace and automotive industry is sought.

2 PROJECT GOALS

2.1 PROBLEM STATEMENT

Alloys with good toughness and elevated temperature properties like A201 are expensive and can be significantly more difficult to process. This results in the use of heavier but less expensive alternatives in many applications where toughness is of concern, such as steels. Common alloys such as A356 and E357 are relatively inexpensive and easy to work with. However, these alloys have considerably lower toughness than premium alloys. This research aims to investigate surface modification treatments that could yield better toughness, at lower cost, in a common aluminum alloy. The process must show significant improvement in said properties, be cost effective, and easily adaptable in a common foundry.

2.2 OBJECTIVES

In fewer terms, this research aims to:

- Improve toughness
- Improve impact strength
- Keep costs low

2.3 BOUNDARY CONDITIONS

Due in part to the objective of keeping costs low and narrowing the scope of this research, boundary conditions were set. These boundary conditions include:

- Processed or treated after initial casting
- Process operates in the standard T6 operating window of heat treatment for a given alloy
- The process is cost effective and adaptable to a typical foundry

3 LITERATURE REVIEW

3.1 BACKGROUND

This chapter provides an overview of the state of the art regarding the aluminum components in the aerospace and automotive industry and with respect to toughness and impact properties. This section presents the argument that a process by which common casting alloys can be improved to the heights of premium alloys can be developed and is needed. A basic introduction to toughness, and impact strength will be provided in addition to the technical challenges that are posed.

3.1.1 CURRENT MATERIALS & LIMITATIONS

Aluminum is one of the most prominent engineering materials that balance high strength and lower weight. It is relatively cheap, easy to work, and highly recyclable compared to magnesium or titanium-based alloys. This metal can accommodate high additions of other elements in terms of solubility, which gives aluminum the capability to alloy with a wide array of elements [1]. Aluminum even has properties to protect itself from further oxidation through its nearly instantaneous passivation. Aluminum is also capable of being manipulated for corrosive or high temperature environments just like steels [5]. These properties, in addition to low cost in material and manufacture, have allowed aluminum to pervade everyday life from household cutlery to aircraft engine housings. Its ubiquity and low cost are the driving forces for further research into improving aluminums' properties and reach [6, 7].

As it pertains to this research, we will only focus on cast aluminum alloys as there are numerous types. In recent years, a trend has been seen with movement towards aluminum in general due to ease of manufacturing, recyclability, and capital savings. The automotive industry for example, has steadily increased the aluminum content per vehicle year after year as shown in Figure 1. Using more cast aluminum components in automobiles has allowed and is continuing to allow manufacturers to remain economically competitive in the market [8]. Aluminum alloys are wildly versatile, can be created to satisfy a broad range of requirements in mechanical properties, can be alloyed with various elements for enhanced properties, and even used in matrix composites. A brief summary of properties of interest are given below in Table 1 and are taken from the ASM Handbook on Aluminum Castings [1, 5]. Impact and fracture properties are specifically of A356 in the T6 condition. Cast parts have the advantage of reducing manufacturing and machining costs by eliminating the need for welding, fluidity of aluminum allows the creation of complex and thin-walled shapes, and costs are generally less than the wrought counterparts [1].

Mechanical Property	**Value**
Tensile Strength [MPa]	70 – 505
Yield Strength [MPa]	20 -455
Elongation [%]	<1 – 30
Young’s Modulus [GPa]	65 - 80
Impact Energy [J][a]	2 - 30
Fracture Toughness $[MPa\sqrt{m}]$[b]	10 - 25

Table 1: Brief summary of mechanical properties of cast aluminum [5]. Fracture Toughness specifically for A356-T6 [9, 10] (b). Impact Energy specifically for A356-T6 in a permanent mold varying solution time (a) [11].

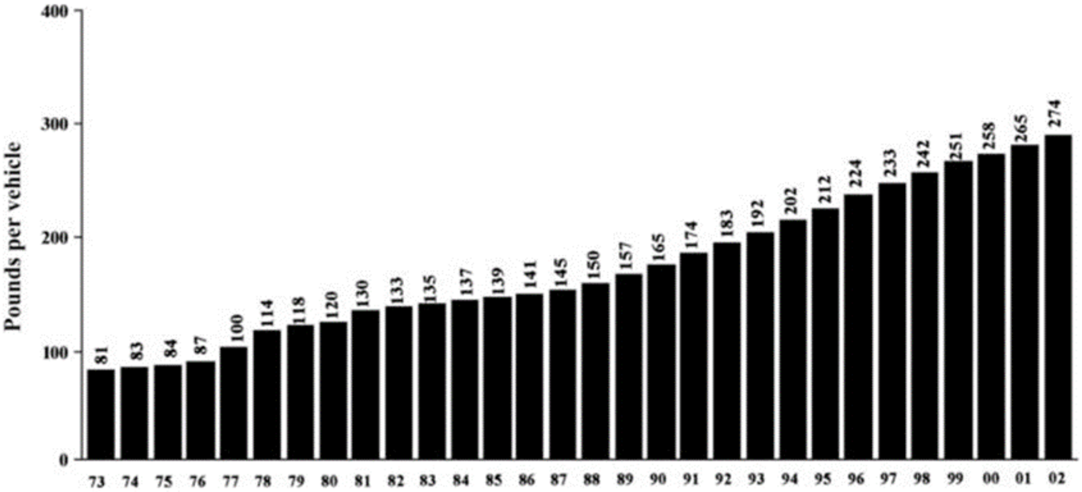


Figure 1: North American light vehicle change in aluminum content, 1973 to 2002 [1].

For this research, it is important to discuss post processing of cast alloys. One major facet is the heat treating of parts to a designated temper. Various tempers have been developed and optimized for a given set of desired properties. In general, cast aluminum parts are found in service with a temper whether it is for high strength or stress-corrosion resistance. The general process of heat treating goes as follows: solutionizing, cooling, and ageing. Some tempers require very specific quenchants, heating methods, natural ageing, etc.

3.2 TOUGHNESS PROPERTIES

Toughness is the measure of a materials ability to permanently (plastically) deform before fracturing entirely. Toughness is a combinatory property in that it considers strength and ductility of a material. Generally evaluated as the area under the stress strain curve, it is measured in energy per volume of the material. A material can have high strength and low ductility which results in low toughness. On the opposite end of the spectrum, a material with very high ductility and low strength is also low in toughness. The ideal mix would be high strength and high ductility which maximizes the area under a stress strain curve for a given material.

3.2.1 RELATIONSHIP TO ALUMINUM CASTINGS

Toughness is an important property for the aerospace and automotive industry. The aerospace industry is constantly in search of high strength and high ductility alloys for the stringent minimum requirements in safety. Generally, as the tensile strength increases in an alloy, the ductility suffers greatly. High strength materials will more likely experience brittle fracture rather than ductile failure which is more desirable of the two. Very high minimum requirements in toughness have been established on materials as yield strength increases for the aerospace industry and this limits the level of yield strengths available to engineers to produce safe aircraft [12].

3.2.2 INFLUENCES ON TOUGHNESS

The metallurgical influences on toughness of aluminum castings is a complex field of study. Clean melts and high cooling rates are requirements for good ductility and ultimately toughness in a material. Removing impurities and porosity reduces crack nucleation sites. Secondary phase morphology has a large impact on the toughness of a material. Secondary phases that are too large can be crack initiation sites due to incoherency with the matrix of aluminum. If the secondary phases have many sharp edges or non-spheroidal morphology, stresses can multiply at the corners and induce cracks much sooner than expected in a material when under tensile stress [13, 14].

3.2.3 IDEAL MICROSTRUCTURE

The ideal microstructure to result in high strength and high ductility for an overall good toughness is generally summed to have small dendrite arm spacing, spheroidal secondary phases, and low porosity. Other considerations are very similar to requirements for impact properties and will be discussed in further detail in the next section.

3.2.4 INDUSTRY SOLUTIONS

Solutions that are like impact properties will be discussed in the next section. Unique solutions will be briefly discussed here. Some study has been pursued into changing alloying chemistry with more cost-effective elements fur extended toughness properties. In one such case, additions of 1.5 wt% copper to an Al-Si-Mg alloy were found to increase the tensile properties by 10-25% with low reductions in ductility [15]. However, this research does not aim to change the bulk alloy chemistry as it is not within the scope of the project.

Tempering with age hardening can have drastic improvements in ductility and strength of a material. Dissolving of hard secondary phases into the aluminum matrix greatly improves the ductile properties but is accompanied by a reduction in strengths. Various tempers have been developed in order to optimize the strength and ductility of materials and is the focus of many studies for all new alloy developments.

3.3 IMPACT PROPERTIES

Impact strength or impact toughness is a measure of a material's ability to resist fracture under dynamic and sudden loading or the amount of energy the material can absorb before catastrophic failure. Impact energy is generally seen in research for a material's impact properties and is denoted in this paper as J_{IE} with units of joules.

A large portion of aluminum research is dedicated to the impact properties as they are vital to industry members. It has been repeatedly found that the microstructure of a casting is the determinant for impact properties in aluminum. Much work has been done studying the effects of casting parameters, alloying elements, ageing parameters, and geometry of parts on the microstructure and consequently impact strength.

3.3.1 RELATIONSHIP TO ALUMINUM CASTINGS

When manufacturing and designing a part for service, such as a landing gear, in aircraft or engine casing, impact strength is an important factor. Landing gears will repeatedly experience high impact upon bringing aircraft down and engine cylinder heads in automobiles experience explosive impact from combustion many times a second [7, 16]. In both cases, periodic and high strain rate loads are experienced and impact properties must be considered for unexpected accidental collision or unusually high explosive loads.

Inherent properties of cast aluminum, such as porosity or necessary elements in an alloy, can detract from the mechanical abilities of a part. This is especially true in aluminum where impurities and foundry casting capabilities greatly affect the final performance of a part [17].

3.3.2 INFLUENCES ON IMPACT STRENGTH

3.3.2.1 CASTING PARAMETERS

Casting parameters are reasonably simple to control to optimize desired properties. Besides clean melt charges and appropriate control of temperature, cooling rates have a significant effect. In aluminum alloys, microstructure and silicon particle morphology determines properties and cooling rates determine microstructure (SDAS) [18]. Shivkumar et al. demonstrated the dramatic effects of modifications to A356 for impact strength [11]. Strontium modified (SM) A356 were examined in Charpy impact tests in varying T6 conditions. Metal molds (high cooling rates) yielded an increase of 5 times higher impact energy than in the as cast state.

3.3.2.2 STRONTIUM (SM)

The SM on A356 did not significantly affect the arm spacing or grain size. However, the silicon eutectic was found to be much finer in the metal molds than sand molds and a process known as quench modification (QM) [11]. This refinement of the silicon morphology is accepted as the primary influencer on impact properties. In QM or SM, finer and globularized or spheroidized silicon eutectics result in significantly enhanced impact properties.

Finer silicon eutectic is obtained through high cooling rates whereas spheroidized silicon eutectic can be obtained through solutionizing in the T6 ageing treatment. During the solution stage, silicon in the unmodified α aluminum matrix experiences necking, fragmentation, diameter shrinkage, and finally spheroidization. The silicon, driven by interfacial energy reduction, is dissolved into α aluminum; at longer solution times (upwards of 168 hours), silicon will begin to coarsen but a significant amount will still not be fragmented and spheroidized. In SM A356, silicon eutectic experiences the same dissolution and spheroidization at shorter time scales (4 hours) and nearly completely. Shivkumar et al. continues to discuss that silicon particle spacing increases as it is being refined which means there is more aluminum matrix surrounding the silicon particles. The aluminum matrix is the main component in crack growth abatement as it is much more ductile and tougher than silicon. Cracks will begin at the silicon particles due to incoherency and more brittle nature of the silicon; if the particles are more spaced apart, cracks must travel farther in order to agglomerate and result in higher toughness and impact properties [11]. These results are in excellent agreement with Meyers and Lyons' work in 1986. Meyers and Lyons demonstrated that fracture toughness (K_{IC}) or static toughness was proportional to average silicon particle spacing λ for A357-T6 [19] whereas Shivkumar et al. demonstrated that J_{IC} in A356-T6 was proportional to $\lambda^{0.89}$.

3.3.2.3 AGEING

In regards to age hardening, when solution treated for the typical 8 to 12 hours, the impact energy doubled to 13.9 J in SM samples compared to the unmodified specimen. SM's effects were more significant when solidification cooling rates were much lower, such as in sand castings or thicker sections of a metal mold. Overall, the impact energy of SM alloys is always higher than the unmodified specimen at all solution times, solidification rates, and casting molds. From this study, increased solutionizing times resulted in increased impact energies. Explained previously, longer solution times led to finer and rounder silicon particles, which result in improved impact properties.

3.3.3 IDEAL MICROSTRUCTURE

In summary, the ideal microstructure for enhanced impact strength has fine and well dispersed silicon eutectic particles. These particles must be globularized and/or as close to spheroidized as possible through SM or QM. Finally, the silicon should be far apart from one another to mitigate crack linking.

3.3.4 INDUSTRY SOLUTIONS

Industry members generally cannot improve impact toughness after casting so great care is taken in the casting process. Steps include modification of the silicon eutectic or grain refinement which may help with silicon segregation at the grain boundaries. However, some work has been done in polishing as a simple method for improving impact strength. Some samples are purposely notched when testing as a standard. In regard to crack nucleation, Srivastava et al. demonstrated that in aluminum alloys, having a notch or not greatly affects the impact strength. Having a notch could reduce impact strength by 80% when compared to un-notched samples. Even a scratch on the surface of the specimen as deep as 0.1 mm was found to decrease the impact absorption by 30% compared to mirror polished samples [20].

3.4 TECHNICAL CHALLENGES

Due to the nature of this research, challenges have inevitably risen concerning measurement and evaluation of the effects. Some of these challenges will be briefly discussed in the following section.

3.4.1 BOUNDARY CONDITIONS

The proposed solutions involving a chemical surface treatment and a boundary condition of a T6 heat treating operating window limits the depth of effect that the treatment can have on the specimen. If the depth of effect of the treatment is limited to subsurface, bulk properties such as toughness and impact may not be affected significantly enough to be measured by conventional ASTM recommended methods.

In addition, most techniques employed to improve impact and fracture are conducted in the casting and cooling procedures. It is well documented that clean melt chemistries, good casting practices, additions of grain modifiers and refiners, and high cooling rates induce excellent parts. Given that the research is narrowed to processes applicable after casting severely limit the total potential improvement in desired mechanical properties.

3.4.2 MEASUREMENT TECHNIQUES

As stated, limited depth of effect will make bulk property measurements more difficult to attain. Bulk measurement instruments such as an impact tester or a compact-tension fracture sample are not directly applicable to surface treatments. Other methods to indirectly measure properties of interest have been suggested in the form of nanoindentation technique and changes in toughness from stress-strain curves.

4 APPROACH

The approach taken for this research focuses on sub-surface microstructural modification. It is well known that dendrite arm spacing, the dominant factor in aluminum's mechanical properties, has the largest effect. In the silicon series of aluminum alloys, silicon modification can substantially help. If the initiation of cracks in these alloys begin at the silicon-aluminum interface and crack mitigation can begin at the surface, then impact and toughness properties have the potential to be improved with just surface modification.

Inspiration for this research comes from the glass industry with regards to chemically strengthened glass. Chemically strengthening glass is a solid-state process in which completely solidified glass is submerged into a molten salt. Relatively large ions (compared to atoms in the glass) are diffused into the glass and induce compressive stresses by overcrowding. This compressive stress creates a very strong glass material that is much more resilient to fracture, impact, crack initiation, etc. A similar approach was proposed for aluminum by method of coatings and diffusion by heat treatment. However, due to the metallic nature of aluminum and amorphous nature of glass, the effect of overcrowding residual stresses will be drastically different. Aluminum may not experience any significant compressive residual stress due to ductility and stress relief experienced in the ageing step of heat treating.

4.1 SOLUBILITY

It will be important to evaluate the solubility of proposed coating materials into the substrate aluminum. To this end, Thermo-Calc software was used to produce phase diagrams of the base substrate A365 (nominal compositions) with varying weight of coating material. Note that in a phase diagram with pure aluminum and pure coating material, solubilities are generally higher. The following diagrams present lower solubilities of the coating material in aluminum due to the addition of alloying elements. Solid solutions in metals generally adhere to the Hume-Rothery Rules which will be listed below [21]:

- **Atomic Size** – Atomic radii must be within about 15% of one another
- **Crystal Structure –** Both atoms must have similar crystal structure
- **Electronegativity –** Similar electronegativity
- **Valences –** Similar valences

4.1.1 A365 – ZINC PHASE DIAGRAM

Figure 2 shows the phase diagram of A365 nominal composition against the composition of zinc. This phase diagram was not zoomed in because the solubility of zinc inside of this alloy is rather high at 500°C. The high solubility supports the idea of having zinc in solid solution to the aluminum matrix. Since a rapid quench is employed after solutionizing, zinc should remain in solution. Zinc has an atomic radius of approximately 1.42 Å and aluminum has a relatively smaller atomic radius of 1.18 Å. A combination of high solubility and larger atomic radius may simulate a strengthening akin to overcrowding experienced in glass ion implantation.

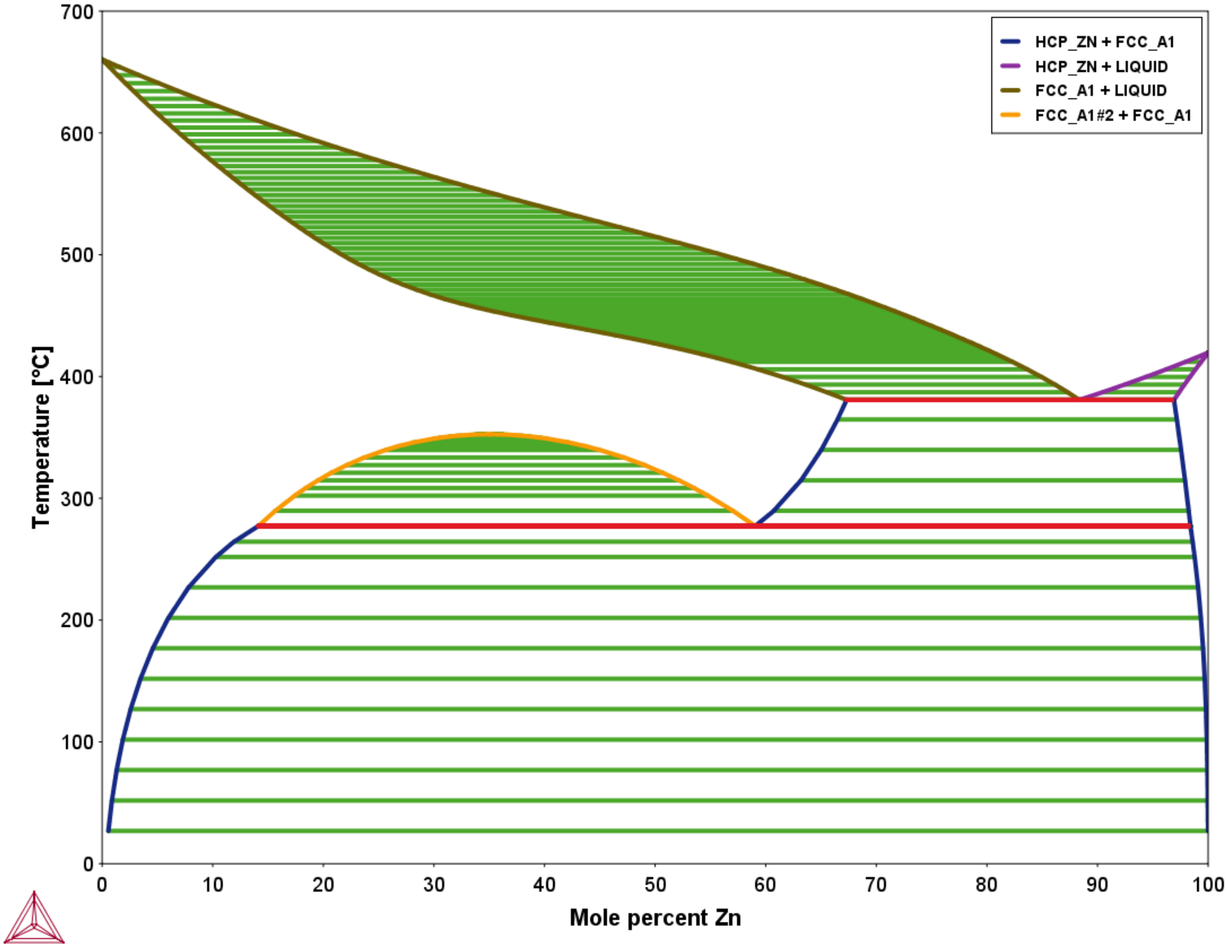


Figure 2: Thermo-Calc phase diagram of A365 nominal composition against composition of zinc. The phase diagram axes are zoomed into to show the solubility at 500°C.

4.1.2 A365 – COPPER PHASE DIAGRAM

This phase diagram in Figure 3 with A365 nominal composition against the composition of copper shows much more limited solubility compared to zinc. Although the solubility of copper is less than that of zinc, copper has a comparable atomic radius of 1.45 Å which may induce solid solution strengthening.

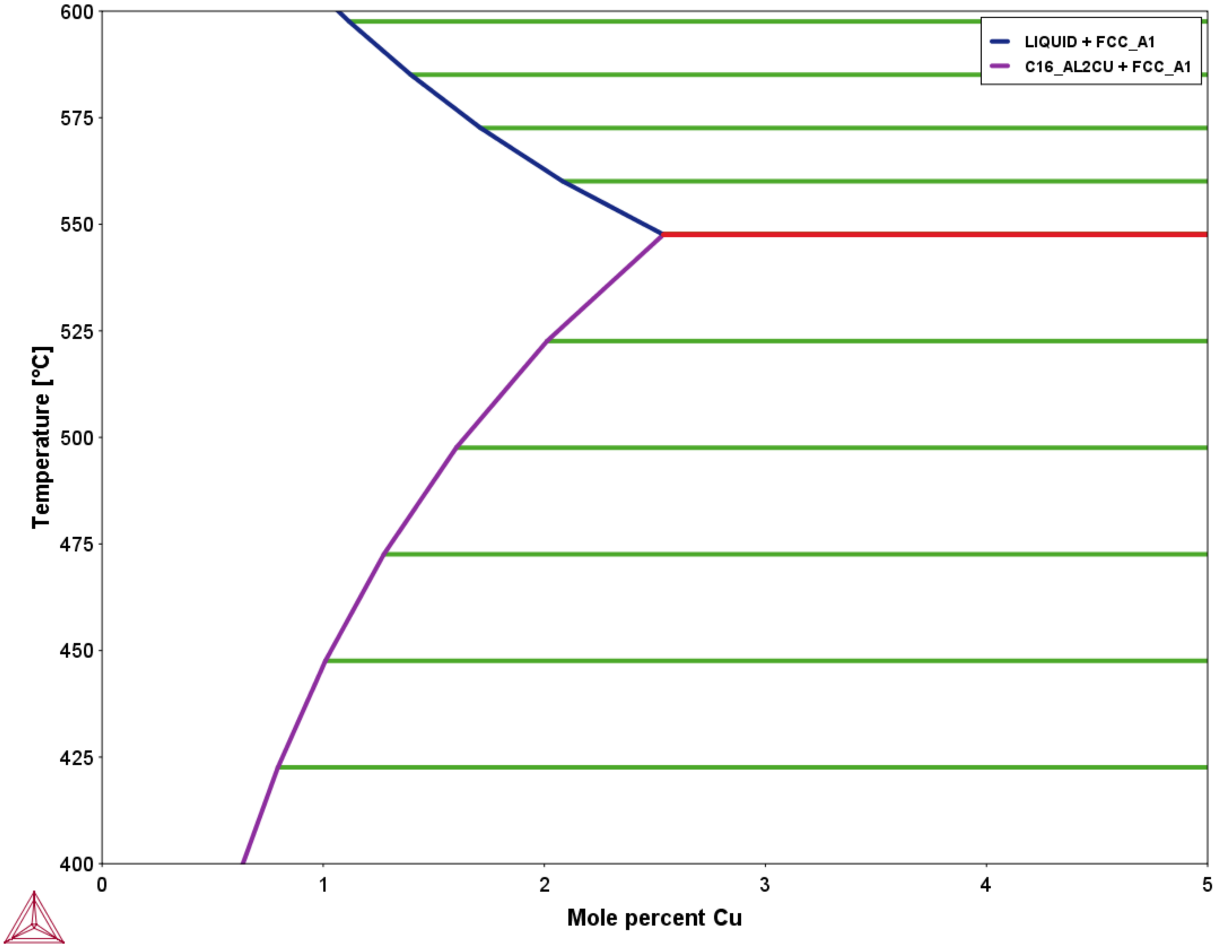


Figure 3: Thermo-Calc phase diagram of A365 nominal composition against composition of copper. The phase diagram axes are zoomed into to show the solubility at 500°C.

4.1.3 A365 – NICKEL PHASE DIAGRAM

Nickel has an atomic radius of 1.49 Å and is shown below in a phase diagram of the nominal compositions of A365.

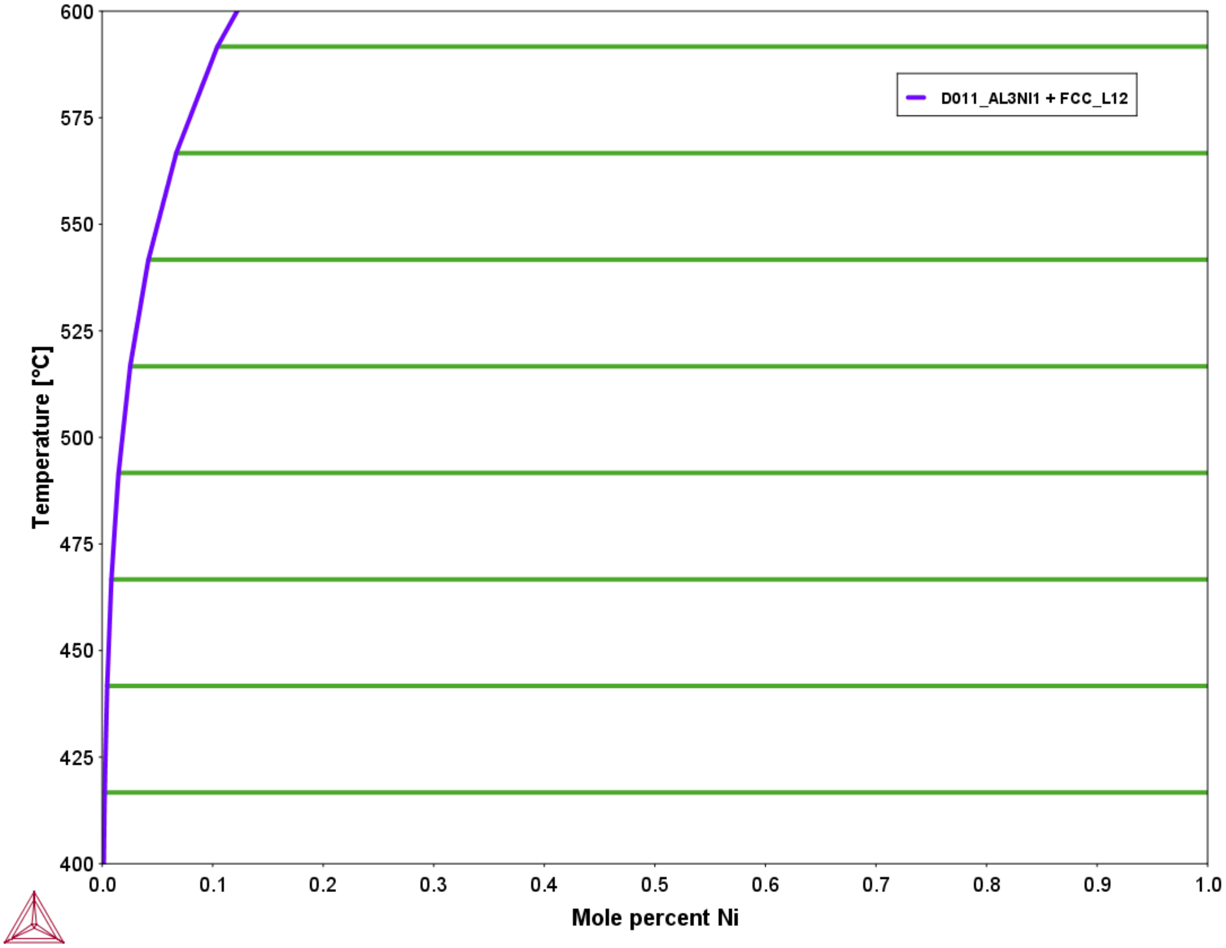


Figure 4: Thermo-Calc phase diagram of A365 nominal composition against composition of Nickel. The phase diagram axes are zoomed into to show the solubility at 500°C.

4.1.4 A365 – TITANIUM PHASE DIAGRAM

Titanium has an atomic radius of 1.76 Å and is shown below in a phase diagram of the nominal compositions of A365.

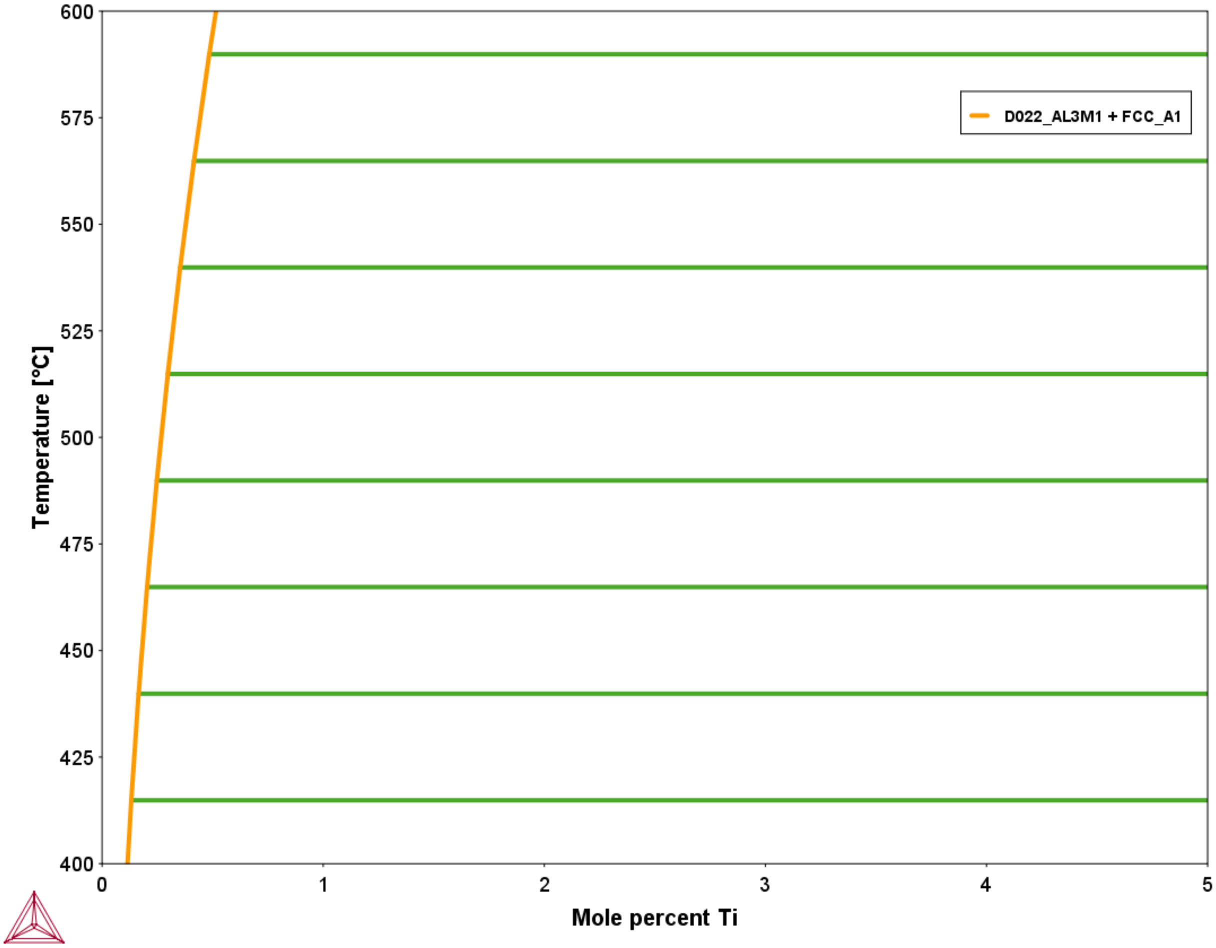


Figure 5: Thermo-Calc phase diagram of A365 nominal composition against composition of Titanium. The phase diagram axes are zoomed into to show the solubility at 500°C.

4.2 THRESHHOLD STRENGTHENING APPROACH

One method of improving impact strength and toughness is by increasing the threshold required to propagate a crack. If a method can significantly increase this, much more energy is required to send an initial crack all the way through a specimen thus increasing impact and toughness. Regarding metals, solid solution strengthening or creating strengthening intermetallics at the surface may aid in this end.

4.3 MATRIX SOFTENING APPROACH

Another method is the reverse in that a much more ductile matrix will improve impact and fracture properties. Work conducted by Shivkumar et al. and Meyers and Lyons [11, 19] support this approach in regards to silicon morphology and aluminum microstructure as discussed earlier.

4.4 METHOD

The overarching theme of both approaches involve the diffusion of atoms into or out of the matrix. Removing or creating hard phases in the matrix or solid-solution strengthening could be a solution to this research problem. To this end, it was proposed that a coating was to be applied to a base material and then a heat treatment was to be applied to facilitate diffusion. Proposed materials to coat aluminum substrates are currently in use for alloying purposes or strengthening mechanisms. The materials included copper, nickel, titanium, zinc, and aluminum. Creating more strengthening phases could potentially raise the crack initiation and propagation threshold which would result in improved properties. On the other hand, softening or increasing ductility in the regions of interest could have much greater effect in improving properties.

The methods of electroplating, electroless plating, hot dip galvanizing, and cold spray were considered and tested in an exploratory fashion. Cold spray was determined to be the best in terms of continuity in coating. The difficulty in the other application methods arise due to the passivating nature of aluminum and the lack of industrial scale equipment to ensure good adhesion. Cold spray has the benefits of being a relatively low temperature process that is effective in adhesion, coatings are highly dense (low porosity), and concurrently peens the surface. Studies have shown that the cold spray method introduces no detrimental fatigue effect to the substrate and actually improves fatigue life [22-24].

A brief exploration of the proposed materials to be coated will be discussed. Aluminum was selected as a coating material because of its ductility. Since pure aluminum is silicon-deficient as compared to the substrate, diffusion of silicon from the substrate to the coating will make the surface of the substrate more ductile. Copper was selected as it is the primary alloying constituent currently used in aerospace applications for these desired mechanical properties. Nickel was selected for the potential benefits found in nickel aluminide materials. Nickel aluminide has excellent high temperature properties but processing at lower temperatures proves to be difficult due to the brittleness of the material. Titanium was selected because of its use in tool steels.

Titanium nitride increases various mechanical properties including impact strength. In aluminum alloys, titanium diboride is used to refine the grains for excellent impact and strength properties. Finally, zinc was selected due to its ductile properties. It is used as coatings in steels, used as a strengthening phase in aluminum, and dissolves quite readily in aluminum as shown in Table 2. Copper and zinc show promise as they can be held in solution in aluminum at high concentrations. This gives some support to solid solution strengthening.

Solubility of Material in Pure Aluminum at 530˚C

Material	Aluminum	Copper	Nickel	Titanium	Zinc
Solubility	100 wt%	5 wt%	0.25 wt%	0.7 wt%	31 wt%

Table 2: Solubility of coating materials in pure aluminum at 530˚C

In moving forward, suggestions for applying these coatings onto aluminum proved difficult. Each material was applied by way of electroplating and hot dipping for even coatings but found that much more stringent cleaning and deoxidizing methods were needed. Professional and industrial platers were sought to conduct the coatings. To ensure even coatings and good contact between the coating material and substrate, cold spray was decided to be the best approach. According to the Applied Research Lab at Pennsylvania State University, they recommended continuing with copper, nickel, and titanium in the time being as they were optimizing the other materials to be sprayed.

4.5 PREPARATION

Sub-size impact specimen will be produced via waterjet cutting from stock high-pressure die cast A365 (HPDC-A365) aluminum donated by Rio Tinto, Montreal, Canada. Dimensions of specimen are in accordance with: ASTM E23-16b in section A3.1 in the V-Notch form for impact testing and ASTM B557M-15 sub-size 6mm wide for tensile testing.

Original HPDC-A365 plates were approximately 229 mm x 76 mm and 3mm thick. Plates were faced in a HAAS Mini Mill to a 2.5mm uniform thickness before waterjet cutting in the Worcester Polytechnic Institute Machine Shops. Parts were waterjet cut by Hydracadabra and Arc Technologies in Amesbury, MA.

Cold spraying of Nickel, Titanium, and Copper was conducted by the Applied Research Lab at Pennsylvania State University in conjunction with the Army Research Lab at Worcester Polytechnic Institute.

4.6 EVALUATION

After machining, the parts are coated via cold spray, heat treated to a T6 temper, and then tested in an Instron Charpy Impact Tester and Instron Mechanical Tester. Bulk impact strength will be evaluated in addition to the energy absorption as obtained from the area under a stress-strain curve. Grips from tensile bars and spared parts from impact testing will also be analyzed for diffusion in a scanning electron microscope for the EDS capabilities.

5 SUMMARY OF RESULTS

5.1 COATING

Prior to the completion of this research, a wide array of methods were explored in order to coat metal onto an aluminum alloy substrate. Desired properties of the coating itself was low porosity, good metal to metal contact, continuous, and relatively uniform. It must be stressed that the coating methodology was not of concern so long as the quality of the coating was good. The primary concern of this research is the effect of the coating after heat treatment and not the efficacy of applying a coating material.

5.1.1 EXPLORED COATING METHODS

Electroplating copper, iron, and cerium, electroless plating of nickel, and zinc hot dipping onto an aluminum substrate proved unsuccessful. In regards to electroplating copper and iron, poor adhesion was achieved such that the coating rubbed off the substrate easily. Many steps were taken to remove the impediment aluminum oxide ranging from NaOH baths, ASTM Universal Deoxidizers, acid baths, zincate solutions, and pre-strikes were employed with little success. This result is not a statement on the coating process but that a lab scale batch process coating method was not successful and a professional plating institution may prove more successful. The results of these coating methods discontinued these methods for this research.

Electroless nickel was applied via a Caswell Plating Kit for hobbyists. A nickel coating was applied that resulted in a tight and clean coating of nickel. However, when undergoing the solutionizing process, the nickel coating oxidized and spalled off upon quenching. This is likely due to the low thickness of the coating itself. After the final step of artificial ageing, it was found that nickel had not diffused in any appreciable amount and the coating method was discontinued. Much more work and discussion can be found in the Appendices on some of these experiments.

5.1.2 ZINC HOT DIPPING

Zinc hot dipping was employed for a short time to adhere zinc to the surface of an aluminum sample. Figure 6 shows a sample that was coated in this manner. The aluminum substrate acted as the heat sink which allows the zinc to solidify on contact. As seen in that photo, an inconsistent coating was applied although the coating was very tight around the sample itself. The red arrow in the photo indicates an example of the tight coating. No gaps were present when the sample was examined. The method of zinc application was successful but the results after applying a T6 heat treating cycle resulted in pitting and corrosion due to the high temperatures. After solutionizing, the zinc coating was melted off. This liquid zinc on aluminum provided the ideal situation for the dissolving of aluminum away from the substrate and into the zinc liquid. This method of coating was discontinued due to a variety of reasons but the coating itself is still of interest as the results after T6 treatment are promising. Zinc samples did not undergo mechanical testing due to the corrosion of the aluminum sample but will be discussed in the section covering electron dispersive spectroscopy.

Figure 6: Aluminum tensile bar hot dipped in a zinc melt.

5.1.3 COLD SPRAY

Cold spray proved to be the best method of coating application explored. One of the major reasons that cold spray was considered and pursued was that oxide removal was less of a concern. In the other cases, oxides were the limiting factor. In this situation, since such high speeds are employed the metals flow like a liquid and oxides are shattered in the process. This provides an excellent metal to metal contact which will facilitate diffusion of the coating into the substrate. Figure 7 shows the A365 samples as they were coated by the Applied Research Lab at Penn State.

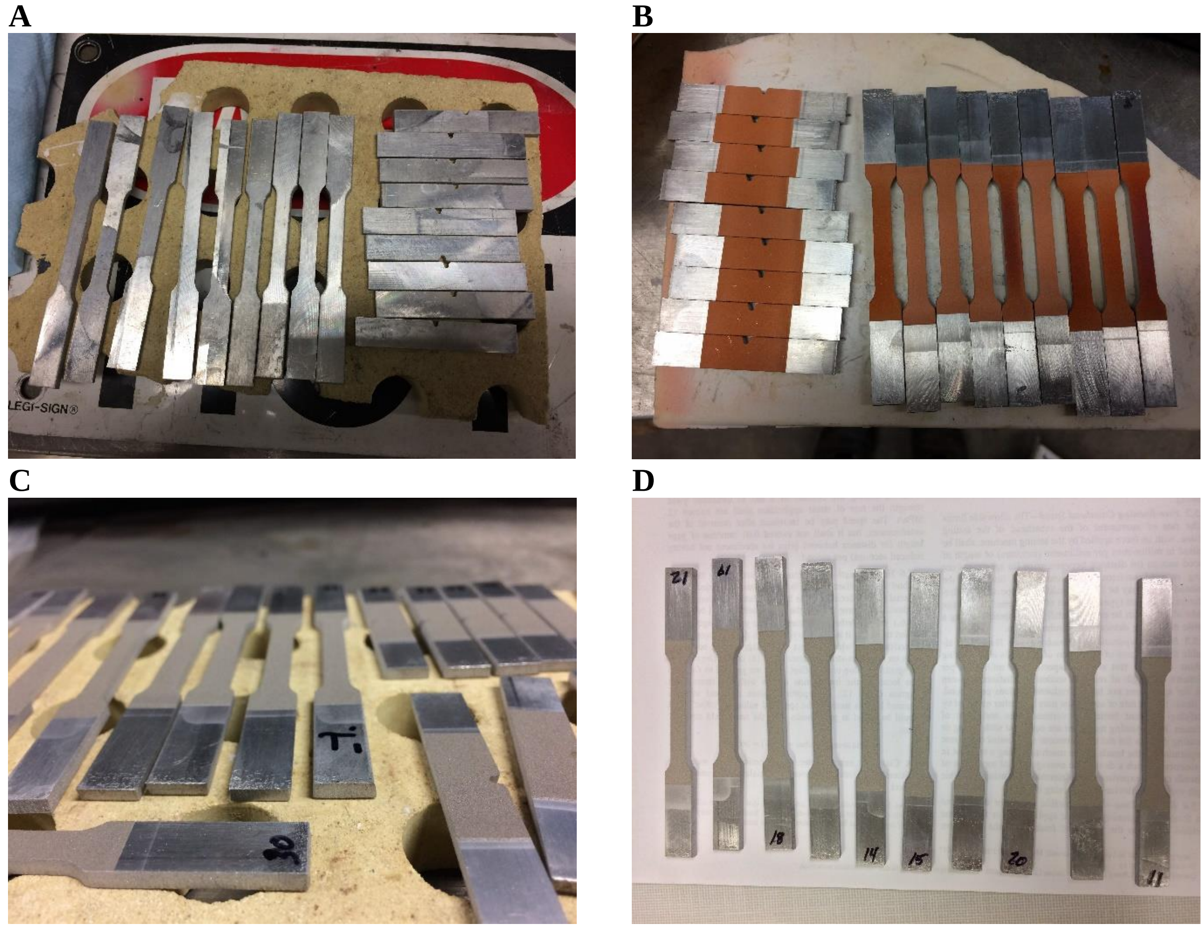


Figure 7: Cold sprayed samples as received. A) Reference as cast A365 HPDC no coating. B) Copper cold sprayed A365, no treatment. C) Titanium cold sprayed A365, no treatment. D) Nickel cold sprayed A365, no treatment.

5.2 HEAT TREATING

Heat treating in the T6 condition was employed to facilitate diffusion between the coating and the substrate aluminum. Optical microscopy was employed to examine the change of the aluminum-coating interface from the as-received condition, to solutionizing, and after ageing. Distinct conditions were examined for reference.

5.2.1 AS RECEIVED/AS CAST

As received samples can be viewed in Figure 7 by the human eye. Sample cross-sections can be seen in Figure 8. The black portions of the photo are the resin used to hold the samples. The orange layer seen is copper in photo B, the dark layer in photo C is titanium, the dark blue layer in photo D is the nickel. As shown in the figure, good metallurgical contact can be seen between the coating layer and the aluminum substrate.

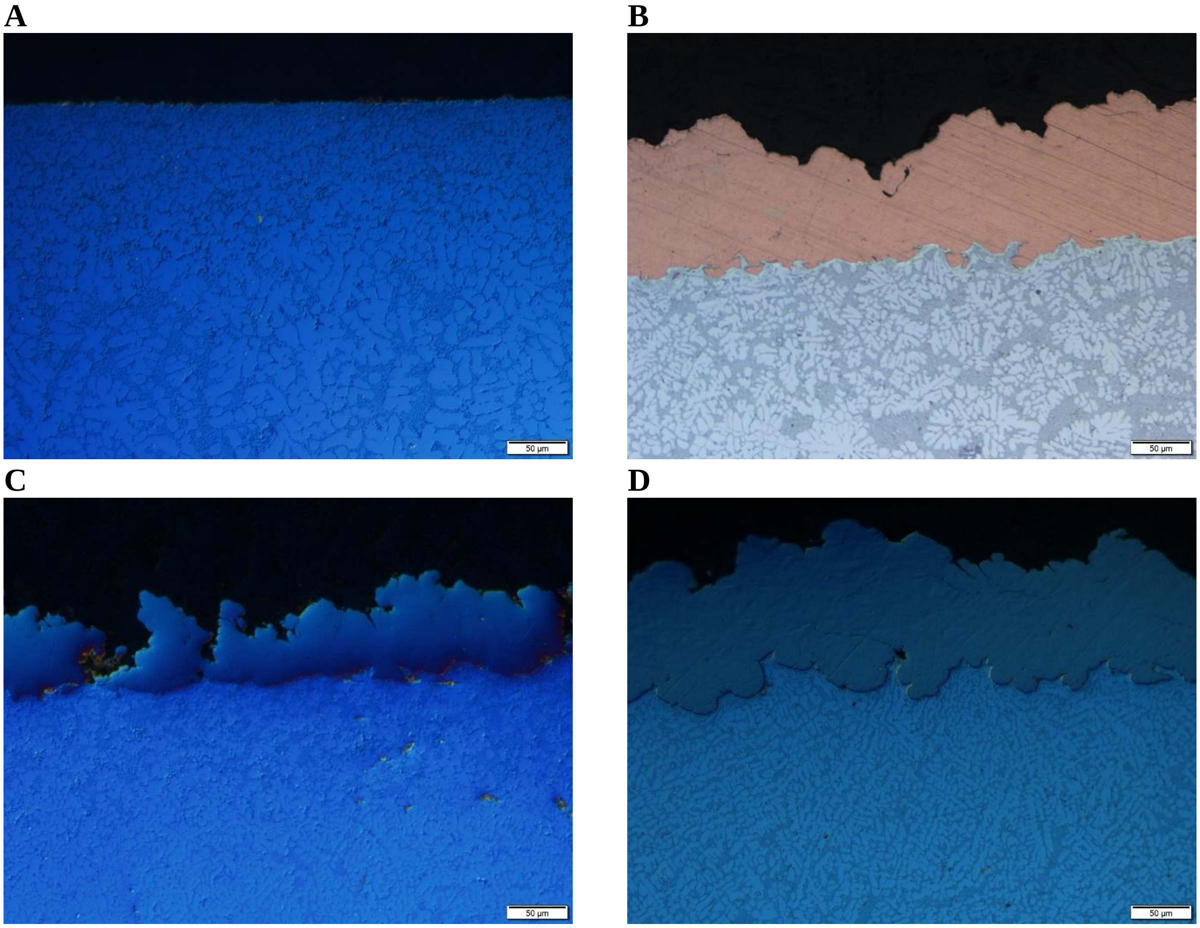


Figure 8: Optical micrographs of the A) As-Cast A365 HPDC, B) Copper cold spray, C) Titanium cold spray, and D) Nickel cold spray samples. Black portions of the image are the resin used to hold the sample.

5.2.2 SOLUTIONIZED

Solutionizing was conducted as recommended by Rio Tinto, the producer of the A365 used in this research. A furnace of 500°C was run for several hours to regulate and stabilize. Samples were placed in the furnace and then allowed to sit until the thermocouples read 500°C again. Once the temperature was reached, a timer for 80 minutes began. Once removed and forced air cooled, the following images were obtained and presented in Figure 9 and Figure 10.

Most of the dramatic events in diffusion will have occurred in the solutionizing step due to temperature. Copper had the most severe diffusion, followed by nickel, and lastly titanium.

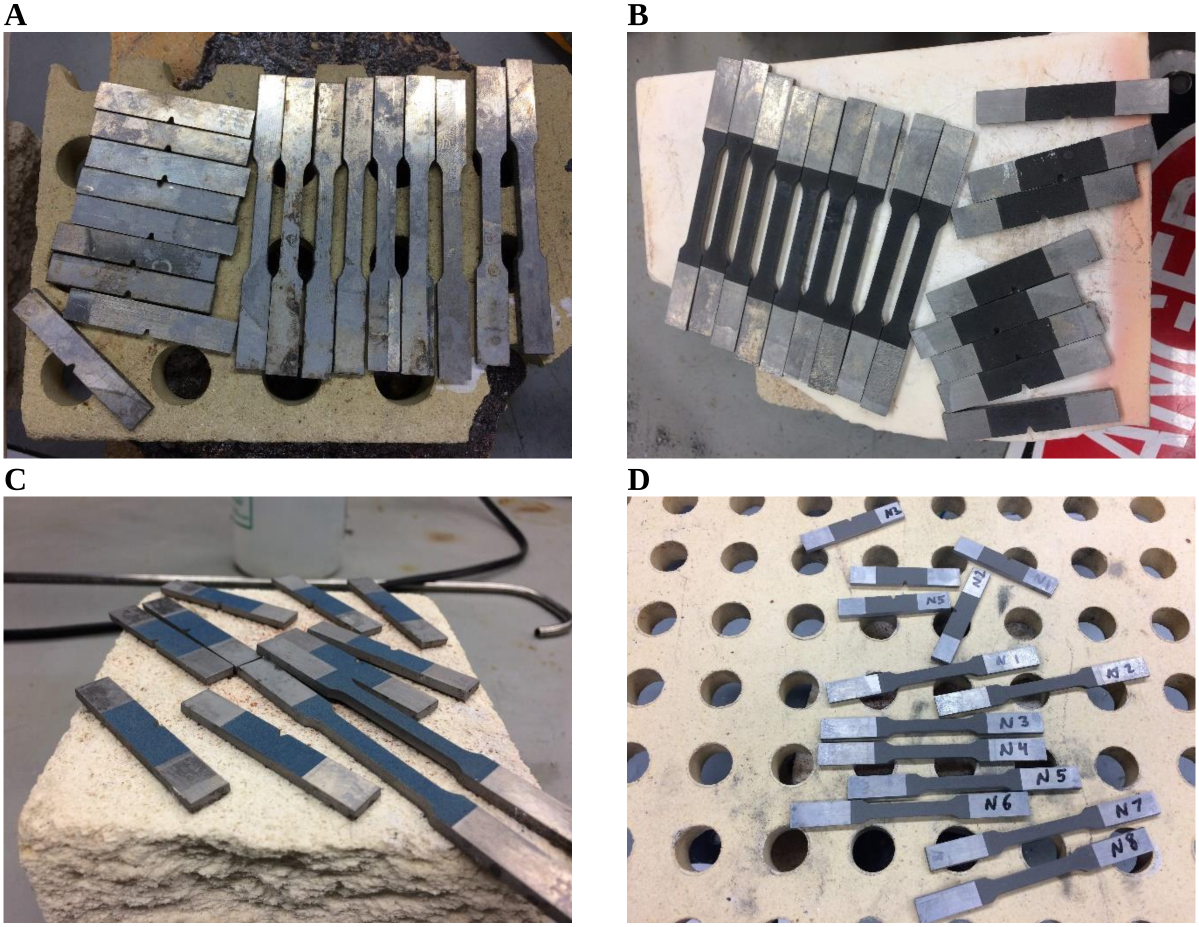


Figure 9: Samples of A365 after solutionizing and forced air cooling A) As cast A365, B) Copper cold sprayed, C) Titanium cold sprayed, D) Nickel cold sprayed.

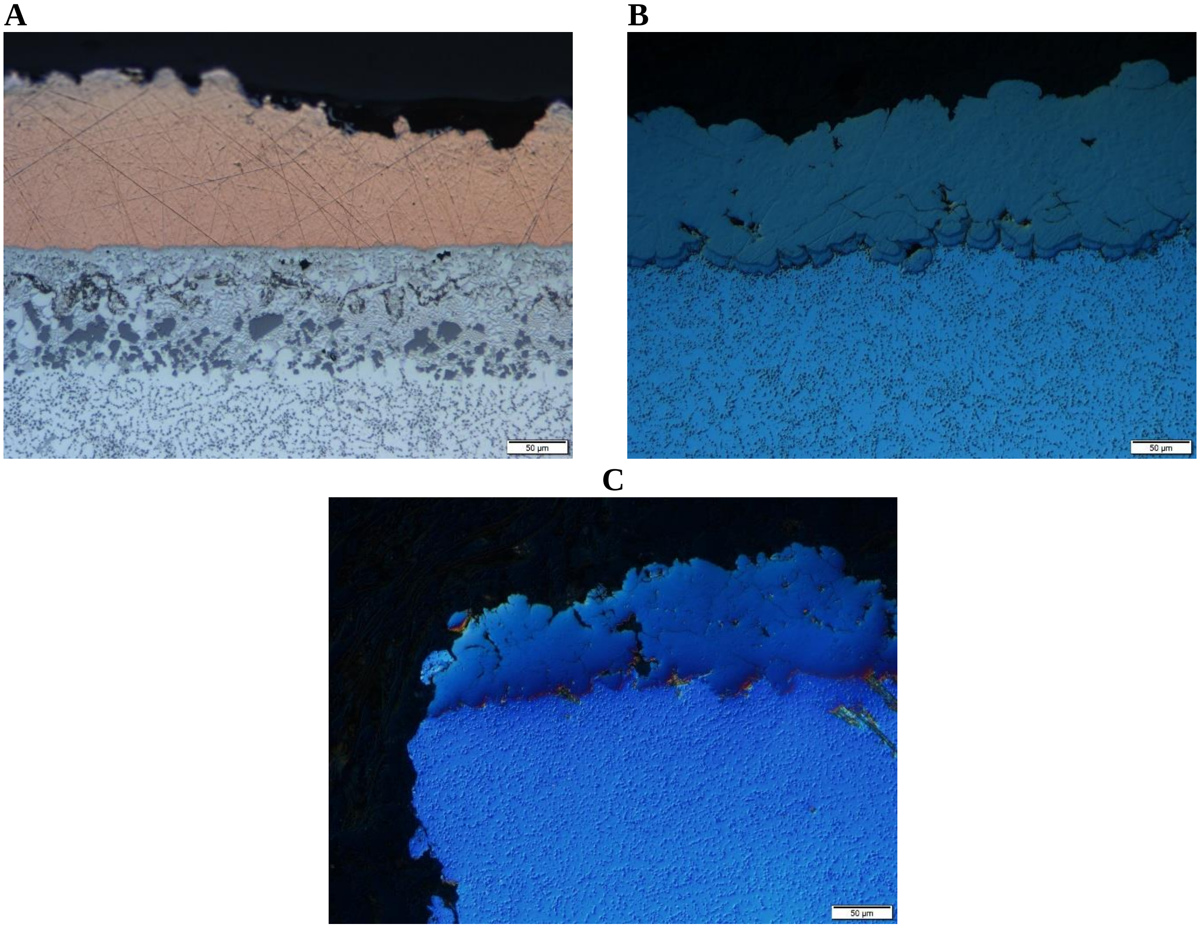


Figure 10: Optical micrographs of A365 samples that were cold sprayed and then solutionized at 500°C for 80minutes. A) Copper cold sprayed, B) Nickel cold sprayed, C) Titanium cold sprayed.

5.2.3 FULLY AGED

Complete ageing consists of, in addition to the solutionizing step, a 24-hour room temperature age, and then an artificial age at 176°C for 8 hours. Fully aged specimen look exactly the same visually as the solutionized samples. No significant oxidation is seen past what was done in solutionizing. Figure 11 shows the optical micrographs of fully aged A365 samples in the T6 temper.

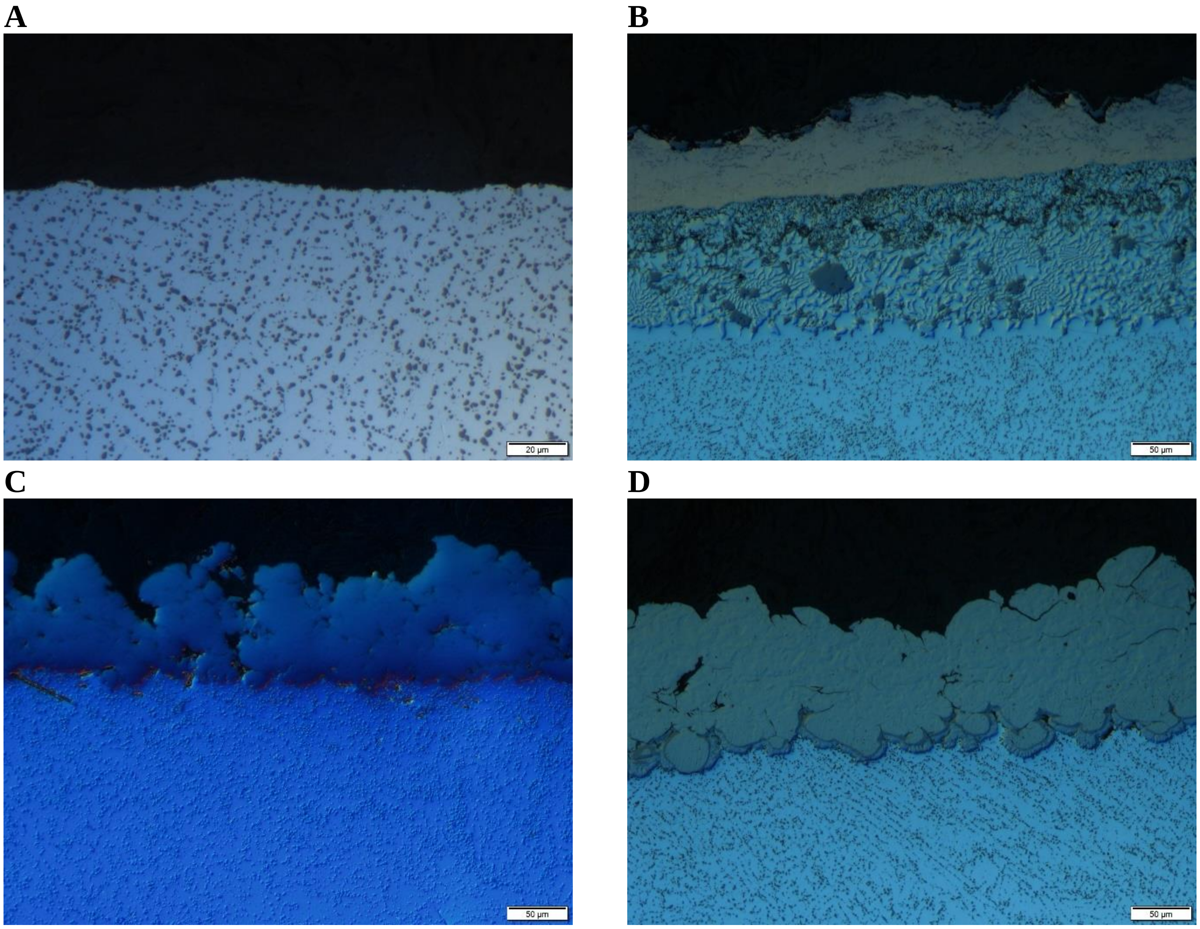


Figure 11: Fully T6 aged A365 samples where A) is as cast, B) is copper cold sprayed, C) is titanium cold sprayed, and D) is nickel cold sprayed.

5.3 ELECTRON DISPERSIVE SPECTROSCOPY

After a full T6 temper heat treating cycle, cross sectioned samples were examined to evaluate the depth of diffusion of the coating material into the substrate, secondary phases formed, changes in silicon morphology, and the overall microstructure. Although zinc samples were not mechanically evaluated, EDS analysis proved to be a useful metric for zinc's future in this area of research.

5.3.1 ZINC

Coatings of zinc were carried out on an earlier substrate of A356 that was employed at the outset of this research. Since the transition was made to A365 as the substrate and due to ineffectiveness of hot dip zinc coating, zinc was discontinued. However, zinc cold spray should be applied for the future. In these experiments, a tensile bar of A356 was dipped into molten Zn – 15Al (Al 15 wt%) and removed immediately. The sample was allowed to cool to room temperature and then solutionized at 530°C for 21 hours. The coating itself melted away and corroded the surface of the aluminum due to the low melting point of the coating. Figure 12 presents micrographs of this sample. Features of note are the large diffusion zone where silicon is appeared to have diffused away. It is predicted that the silicon migrated towards the silicon deficient Zn – 15 Al coating. This coating then melted away taking the silicon with it. In the bottom of the micrographs, the raised structures are a zinc – silicon phase that did not completely leave the substrate.

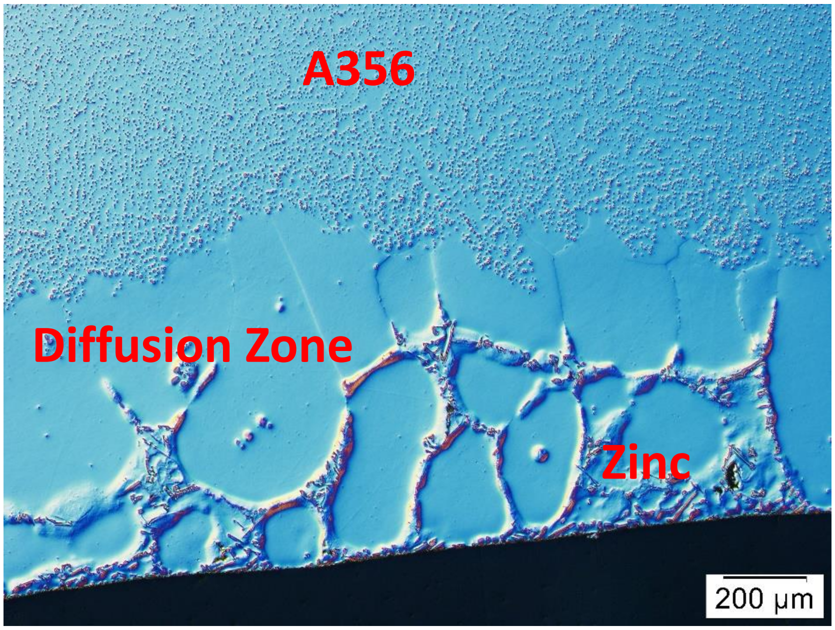


Figure 12: A356 substrate coated with Zn - 15 Al and solutionized for 21 hours at 530°C

In Figure 13, an EDS line scan shows that zinc had in fact diffused into the substrate. Given that the 21-hour solutionizing step is much higher than typical for T6 temper in A356 at about 6 hours, the diffusion depth is about 1000 µm before approaching expected composition of zinc in A356 by alloy of about 0.1 wt%. From these same scans, no formation of intermetallics were found which means that zinc has stayed in solid solution to the aluminum matrix.

One interesting note for these samples were that no prior cleaning procedures were taken. No pickling, etching, polishing, or other surface preparation was conducted. The adherence seems to be purely mechanical bonding. Once the coating melted and formed a liquid on the aluminum parts, the zinc was able to diffuse readily through the aluminum oxide.

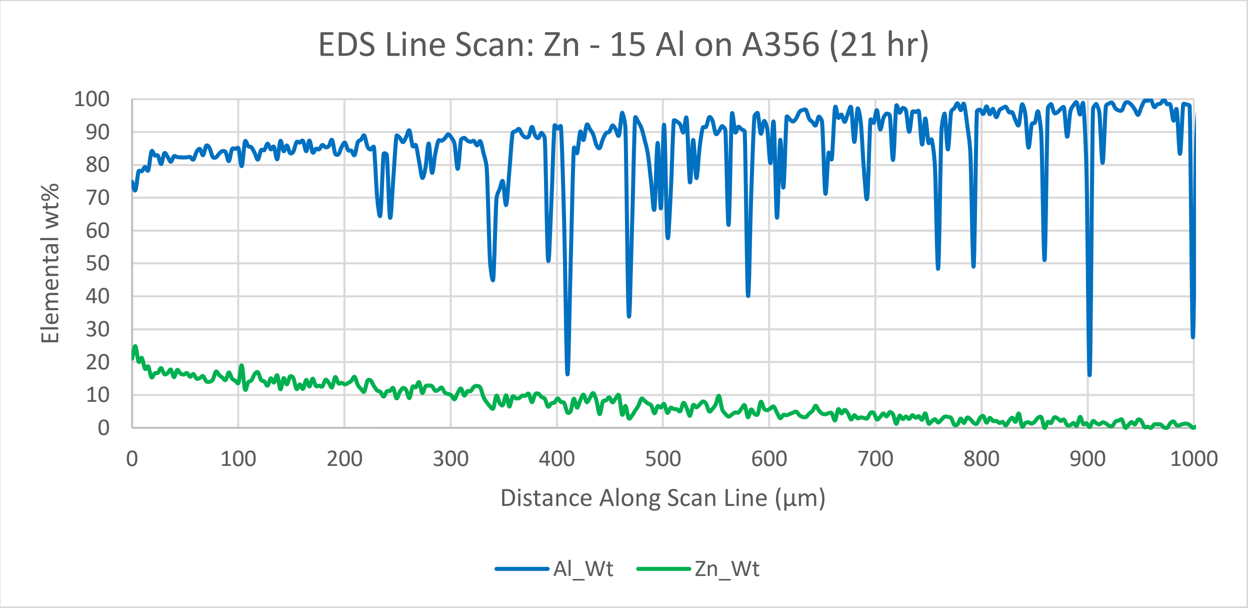


Figure 13: EDS line scan of A356 substrate coated with Zn - 15 Al and solutionized for 21 hours at 530°C.

5.3.2 COPPER

Copper cold spray coatings onto A365 underwent a T6 treatment cycle. Results previously discussed in Figure 11 displaying a micrograph of the multilayered structure show 3 distinct regions. The first layer comprised of the copper coating, the second layer is the diffusion zone, and the final layer is the A365 substrate. EDS mapping shows the contents of each of these regions.

5.3.2.1 COPPER COATING LAYER

The copper coating is dense with little to no porosity. The high impact of cold spray closes all gaps and provides an excellent coating method in this regard. Black streaks can be seen towards the top of the image and these are bands of copper oxide. Copper oxide is expected due to the high temperature and exposure to air in the solution step of the T6 process.

5.3.2.2 DIFFUSION ZONE

In the copper diffusion zone seen in Figure 15, there are many features that have formed. A thin layer between the copper coating and the aluminum has formed which has been determined to be a continuous phase of aluminum – copper, which is expected. According to EDS line scans in Figure 14, all secondary phases of aluminum – copper are Al_2Cu. Since the solution time is only 80 minutes at 500°C, other intermetallics along the equilibrium phase diagram formed such as in Funamizu's work [25]were not found in these results If a significantly longer solution time was allowed, 4 other phases may have appeared.

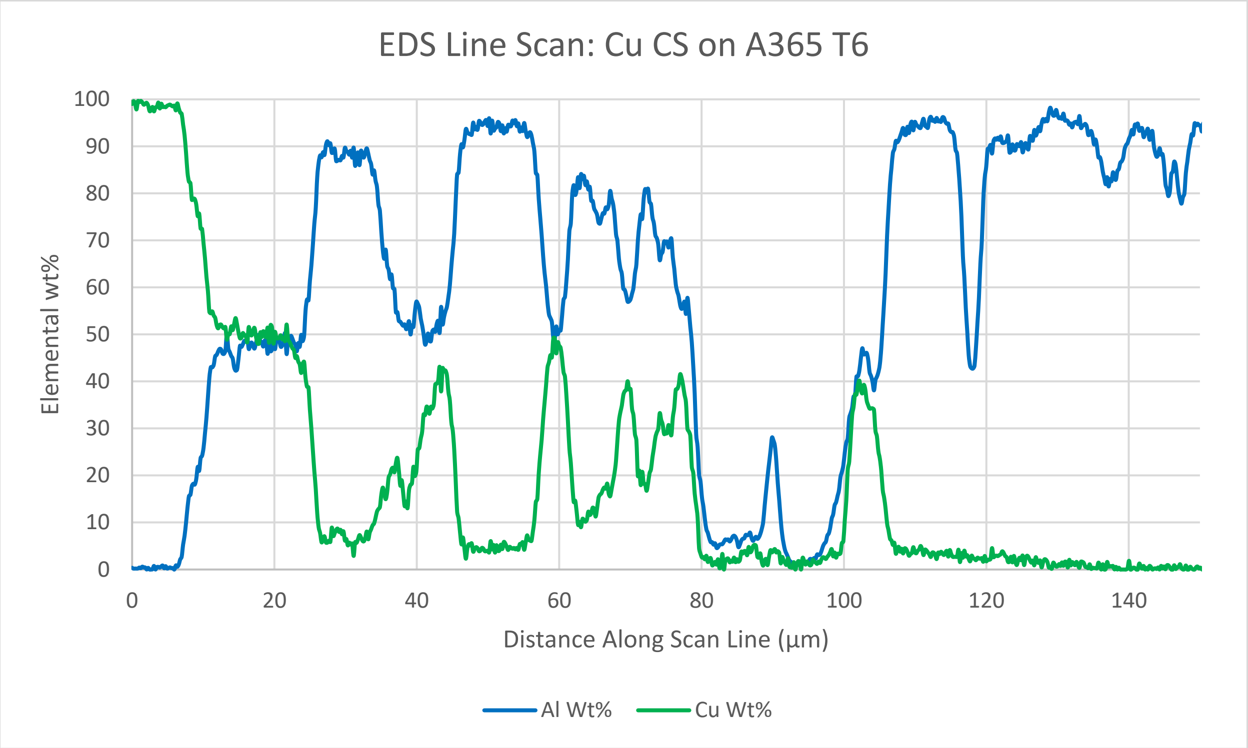


Figure 14: EDS line scan of A365 substrate cold spray coated with copper and solutionized for 80 minutes at 500°C.

The finger-like phases in the bulk of the diffusion zone are also Al_2Cu but formed in a discontinuous manner. Another feature of note are the large silicon phases that form in the diffusion zone. The silicon agglomerated together in the region where significant copper diffusion occurred. Driving forces for this agglomeration could arise from copper being held in solid solution to the aluminum matrix and kicking out silicon. It is predicted that for silicon to reduce its energy while in the aluminum matrix silicon agglomerated into large polygons. Copper, when not in an intermetallic phase, was found to be about 5 wt% in solid solution to a depth of 100μm below the copper – aluminum interface and in those same regions silicon was not generally found in solution.

Black 'holes' that appear to look like porosity in the diffusion zone were found to be magnesium oxide. EDS mapping found in Figure 15 show that on the black holes, magnesium and oxygen signals are strongly detected. Approaching the bottom of the diffusion zone, when copper was no longer detected, phases of Al_2Cu no longer appear and finer silicon precipitates expected in the bulk are well dispersed.

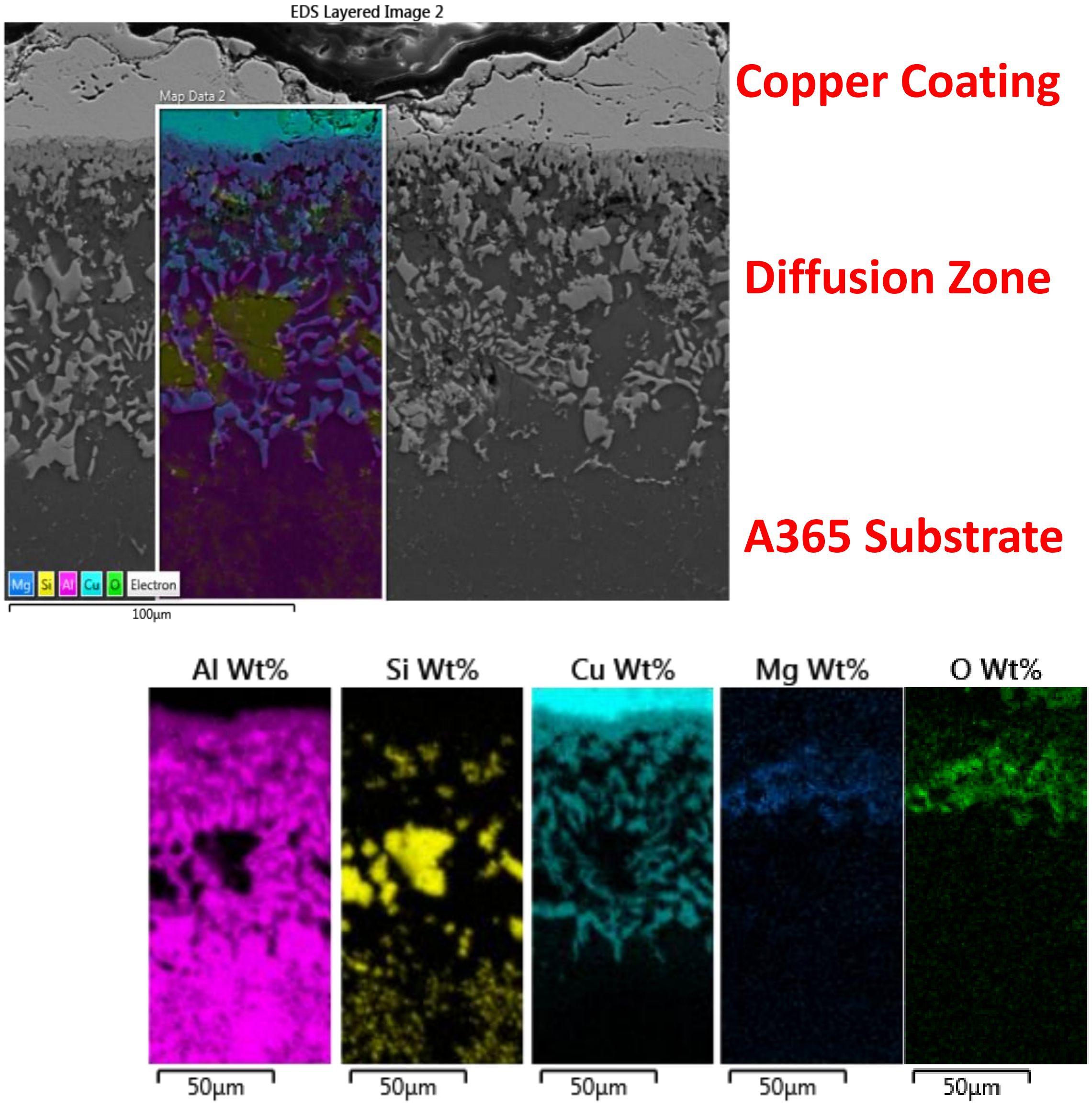


Figure 15: EDS Mapping of A365 with a copper cold sprayed coating and after a T6 treatment.

5.3.3 NICKEL

Nickel samples differed from both copper and zinc results in that very little, if any, nickel was held in solid solution. Intermetallics of nickel and aluminum formed but EDS was not the appropriate method for differentiating the potential phases formed due to the small thickness of each layer and similarity of compositions. Potential phases to have formed include Ni_2Al_3, $NiAl_3$, and NiAl according to the EDS line scans conducted. If longer solution times were available, all intermetallics expected should form.

A feature of note for the nickel diffusion zone is how continuous and relatively smooth the intermetallic layer is compared to the intermetallic layer of copper. Nickel does not appear to have been held in solid solution to the aluminum matrix.

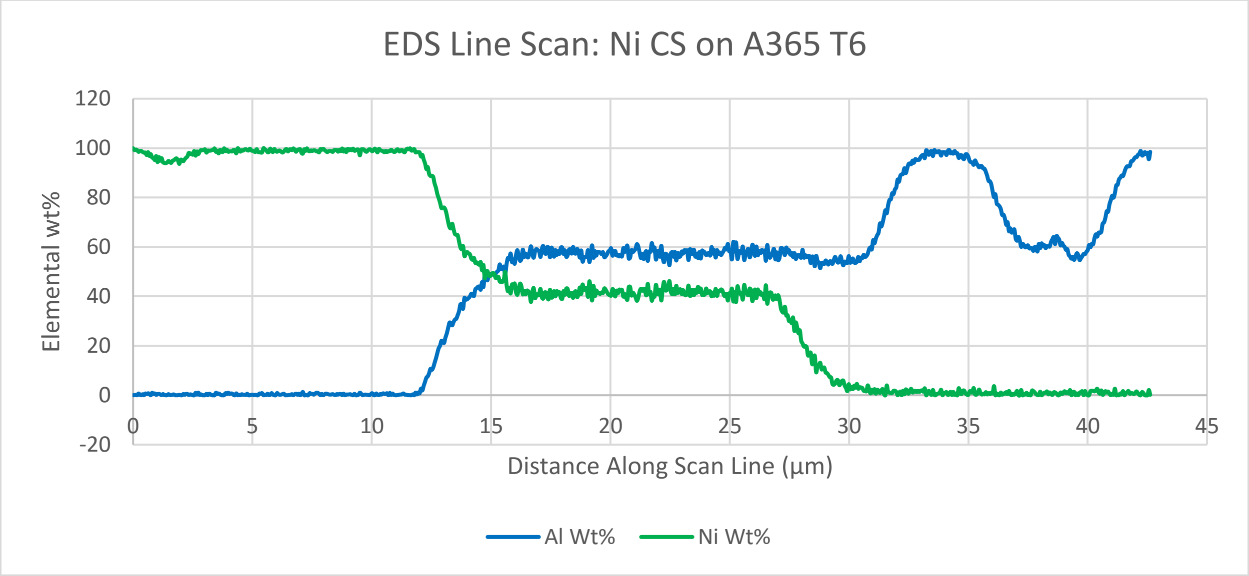


Figure 17:EDS line scan of A365 substrate cold spray coated with nickel and solutionized for 80 minutes at 500°C.

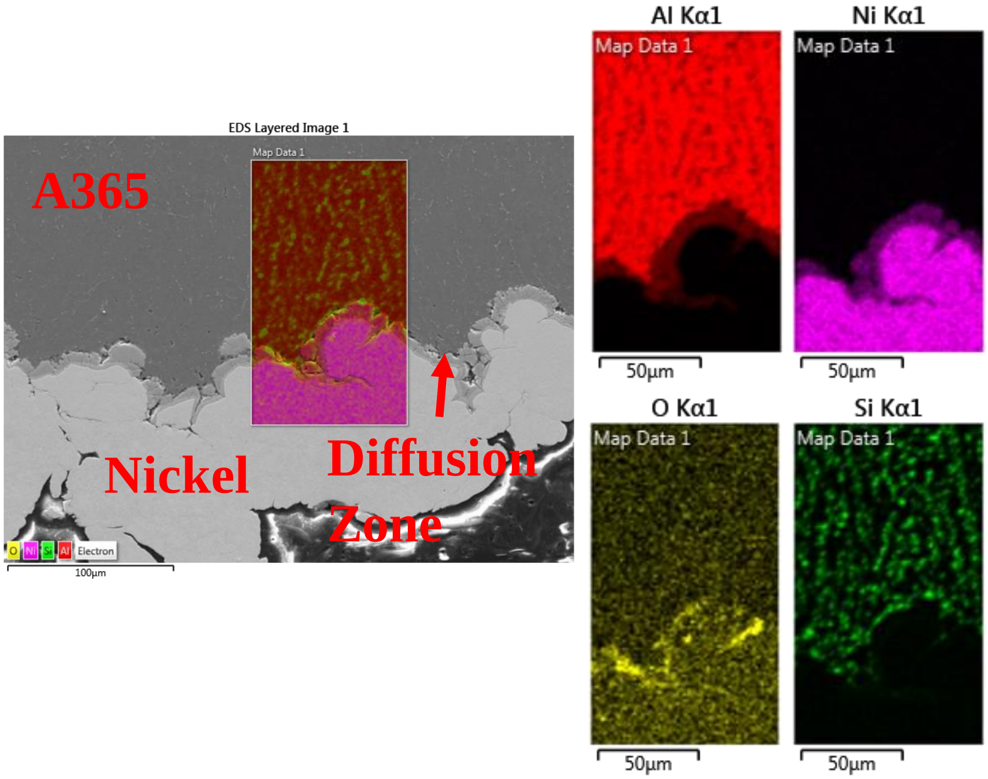


Figure 16: EDS Mapping of A365 with a nickel cold sprayed coating and after a T6 treatment.

5.3.4 TITANIUM

Titanium results from EDS show no significant diffusion into the surface of the aluminum substrate. Figure 18 shows the line scans of aluminum and titanium against distance along the scan. In this figure, the titanium coating began on the right-hand side and moved leftwards. An insignificant amount of titanium can be found in the aluminum substrate due to the probe size of the electron beam in EDS analysis. Dips in aluminum content along the scan are due to formations of silicon phases in the bulk of the sample.

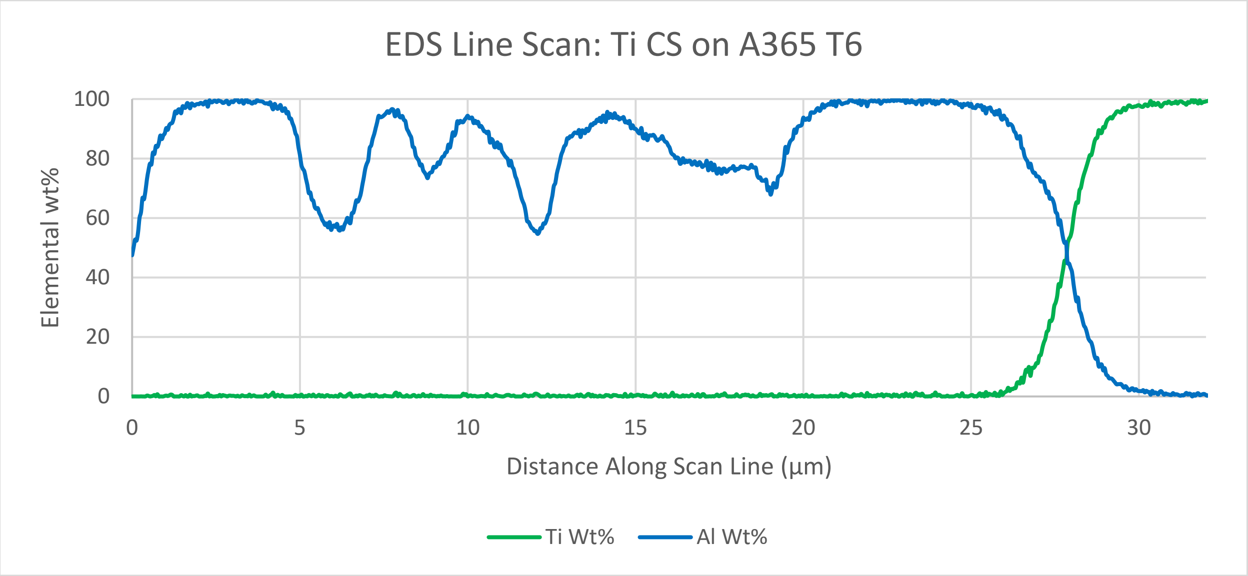


Figure 18: EDS line scan of A365 substrate cold spray coated with titanium and solutionized for 80 minutes at 500°C.

5.4 IMPACT STRENGTH

Impact strength of as cast A365 HPDC, as cast A365 HPDC – T6, CuCS A365 – T6, NiCS A365 – T6, and TiCS A365 – T6 were evaluated in an Instron Impact Tester. Both conditions of A365 AC and A365 AC – T6 are provided as references. All impact tests were conducted at room temperature.

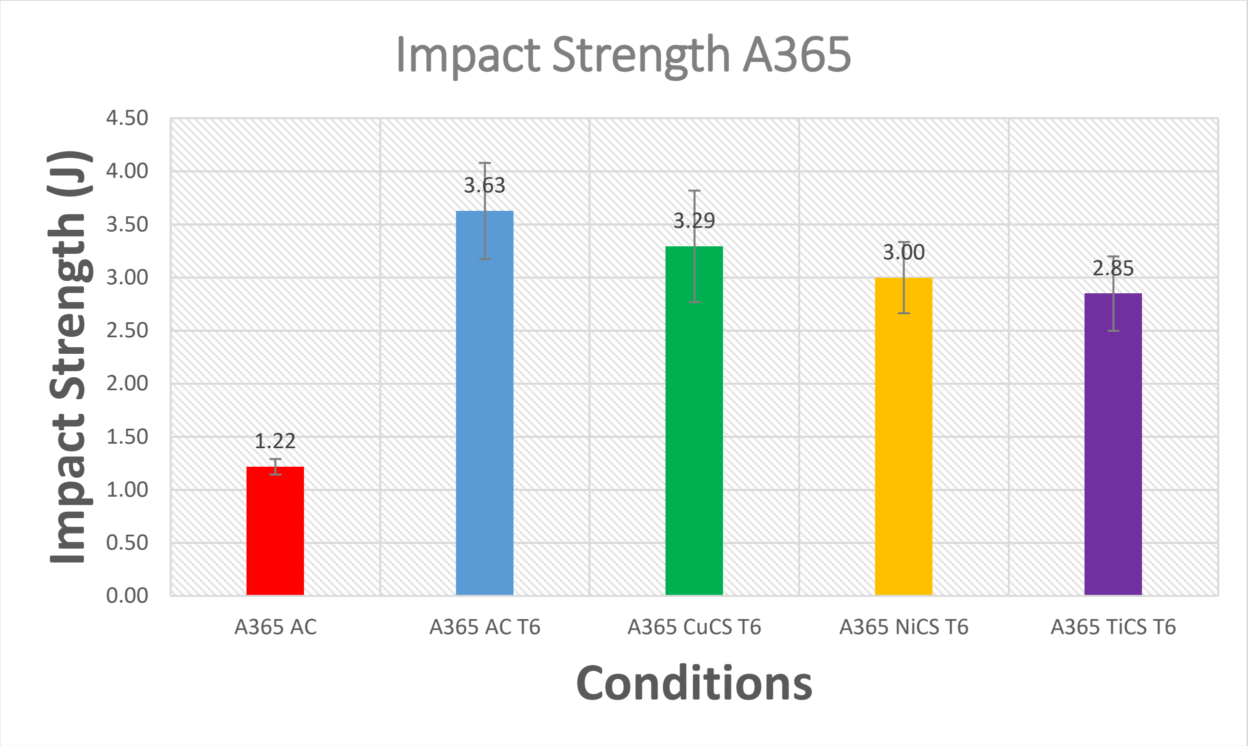


Figure 19: Impact strengths of A365 in various conditions conducted at room temperature.

As seen in Figure 19, applying the T6 temper on as cast samples induces a dramatic increase in impact strength as measured in energy absorbed (J). Cold spray coatings seem to reduce the efficacy at which A365 can absorb impact energy. Recalling Figure 8 A and Figure 11 A, as cast and as cast in the T6 temper respectively, the silicon particles are much more spheroidized in the T6 temper. A combination of factors from spheriodicity and dispersion of silicon particles, as well as the formation of the strengthening nano sized Mg_2Si in the aluminum matrix provides the increased impact strength of A365 in this temper [11, 26].

The addition of a coating and a T6 temper resulted in poorer energy absorption. A combination of surface roughness from unpolished cold spray surfaces [20] and brittle intermetallics formed reduced the ability of A365 to absorb energy. In the case of copper, the diffusion zone with intermetallics ranged from 100 µm to 200 µm thick on both broad faces of the samples. This causes a reduction upwards of 400 µm in the effective ductile (impact strong) cross section to absorb energy. In addition to the intermetallics formed, the brittle oxide surface of the coatings provides an unfavorable condition for impact strength as these are excellent crack initiators. An interesting feature of this plot however is the decrease in impact strength decreases as the coating's relative hardness increases. In other words, a softer coating resulted in less detriment to the impact strength of the A365 substrate.

5.5 TENSILE STRENGTH

Tensile strengths of the various samples were conducted at room temperature.

5.5.1 A365 AC – T6 vs A365 CuCS – T6 STRESS-STRAIN CURVES

Figure 20 shows the stress strain curves of A365 as cast in the T6 temper against copper cold sprayed coated A365 in the T6 temper. Red curves are of the copper sprayed samples. Features of note are the reduction in tensile strengths of the copper cold sprayed samples compared to the as

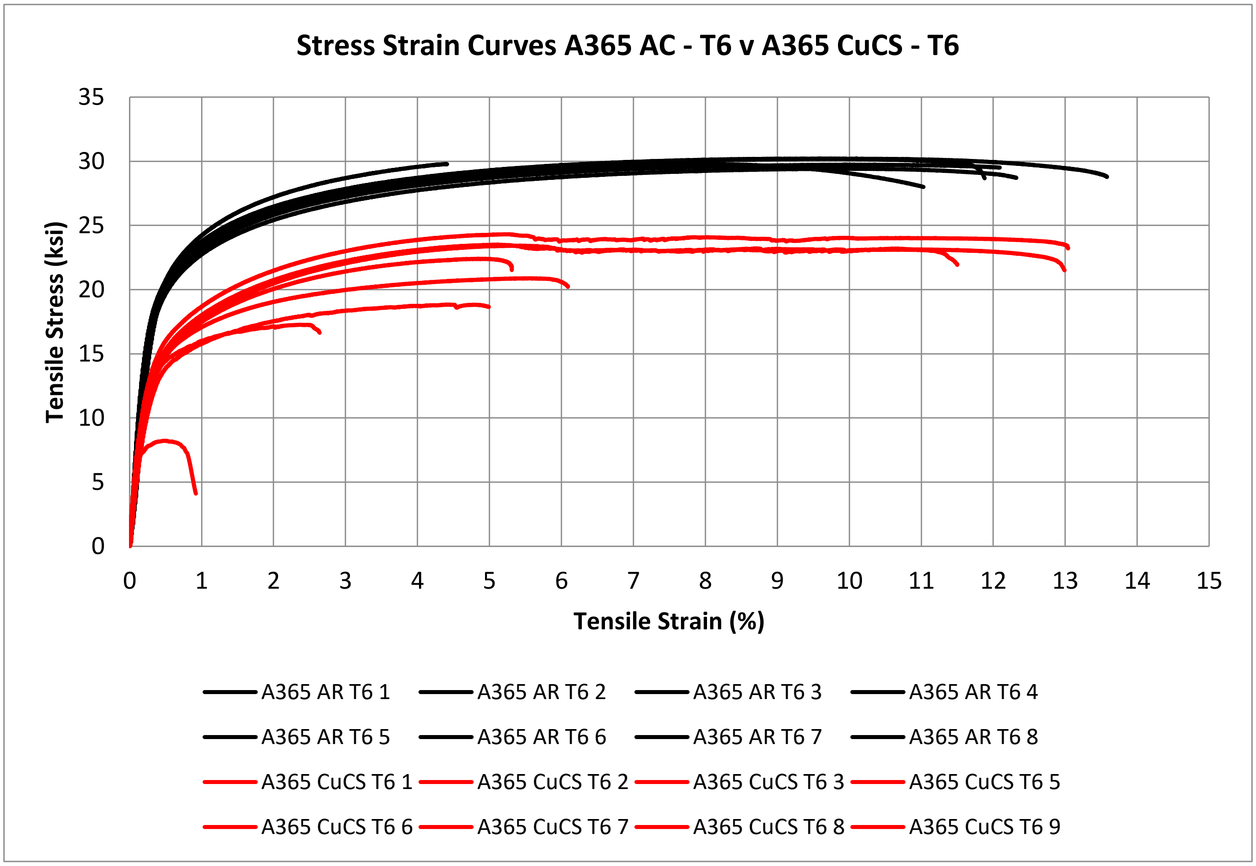


Figure 20: Stress-strain curves for A365 AC in the T6 temper and A365 copper cold spray in the T6 temper.

cast and tempered samples. Within the red curves themselves, two distinct regions exist where some achieved the ductility as expected in A365 T6 and those that did not. The copper samples that did reach expected elongation had copper delaminating from the substrate. Since the brittle intermetallics and coating delaminated, the substrate was allowed to elongate to the expected lengths. On the other hand, the samples that only elongated to about half of the expected elongation had the copper coating adhere to the surface. The brittle nature of the intermetallics and coating reduced the elongation significantly. Upon inspection of the delaminated samples, no intermetallics were found on the substrate. The intermetallic region was ripped away from the substrate and remained on the copper coating.

5.5.2 A365 AC – T6 vs A365 NiCS – T6 STRESS-STRAIN CURVES

Figure 21 shows the stress strain curve of A365 as cast in the T6 temper against nickel cold sprayed coated A365 in the T6 temper. The red curves are of the nickel coated samples. A feature of interest is that in these samples, very little reduction was found in tensile strengths of coated against uncoated in nickel. Elongation, however, was in fact reduced in the nickel cold sprayed samples.

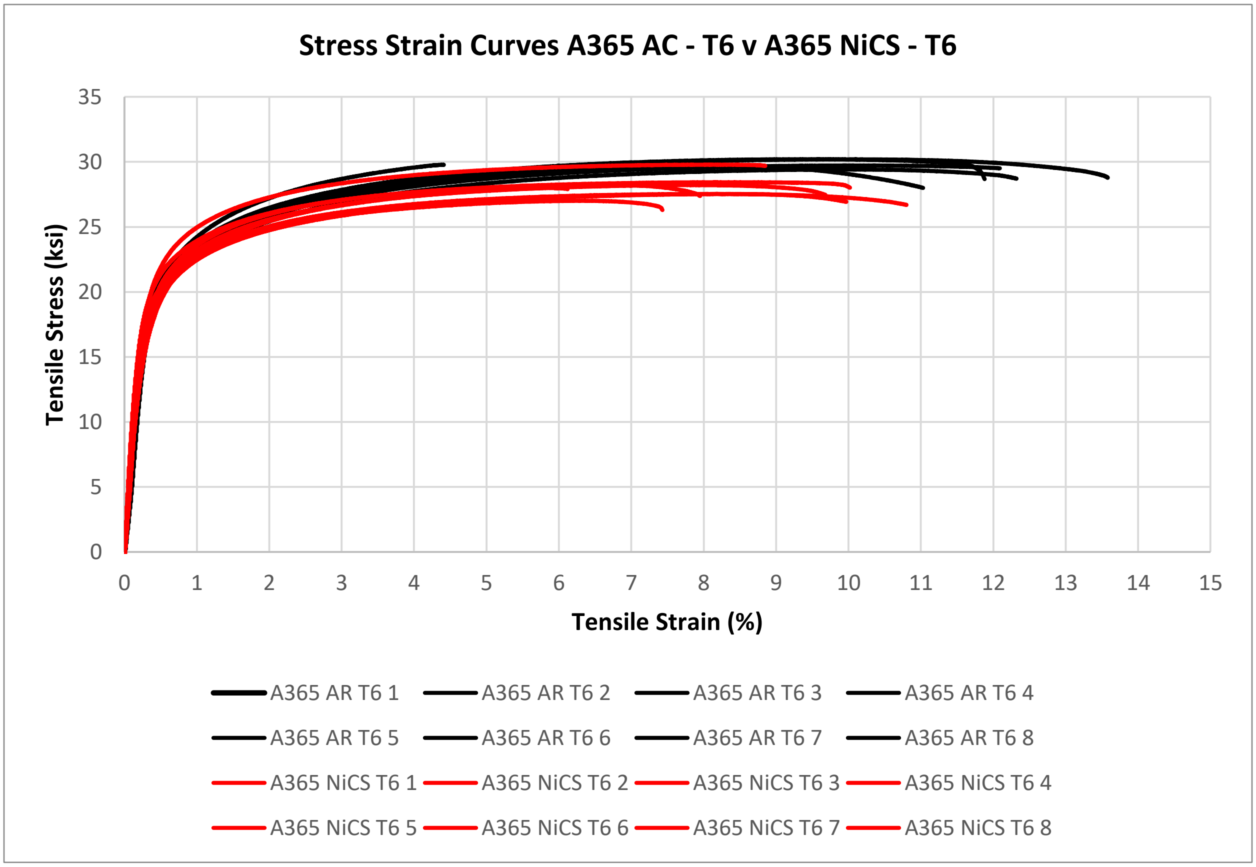


Figure 21: Stress-strain curves for A365 AC in the T6 temper and A365 nickel cold spray in the T6 temper.

No samples of nickel delaminated from the surface of the substrate meaning the intermetallics formed were not detrimental to tensile strength but was detrimental to the ductility of the substrate.

5.5.3 A365 AC – T6 vs A365 TiCS – T6 STRESS-STRAIN CURVES

Figure 22 shows the stress strain curves of A365 as cast in the T6 temper against titanium cold sprayed coated A365 in the T6 temper. The red curves are of the titanium coated samples. Titanium showed interesting results. Unlike copper or nickel, titanium did not reduce tensile strengths significantly. Some variation has been found in elongation but no samples elongated more than the reference A365 T6 samples. No samples were found to delaminate from the substrate during testing.

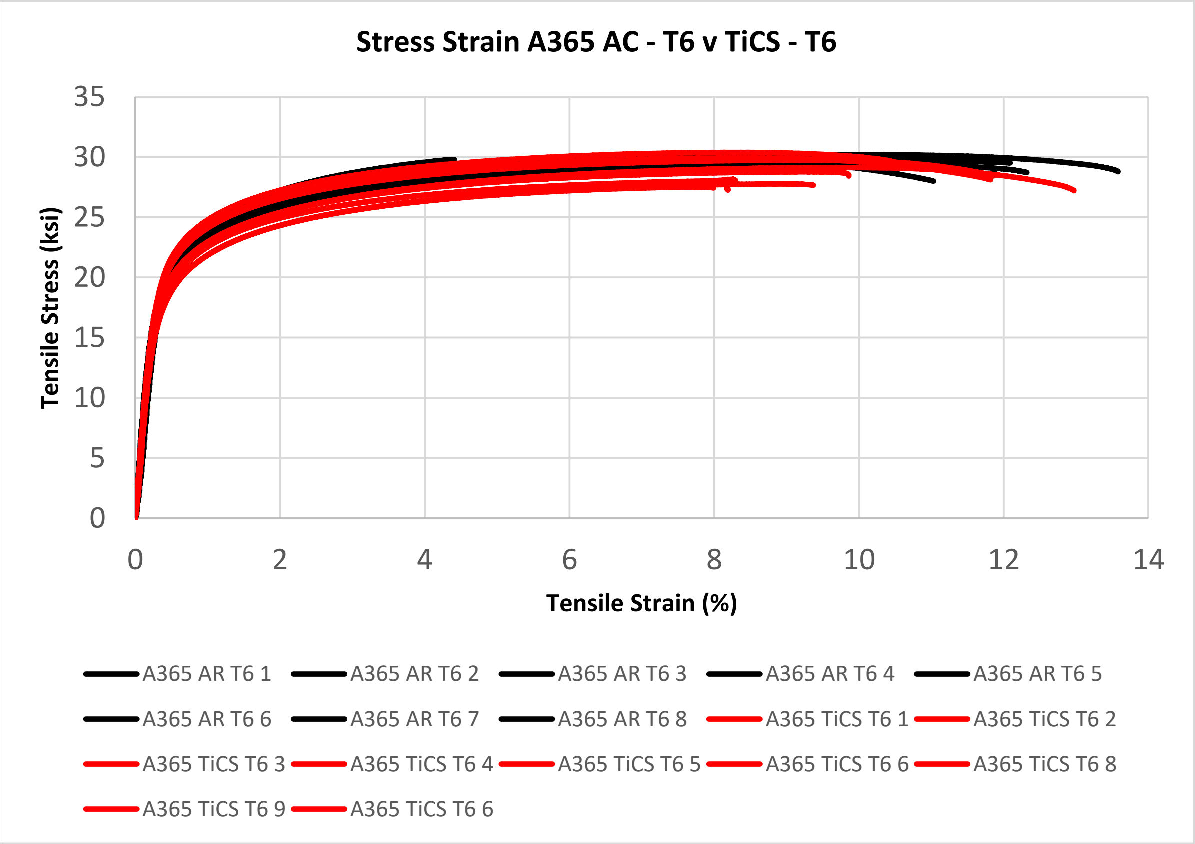


Figure 22: Stress-strain curves for A365 AC in the T6 temper and A365 titanium cold spray in the T6 temper.

6 DISCUSSION & FUTURE WORK

A summary of what was learned and what could be done will be discussed in this section. The main purpose of this research was to improve toughness and impact in cast aluminum with inspiration from the glass industry. Using foreign atoms in the surface of target substrates, an increase in toughness and impact properties was desired. It is well known that foreign atoms inducing compressive residual stresses works in glasses due to the amorphous properties. Metals however are metallic and can accommodate small variations such as foreign atoms substitutionally or form intermetallics which are generally detrimental to these mechanical properties.

6.1 CANDIDATE COATING MATERIALS

It is reasonable to say that copper, zinc, and aluminum are highly recommended candidates to be coated onto A356 or A365 and used in tandem with the typical T6 heat treatment process. This combination of coating and heat treating has the effect of controlling, removing, and redistributing the silicon secondary phase found in this series of alloy. Since silicon is a strengthening phase, removing the phase completely will be detrimental to the overall strength of the base material. However, if the silicon can be redistributed away from the subsurface region, improvements in fracture and impact can potentially be obtained while retaining the strengths of the cast material in the T6 temper. Additionally, strengthen from solid solution will play a role on the resulting mechanical properties. Nickel nor titanium was found to diffuse in significantly to strengthen via solid solution in terms of toughness. It was found that in fact copper, nickel, and titanium were detrimental to impact strength and toughness.

6.2 COATING METHOD

Various methods of applying a coating have been explored. Limitations on the lab scale prevent good quality metal to metal contact. This lack of contact will inhibit diffusion of the coating into the substrate. At this current time, cold spray seems to provide an excellent entry into good metal to metal contact for applying the coating. Cold spray seems to offer more agility in regards to spot treating on a shop floor. Instead of coating and heat-treating entire parts, coating just high-risk sections can prove to be a useful ability. Cold spray also offers good coating to substrate contact while also removing oxides which inhibit diffusion.

6.3 MECHANICAL RESULTS

Copper coated samples resulted in reduced tensile strengths and reduced elongation if the samples did not delaminate. However, if the samples did delaminate elongation was allowed to proceed towards the values shown by as cast A365 in the T6 temper. Nickel samples resulted in similar tensile strengths, but reduced ductility compared to the as cast A365 T6 samples. Finally, titanium samples resulted in comparable tensile strengths and elongation as the A365 T6 samples. A major caveat to these inconclusive results is that much more samples are required to validate the findings.

In regards to impact strengths, A365 T6 results had the highest absorbed energies. Copper, nickel, and titanium resulted in slightly reduced impact strengths. An interesting feature is that as the coating hardness increases, the impact strength is decreased. As the coating becomes more ductile, impact strengths may increase. Like the inconclusive results in tensile testing, many more samples are required to validate these findings.

6.4 FUTURE WORK

6.4.1 COATING MATERIALS

Copper, although seen to create a detrimentally thick diffusion zone, should be further explored. The T6 temper used for A365 may not be appropriate to facilitate solid solution strengthening due to the formation intermetallics. However, copper is used as a strengthening phase in other aluminum alloys and a temper should be developed similarly for copper coatings on A365.

Zinc is highly recommended for its high solubility and generally more ductile properties. Early experiments show that zinc has the best promise for improving toughness and impact strength but a method of application was not easily attainable in the timeframe of this research.

6.4.2 MODIFIED TEMPERING CYCLES

In addition, a modified heat-treating cycle should be explored to avoid pitting as can be found in zinc and copper coatings on aluminum. There may potentially be a temperature at which satisfactory solutionizing and coating diffusion occur but for longer time cycles. The modified heat-treating cycle should be at sufficient temperatures and time scales to manipulate silicon while also avoid pitting and corrosion of the aluminum substrates. Considerations must be taken for optimizing coating alloys to mitigate aluminum dissolving into the coating itself.

6.4.3 SAMPLE GEOMETRY

Another area of exploration should be conducted on part and specimen geometry. Samples explored in this research were rectangular. Circular tensile bars would provide and interesting look into the effect of the coatings without the effect of sharp edges and would include complete coverage by the coating.

7 APPENDICES

7.1 APPENDIX A

7.1.1 A356 AGEING PROCEDURE – T6

- Solutionize in a furnace at 540°C for 6 hours
- Water quench
- Natural age (Room Temperature) age for 24 hours
- Artificial age in a furnace 170°C for 8 hours

7.1.2 A365 AGEING PROCEDURE – T6

- Solutionize in a furnace at 500°C for 80 minutes
- Forced air quench until room temperature
- Natural (Room Temperature) age for 24 hours
- Artificial age in a furnace at 176°C for 8 hours

7.1.3 6061 AGEING PROCEDURE – T6

- Solutionize in a furnace at 530°C for 6 hours
- Forced air quench until room temperature
- Natural age (Room Temperature) age for 24 hours
- Artificial age in a furnace 176°C for 8 hours

7.2 APPENDIX B

DIFFUSION DATA

Diffusing Species	Atomic Radius Å	Host Metal	D_0 $[\frac{m^2}{s}]$	Temperature [°C]	Calculated D_0 $[\frac{m^2}{s}]$
Zinc[b]	1.42	Aluminum	1.1×10^{-4}	500	7×10^{-14}
Magnesium[a]	1.45	Aluminum	1.2×10^{-4}	500	1.9×10^{-13}
Iron[a]	1.56	Aluminum		-	-
Copper[a]	1.45	Aluminum	6.5×10^{-5}	500	4.1×10^{-14}
Nickel[a]	1.49	Aluminum			
Titanium[a]	1.76	Aluminum			
Aluminum[a]	1.18	Aluminum	2.3×10^{-4}	500	4.2×10^{-14}

Table 3: Selected interstitial diffusion data for elements in host aluminum taken from Smithells Metals Reference Book (a) [27], Hilliard et al. (b) [28] . Aluminum in aluminum is substitutional diffusion.

7.3 APPENDIX C

NOMINAL COMPOSITION DATA

Wt%	Si	Fe	Cu	Mn	Mg	Zn	Ti	Al
A201	0.05	0.10	4.0-5.0	0.20-0.40	0.15-0.35		0.15-0.35	Bal.
A365	9.5-11.5	0.15	0.03	0.50-0.801	0.10-0.60	0.07	0.04-0.15	Bal.
A356	6.5-7.5	0.20	0.20	0.10	0.25-0.45	0.10	0.20	Bal.
6061	0.40-0.80	0.70	0.15-0.40	0.15	0.80-1.2	0.25	0.15	Bal.

Table 4: Nominal composition data denoting limits on alloying species. Data obtained from ASM Handbook [1].

7.4 APPENDIX D

GENERAL COMPARATIVE DATA

	A201 (T7)	A356 (T6)
Yield Strength [MPa]	415	210
Tensile Strength [MPa]	345	275
Fracture Toughness [MPa √m]	-	10-25
Impact Strength [J]	8-11	1-4

Table 5: Comparative mechanical data on A356 and A201 at room temperature [29].

7.5 APPENDIX E

7.5.1 ELECTROLESS NICKEL PLATING

In order to plate nickel with even coatings, electroless was used. Electroplating is direction dependent and does not accommodate complex shapes or cavernous geometries. A commercially available electroless kit was used on a smaller scale from Caswell Inc. A brief summary of procedure is as follows:

- Acetone and ultrasonic shaker for 60s
- Allow time to dry in air
- 10 wt% NaOH solution in Deionized Water for 30s
- Deionized water rinse
- ASTM B253-11 X1.9 Universal Deoxidizer for 30s; no rinse
- Caswell Inc. zincate solution 30s; no rinse
- Universal Deoxidizer again for 30s; no rinse
- Zincate again for 30s; no rinse
- Immediately plate into solution for 30 minutes according to kit instructions

7.5.2 ZINC HOT DIPPING

Zinc plating was conducted as an insert casting type procedure with no pickling steps prior. An alloy of Zn – Al 15 wt% was used in order to supersaturate the zinc with aluminum. This was done in order to mitigate aluminum dissolving from the substrate into the coating melt at elevated temperature.

- Melt Zn – Al 15 wt% alloy to 450°C
- Dip samples for 30s, 60s, 180s
- Air cool

7.6 APPENDIX F

Previous work will be discussed in this section as they may prove valuable to future researchers. All previous work done has led the research team to the end of this research that is discussed in depth in the prior sections.

7.6.1 SKIN MELTING

At the beginning of this research, one objective to improve properties was via compressive residual stresses like chemically strengthened glass. Initial work began with skin melting and pertained to inducing compressive residual stresses thermally on the surface of a casting. The results of this experiment supported the end of employing skin melting but will be further explained in this section.

7.6.1.1 INTRODUCTION

Solidification rates affect the microstructure of cast aluminum. It is known that the mechanical properties of cast aluminum are heavily dependent on the final microstructure. There is already much research in age hardening and microstructure so tight controls can be implemented for optimization of the desired property and consequently, the grain structure. Microstructure can vary from the outer walls of castings to the center so a solutionizing step can be utilized to alleviate this. If it is assumed that the casting has a uniform structure, modifying the outer surface microstructure can yield interesting results. A patent in the late 1970s was based on the very idea of modifying the surface or the “skin” of casting by precisely melting and rapidly cooling it [30]. By rapidly cooling a molten material, the microstructure does not have time to grow too large, which results in a finer structure. A finer structure is associated with better mechanical properties. Much of the current research into skin heating is generally done with lasers as they can deliver large amounts of heat with great precision and speed to only the surface by controlling some process parameters. The air or even the work piece itself works as a heat sink to quickly remove the heat from the surface. This process is generally classified as surface laser treatments.

Surface laser treatments are very costly due to the laser itself and the development of optimized process parameters for a given part, and it is slow even for small parts. However, molten salts are available for many applications. Some are used in solar energy plants or as quenchants for steel when temperatures above the boiling point of water are needed. Ideally, this medium would not evaporate like water, catch on fire like some oil quenchants, could be reusable, and have a fairly high melting point. One of the major benefits of a molten salt medium for heat transfer in skin melting is that the heat transfer is faster than a gas environment and the transfer is uniform around complex pieces. The transfer of heat may not be as fast as a laser, but the costs are drastically lower.

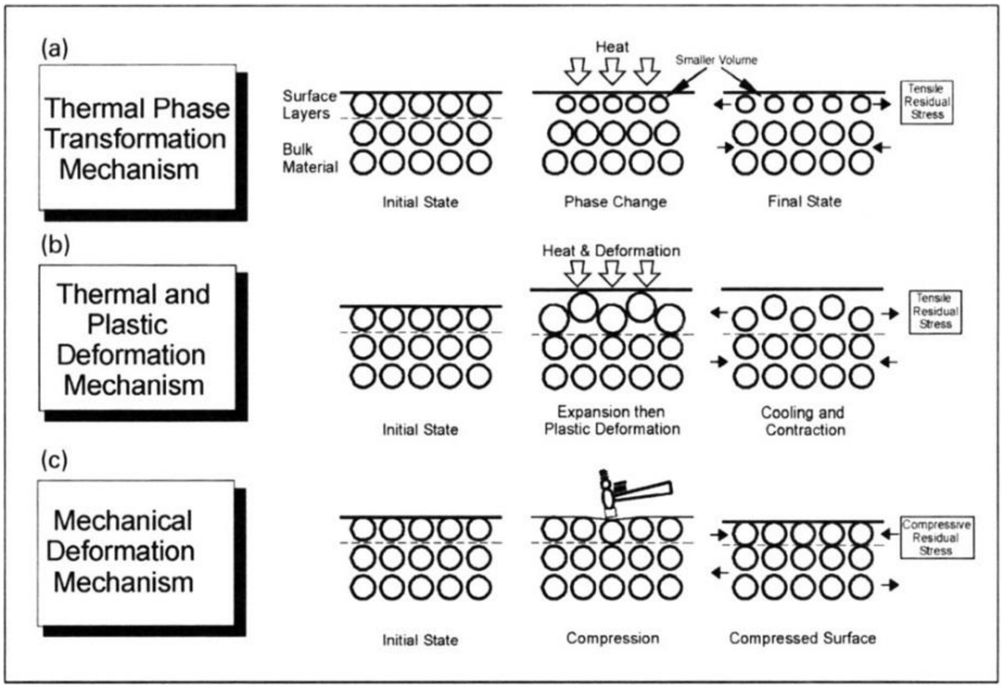


Figure 23: Griffith's depiction of residual stress origination [31].

It is known that compressive residual stresses can originate from mechanical or thermal means or a combination of the two. Since the laser applied a focused amount of heat to a localized region, only the skin melted and solidified which induced compressive residual stresses. In order to meet the cost effective criteria, molten media and rapid quenching was employed to primitively simulate laser skin melting. Although, in the case of this research, skin melting was not achieved due to the rate of heat input and conductivity of aluminum, the nomenclature was maintained.

7.6.1.2 METHOD

The various molten media explored included molten salt, a steel salt quenchant, and pure molten zinc. The melt temperatures were 810°C, 600°C, and 550°C respectively. The steel salt quenchant was graciously donated by DuBois Chemical (Ohio). Quenching media explored included room temperature water, ice water, and liquid nitrogen at ~23°C, 0°C, and -196°C respectively.

The process by which these experiments were conducted were to melt the molten media to the prescribed temperatures. Once at temperature, the media were allowed to settle at that temperature for 3 hours. Cleaned and polished aluminum samples were dipped into the molten media for 3 seconds, removed, and then submerged with agitation into the quenching media.

7.6.1.3 EVALUATION

Due to the complex nature of measuring residual stresses in a very precise location, nanoscale measurements are required. Area of effect was localized to the subsurface region of a casting and classical X-ray diffraction did not provide the accuracy required to evaluate. Nanoindentation were conducted using the Keysight G200 Nanoindenter. Macro-scale indentations such as Vickers or Knoop use probes that are far larger than the case depth that is of interest. Nanoindentation allow for the measurement of significantly smaller depths with orders of magnitude higher precision in regards to depth of penetration. Due to the smaller scale of metrics, residual stresses should show exaggerated effect which should be easier to detect.

From nanoindentation results, a method of evaluating and approximating residual stress can be used. One particular method developed by Lee et al. [32] estimates residual stress by using load displacement curves and a low-stressed reference sample. The results from their research showed very good agreement with strain gauge measurements and Finite Element Simulation approximations. Khan et al. and Zhao et al. [33, 34] employed Lee’s approximation models with reasonably good fit and results. In each of these experiments, the researchers conducted studies on thin films, the materials under study were very homogenous, and it is assume that biaxial equivalent stresses were present. In this research, A356 (the alloy under study at the time) is not a homogenous material nor was it a thin film.

A slow stress reference samples was created by annealing a sample in the furnace at 400°C for 4 hours and allowing to cool inside the furnace over the course of a day to room temperature.

7.6.1.4 RESULTS

The following results from this approximation are displayed below in Figure 24. These results are inconclusive and do not tell much about any of the combinations of molten media and quenchants. The naming scheme in this figure describe the temperature at which the sample was submerged followed by the quenchant used. The negative numbers presented denote a compressive residual stress but some of these residual stresses are even higher than the compressive yield strengths capable for A356 in any temper. One such source [35] stated that the compressive yield strength of A356 was 195 MPa. Most of the results in Figure 24 show that the sample should have succumb to the stresses induced. No changes were found or expected in the microstructure of the subsurface region of skin melted samples. Not enough time or heat was applied to the samples to melt and resolidify the surfaces via optical microscopy.

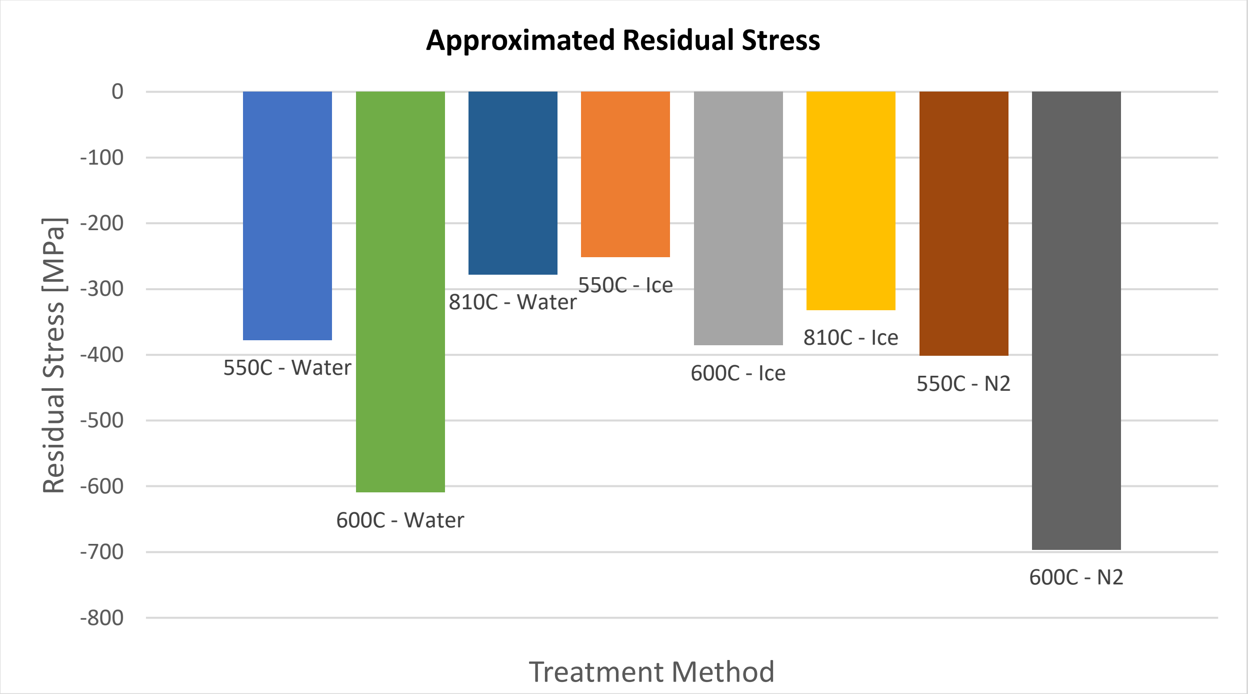


Figure 24: Lee Approximations of residual stress in skin melting experiment.

One source of the incorrect results could be the homogeneity of the A356 alloy. This casting alloy is not nearly as pure in aluminum as the wrought samples that were studied in previous literature. This method of approximating has yet to be optimized for this alloy. Due to these results and lack of methodology to evaluate residual stresses accurately, skin melting and residual stress evaluation were discontinued.

7.6.2 COPPER COLD SPRAY ON 6061

Copper cold spray on 6061 was not an unsuccessful experiment and more of an exploratory experiment. At the time of this research, no method of coating was established to be completely reliable. Cold spray became an option after the optical micrographs provided insight into the quality of contact between the coating and the substrate. Later in the appendices, electroplating, hot dipping, and electroless plating were explored as methods for application but did not yield good results.

7.6.2.1 INTROIDUCTION

Leftover samples of copper cold sprayed onto 6061 were given to this project graciously by the Army Research Lab at Worcester Polytechnic Institute. The sample was provided as shown in Figure 25. A portion of the specimen was cut and examined in the optical microscope as shown in Figure 26. After a T6 heat treatment that was recommended by the Army Research Lab at Worcester Polytechnic Institute, the following micrographs were obtained in Figure 27 and Figure 28.

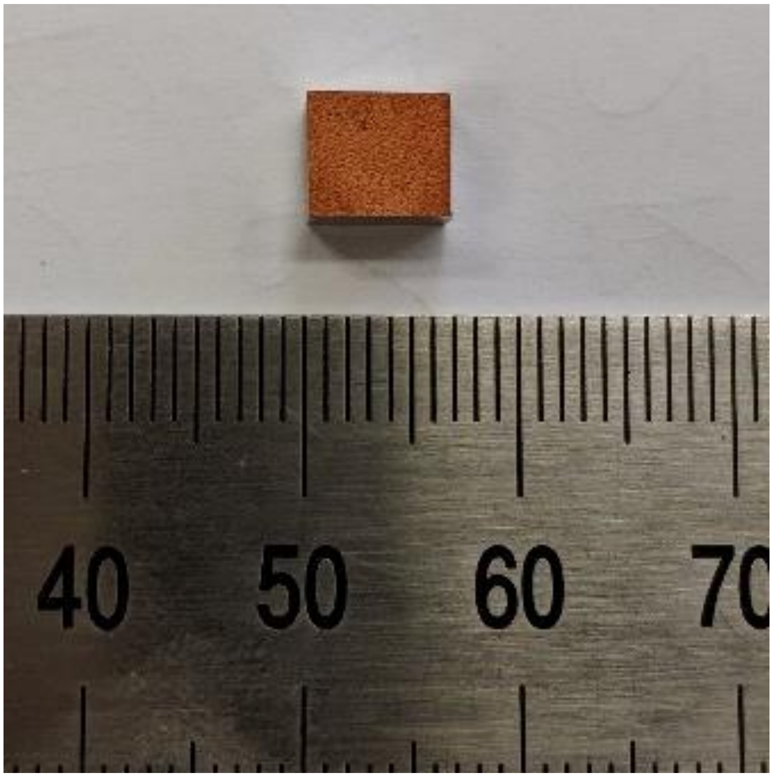


Figure 25: As received copper cold sprayed onto 6061. Ruler is in mm units.

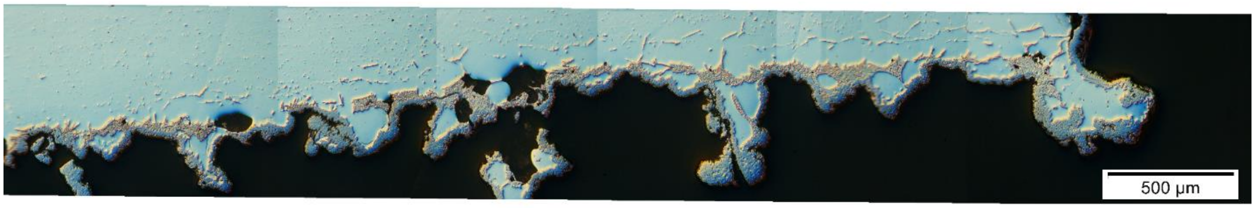


Figure 26: Optical micrograph of copper cold sprayed 6061 in the as received condition.

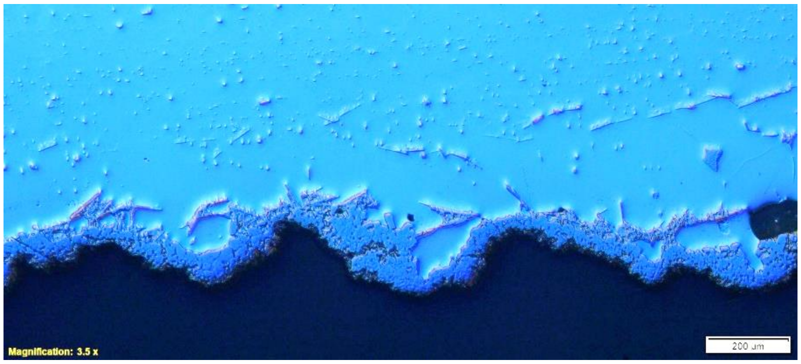


Figure 27: Copper cold sprayed onto 6061 in the T6 temper stitched photos. Upper portion of image is 6061 substrate with the copper on bottom.

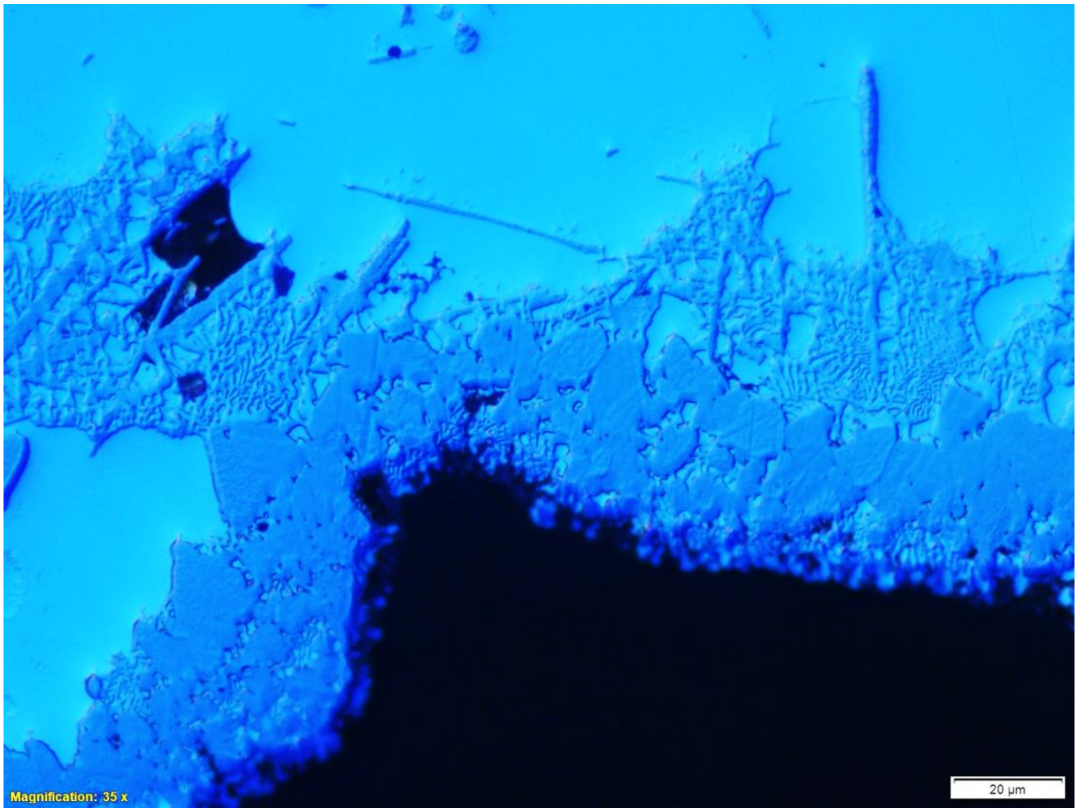


Figure 28: Copper cold sprayed onto 6061 in the T6 temper. Lamellar like structure is Al_2Cu.

7.6.2.2 EVALUATION

At this point in the research, methods of evaluating improvements in mechanical properties was carried out via Vickers indentation for changes in hardness. Tensile specimen and impact specimen were not made at this point as a method of coating the specimen was first sought. In order to evaluate the efficacy of this coating method, EDS analysis was conducted in addition to Vickers indentation.

7.6.2.3 RESULTS

Results from EDS shown in Figure 29 show that copper diffused in and created an intermetallic of Al_2Cu in the subsurface region. Additional instances of these intermetallics can be seen further inwards of the substrate and away from the copper coating itself.

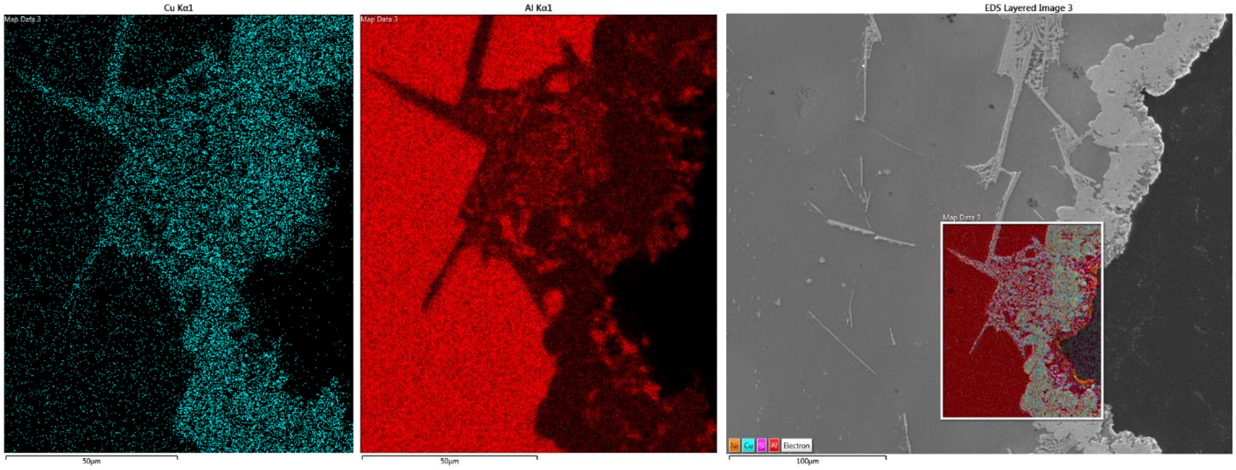
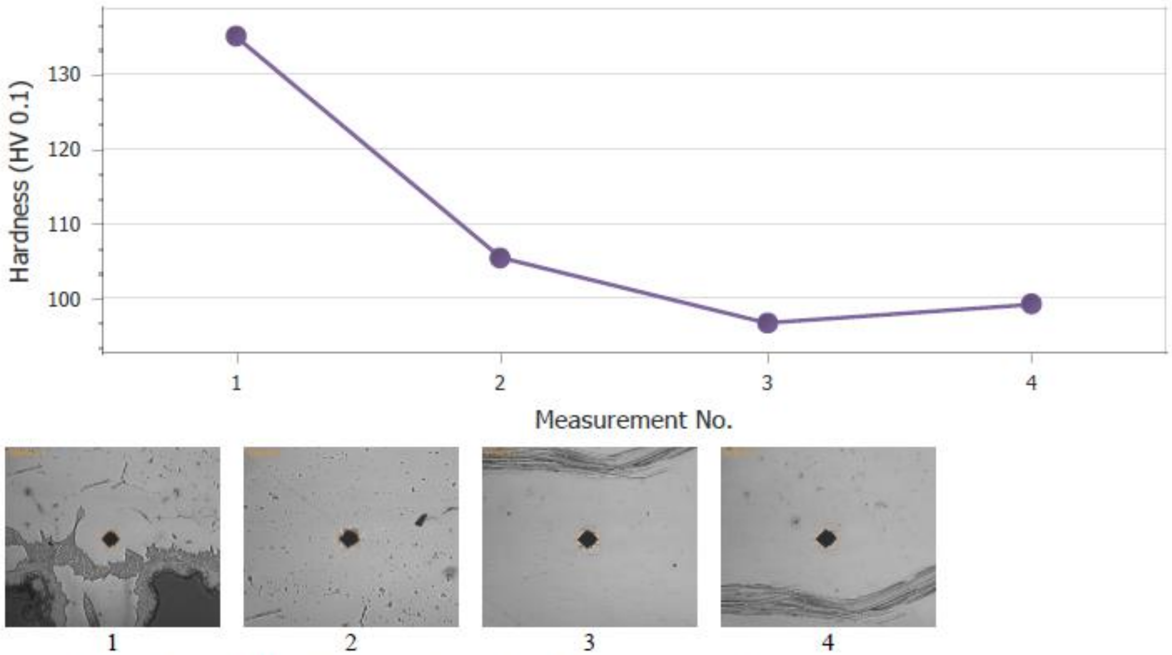


Figure 29: EDS analysis of copper cold sprayed 6061 in the T6 temper.

In addition to results seen as intermetallics, a Buehler hardness indenter was employed to conduct a hardness profile on these samples. Figure 30 shows a hardness profile created on the hardness of the samples. The first indent was conducted at 50µm below the aluminum – copper interface (subsurface region) and subsequent indents were conducted 300 µm apart to avoid effects of other indents. Multiple profiles were measured on each sample and each profile was similar to the results presented in Figure 30. The subsurface region was found to be much harder than the regions in towards the sample. This was an unexpected result due to the little solid solution of copper in aluminum in this sample and the fact that the first measurement was taken towards the edge. Generally, the hardness of a sample is lower towards the edge due to the material having more space for material pile up. As the indenter presses into the sample, material is moved and the sample is deformed. Since the edge is closest to the softer resin, the hardness should be lower than the bulk but the opposite was found. The hardness as the measurements moved in towards the bulk of the sample approached the expected bulk hardness.



Point	Distance	Hardness	Diagonal X	Diagonal Y	Comments
1	0.0 µm	135 HV 0.1	36.2 µm	37.9 µm	
2	300.0 µm	105 HV 0.1	42.7 µm	41.2 µm	
3	600.0 µm	97 HV 0.1	44.1 µm	43.6 µm	
4	900.0 µm	99 HV 0.1	43.2 µm	43.3 µm	

Figure 30: Hardness profile of 6061 with copper cold spray coating in the T6 temper.

Improvements in hardness, though not an accurate measure of toughness or impact properties, showed a significant change compared to a sample without cold spray. The good metal to metal contact achieved by cold spray continued the use of cold spray for the remainder of this research.

7.6.3 ELECTROLESS NICKEL PLATING

Electroless nickel was explored as a possible coating method due to its frequent use in industry for wear resistance and use in high temperature applications. For the purposes of this research, a kit created by Caswell was used to adhere nickel onto aluminum. Much care was taken to alleviate the aluminum oxide layer such that good metal to metal contact was achieved. The process by which electroless nickel was plated onto aluminum can be found in the appendices.

7.6.3.1 EVALUATION

At the time of these results no accurate method indentation was available for this research. It must be stressed that indentation was not the metric of choice but merely a gauge as to whether a process was to be continued to tensile and impact. EDS analysis, however, was still conducted to evaluate diffusion of nickel into aluminum if any.

7.6.3.2 RESULTS

Photographs of an A356 (old alloy) coated in electroless nickel and then tempered to T6 can be seen in Figure 31. All other samples spalled off due to the thermal shock of quenching the sample after solutionizing at such a high temperature. This is most likely due to how low the thickness of the coating was. The nickel could not handle the thermal shock of water quenching.

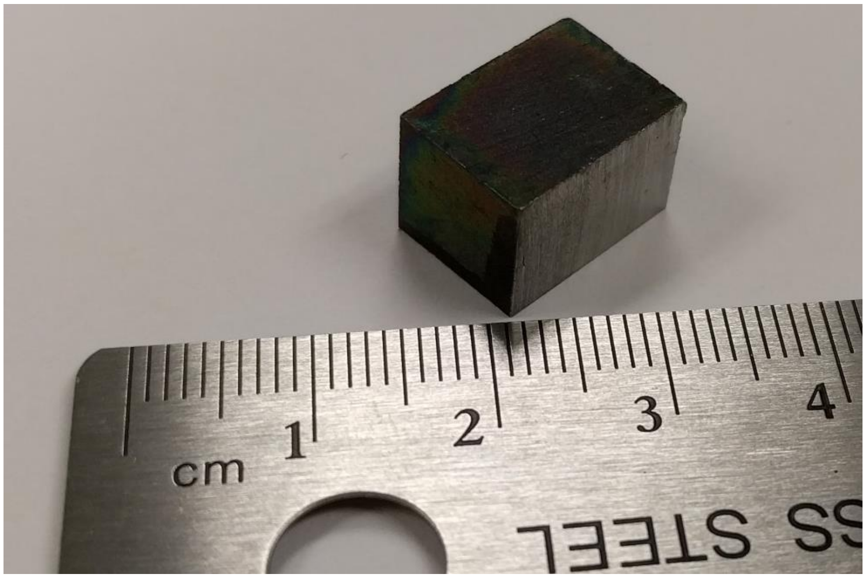


Figure 31: A356 aluminum electroless nickel coated and then T6 tempered.

The image shown in Figure 32 depicts an SEM image of A356 coated in electroless nickel and in the T6 temper. On the left hand side is the A356 substrate and the coating on the right is nickel. As can be seen from the figure, the coating did not adhere well to the substrate. This cracking can be seen on the entire sample. Upon further inspection via EDS as shown in Figure 33, only one instance of nickel aluminum could be found in the upper right hand corner.

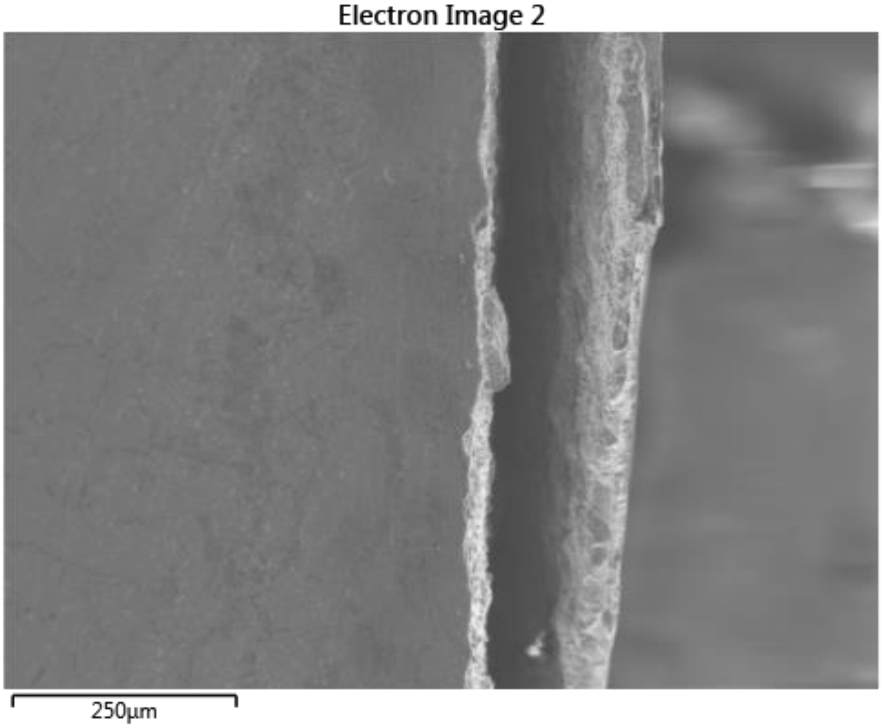


Figure 32: SEM image of A356 with an electroless nickel coating and in the T6 temper.

Contrary to results found in this experiment, nickel cold spray yielded many intermetallics of nickel and aluminum which indicate good metal to metal contact. In this case, a shell was created of nickel but little contact was made between the substrate and the coating. Electroless nickel plating was therefore discontinued as a method to apply a coating onto the substrates for this research.

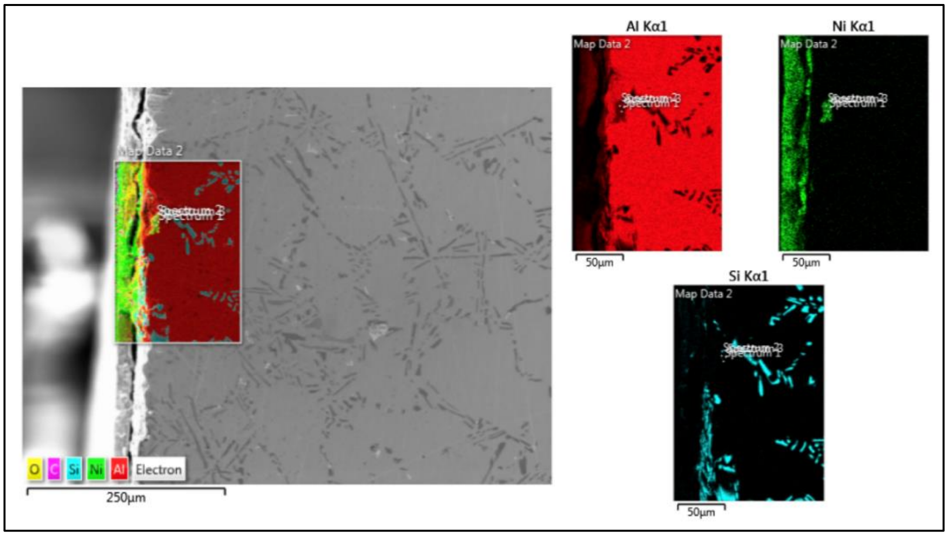


Figure 33: EDS analysis of electroless nickel coated onto A356 in the T6 temper.

7.6.4 CERIUM ELECTROPLATING

Some of the first suggestions and experiments were conducted on electroplating copper and cerium onto aluminum. Great attention must be paid to cleaning prior to applying the coatings. Electroplating offered an excellent opportunity for a cost effective solution as the processes for electroplating has been well studied.

Of these two materials that were explored to be plated, one is unique in that it is a rare earth element. Copper is used in premium aluminum alloys for excellent strength and toughness whereas cerium is a byproduct of rare earth mining. Because of this, cerium will be discussed as a background and copper has been covered in the body of this project.

7.6.4.1 INTRODUCTION

These rare earth metals are generally used for energy production and storage, magnets, data storage, catalysts, ceramics, and even cellphones. Cerium is a rare earth metal but is considered a byproduct of other rare earth extraction for metals like neodymium or gadolinium, which makes this metal valuable to large scale industries like aluminum casting [36]. Cerium additions in aluminum castings have shown potential for improving high temperature applications which may replace denser iron based components [37].

Research from the early 1980s on cerium additions in powder metallurgy aluminum alloys showed excellent high temperature mechanical properties and surpassed the best alloys available at the time. When the research was conducted, cerium costs were prohibitively expensive so the work was not continued but serves as a beginning for this research [37]. Ductility and longer service life at high temperatures have been shown to increase by the introduction of small amounts of cerium into the alloys [38, 39].

Ductility, a desirable property at high temperatures, can be improved through the additions of cerium into the alloy. Research has shown cerium’s effects on ductility in aluminum, magnesium, and even steel alloys [37-39]

7.6.4.2 METHOD

Electroplating was determined to be the best method for applying a layer of cerium onto the aluminum substrate for the equipment setup available. Melting temperatures of Cerium and its salt ($CeCl_3$) have much higher melting temperatures than aluminum. However, $CeCl_3$ can have a reduced melting point when used at the eutectic with Lithium Chloride and Potassium Chloride.

The eutectic melting point was determined to be about 450°C - 475°C which is a safer application temperature for this experiment at a current density of about $10\frac{mA}{cm^2}$. The eutectic composition is as follows: KCl (30.4g), LiCl (40.4g), and CeCl3 (23.7g). The aluminum substrate was the target anode and a graphite rod was used as the cathode. Prior to dipping and electroplating, the aluminum substrate was cleaned with acetone, dipped into NaOH for etching the oxide off of the surface and then covered in a thin layer of zincate. The zincate layer facilitates adhesion of plating materials onto aluminum acting as a flux.

7.6.4.3 RESULTS

Cerium electroplating yielded poor results. Samples were etched in NaOH and zincated twice to help facilitate adhesion onto A356 pieces. The elevated temperature required for the melt and potential chlorine gas production made for a dangerous environment to work. Since the melting temperature needed for the salt was high, aluminum became oxidized before any plating could be conducted and molten salt solidified on contact with the piece. The aluminum piece was submerged for 60s, removed and allowed to cool. Figure 34 shows the results. If a preheating of aluminum is required to reduce the likelihood of solidified salt, the aluminum will readily oxidize and the protective intermediate coating will evaporate away. Another more appropriate setup is required for a successful cerium electroplating if it is to be successful.

Figure 34: The result of an attempt to electroplate cerium onto A356 from a eutectic salt at 450°C for 60s. The white coating is the solidified eutectic salt.

8 BIBLIOGRAPHY

1. Kaufman, J., *Introduction to Aluminum Casting Alloys*. ASM Handbooks, ed. A. International. Vol. Supplement. 2011, Ohio: ASM International.
2. Secretary, O.o.t.P. *Obama Administration Finalizes Historic 54.5 MPG Fuel Efficiency Standards*. [Online Web Page] 2012 [cited 2018 4/27/2018]; Available from: https://obamawhitehouse.archives.gov/the-press-office/2012/08/28/obama-administration-finalizes-historic-545-mpg-fuel-efficiency-standard.
3. Energy, U.S.D.o. *Lightweight Materials for Cars and Trucks*. [Web Page] [cited 2018 4/27/2018]; Available from: https://www.energy.gov/eere/vehicles/lightweight-materials-cars-and-trucks.
4. *Aircraft & Aerospace*. [Web page] 2018 [cited 2018 8/23/2018]; Available from: http://www.aluminum.org/product-markets/aircraft-aerospace.
5. Kaufman, J., *Aluminum Alloy Castings: Properties, Processes, and Applications*. 2004, Materials Park, OH: ASM International.
6. Kaufman, J.G., et al., *Fracture resistance of aluminum alloys: notch toughness, tear resistance, and fracture toughness*. 2001, Materials Park, Ohio;Washington, D.C;: Aluminum Association.
7. Merlin, M., L. Pivetti, and G.L. Garagnani, *Effect of eutectic modification and the solidification rate on the impact strength of a356 aluminum-silicon alloys.* CORRELATION BETWEEN MICROSTRUCTURAL AND MECHANICAL PROPERTIES OF ALUMINUM ALLOY CASTINGS PRODUCED BY DIFFERENT FOUNDRY PROCESSES, 2008. **26**(1): p. 43.
8. Merlin, M., et al., *Impact behaviour of A356 alloy for low-pressure die casting automotive wheels.* Journal of Materials Processing Technology, 2009. **209**(2): p. 1060-1073.
9. Chan, K.S., P. Jones, and Q. Wang, *Fatigue crack growth and fracture paths in sand cast B319 and A356 aluminum alloys.* Materials Science & Engineering A, 2003. **341**(1): p. 18-34.
10. Lee, K., Y.N. Kwon, and S. Lee, *Effects of eutectic silicon particles on tensile properties and fracture toughness of A356 aluminum alloys fabricated by low-pressure-casting, casting-forging, and squeeze-casting processes.* Journal of Alloys and Compounds, 2008. **461**(1): p. 532-541.
11. Shivkumar, S., L. Wang, and C. Keller, *Impact properties of A356-T6 alloys.* Journal of Materials engineering and performance, 1994. **3**(1): p. 83-90.
12. Hahn, G. and A. Rosenfield, *Metallurgical factors affecting fracture toughness of aluminum alloys.* Metallurgical Transactions A, 1975. **6**(4): p. 653-668.
13. Alexopoulos, N. *Impact properties of the aircraft cast aluminium alloy Al-7Si0. 6Mg (A357)*. in *EPJ Web of Conferences*. 2010. EDP Sciences.
14. Zeren, M., *Effect of copper and silicon content on mechanical properties in Al–Cu–Si–Mg alloys.* Journal of Materials Processing Technology, 2005. **169**(2): p. 292-298.
15. Shabestari, S. and H. Moemeni, *Effect of copper and solidification conditions on the microstructure and mechanical properties of Al–Si–Mg alloys.* Journal of Materials Processing Technology, 2004. **153**: p. 193-198.
16. Ma, Z., et al., *Effect of Fe content and cooling rate on the impact toughness of cast 319 and 356 aluminum alloys.* AFS Trans, 2003. **111**: p. 255-266.

17. Casari, D., et al., *The effect of Ni and V trace elements on the mechanical properties of A356 aluminium foundry alloy in as-cast and T6 heat treated conditions.* Materials Science and Engineering: A, 2014. **610**: p. 414-426.
18. Apelian, D., S. Shivkumar, and G. Sigworth, *Fundamental aspects of heat treatment of cast Al-Si-Mg alloys.* AFS transactions, 1989. **97**: p. 727-742.
19. Meyers, C. and J. Lyons, *Fracture Toughness—Second Particle Interactions in A357 Alloys.* Technology for Premium Quality Castings, 1986: p. 151-179.
20. Srivastava, M., et al., *Energy absorption of HPDC aluminium and magnesium alloys.* Proc. High Tech Die Casting, 2006.
21. Hume-Rothery, W., G.W. Mabbott, and K.C. Evans, *The freezing points, melting points, and solid solubility limits of the alloys of silver, and copper with the elements of the B sub-groups.* Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character, 1934: p. 1-97.
22. Sienicki, J., et al., *Cold spraying and laser cladding as an alternative to electroplating processes.* Aircraft Engineering and Aerospace Technology, 2018.
23. Shaha, S., S. Dayani, and H. Jahed. *Fatigue life enhancement of cast Mg alloy by surface modification in cold spray process*. in *MATEC Web of Conferences*. 2018. EDP Sciences.
24. Dayani, S., et al., *The impact of AA7075 cold spray coating on the fatigue life of AZ31B cast alloy.* Surface and Coatings Technology, 2018. **337**: p. 150-158.
25. Funamizu, Y. and K. Watanabe, *Interdiffusion in the Al–Cu system.* Transactions of the Japan Institute of Metals, 1971. **12**(3): p. 147-152.
26. F. Brenton, J.F. *Alloys with high strength and ductility for high pressure vacuum die casting in automotive body structure applications: Impact of heat treatment on mechanical properties*. in *NADCA DIE CASTING NOGRESS & TABLETOP*. 2016. Arlington Heights, IL: NADCA.
27. Brandes, E.A., et al., *Smithells metals reference book*. 7th / by E.A. Brandes and G.B. Brook.;7th; ed. 1998, Oxford;Boston;: Butterworth-Heinemann.
28. Hilliard, J.E., B.L. Averbach, and M. Cohen, *Self and interdiffusion in aluminum-zinc alloys.* Acta Metallurgica, 1959. **7**(2): p. 86-92.
29. *ALUMINUM A201 (Heat-Treatable Aluminum Casting Alloy)*. 1952, ASM International. p. 1-2.
30. Conrad Martin Banas, E.M.B., Bernard Henry Kear, Anthony Francis Giamei, *Skin Melting*, in *Google Patents*, U.S. Patent, Editor. 1978.
31. Griffiths, B., et al., *Manufacturing surface technology: surface integrity & functional performance*. 1 ed. 2001, New York, NY: Taylor & Francis.
32. Lee, Y.-H. and D. Kwon, *Estimation of biaxial surface stress by instrumented indentation with sharp indenters.* Acta Materialia, 2004. **52**(6): p. 1555-1563.
33. Khan, M., et al., *Effect of residual stress on the nanoindentation response of aerospace aluminium alloys.* Computational Materials Science, 2011. **50**(10): p. 2967-2976.
34. Zhao, X. and P. Xiao, *Residual stresses in thermal barrier coatings measured by photoluminescence piezospectroscopy and indentation technique.* Surface and Coatings Technology, 2006. **201**(3-4): p. 1124-1131.
35. MatWeb, L., *MatWeb: Material Property Data.* línea]. Available: http://www. matweb. com/search/DataSheet. aspx, 2013.
36. Binnemans, K., et al., *Recycling of rare earths: a critical review.* Journal of cleaner production, 2013. **51**: p. 1-22.

37. Sims, Z.C., et al., *Cerium-based, intermetallic-strengthened aluminum casting alloy: High-volume co-product development.* JOM, 2016. **68**(7): p. 1940-1947.
38. Schüler, D., et al., *Study on rare earths and their recycling.* Öko-Institut eV Darmstadt, 2011.
39. Gupta, C. and N. Krishnamurthy, *Extractive metallurgy of rare earths.* International Materials Reviews, 1992. **37**(1): p. 197-248.