Tensile Bar Manufacturing and Processing for the Further Development of High Entropy Aluminum Alloys

A Major Qualifying Project Report
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Abstract

Measuring the tensile properties is a challenge for aluminum alloys with poor castability due to the difficulty of making a standard circular tensile bar. The current project is to design small tensile bars for the novel high entropy aluminum alloys developed by WPI Advanced Casting Research Center (ACRC). A Computer Numerical Control (CNC) machining experimental procedure was used to make the small tensile bars. It is observed that a similar trend on yield strength and elongation with the standard circular tensile bar in the benchmark test. In addition, there are two more benefits of making small tensile bars. One, it only uses 5% of the standard circular tensile bar. Second, it is able to provide the tensile properties trend of aluminum alloys with poor castabilities.

Acknowledgments

I would like to show my appreciation to the following people for without their help this project and my part in it may not have been fruitful. Firstly, a special thanks to the Metal Processing Institute (MPI) and the Advanced Casting Research Center (ACRC) for making the project possible through their funding of the project. I also extend my sincerest gratitude to Dr. Mohammad Asadikiya for his instruction and guidance throughout the project. I would like to thank Michael Collins for his help in learning proper safety, his instruction on using the lab equipment and assistance in navigating the lab. I thank Dr. Libo Wang for his guidance in the Foundry and teaching me the casting process. Ian Anderson was a great help and mentor during the brainstorming for the manufacturing process of the tensile bars. I would like to extend my gratitude to Mr. Connor Lemay for his assistance and guidance in manufacturing and experimental processes. Lastly, I thank my advising professor, Dr. Yu Zhong, for his mentorship and assistance at every step of the process.

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1.0. Introduction

Material science has seen a drastic increase in attention in the past decade partly due to the new development of high entropy alloys (HEA) and the possibilities for future applications. Although there is no official definition for a high entropy alloy it is largely accepted as an alloy that incorporates multiple elements into its mixture with at least 4-5 elements in its crystal structure. High entropy alloy experimentation by its modern definition can be traced as far back as 1788 with the German scientist Karl Franz Achard who experimented with ternary systems up to seven material systems. Unfortunately, this publication was largely undiscussed until 1963 when Cyril Stanley Smith, famous for his contribution to the Manhattan Project, brought it back into the light. Even then it would be nearly four decades during the turn of the 20th century before Brian Cantor in the UK and Jein-Wei Yeh in Taiwan would, through two independent investigations, start the boom of high entropy alloy. The increase in publications can be observed over the last two decades by the figure [1]. The purpose of this exploration into high entropy alloys is to create new materials that have properties that are unachievable through simpler material combinations. This addition of many materials acts to distort the material lattice and these distortions can lead to improved physical properties in the materials. Many materials have already proven the concept of lattice distortion, a common example being Gorilla Glass, a ceramic commonly used for smartphone screens. During processing the alkali-aluminosilicate is submerged in a potassium ion salt bath that causes potassium ions to replace sodium ions in the lattice interstitially. This invasion of potassium ions places the surface of the glass in high compression which gives it its surface strength and resistance to cracking [2]. While the process for the aluminum alloy that was worked on by the WPI high entropy alloy team was very different

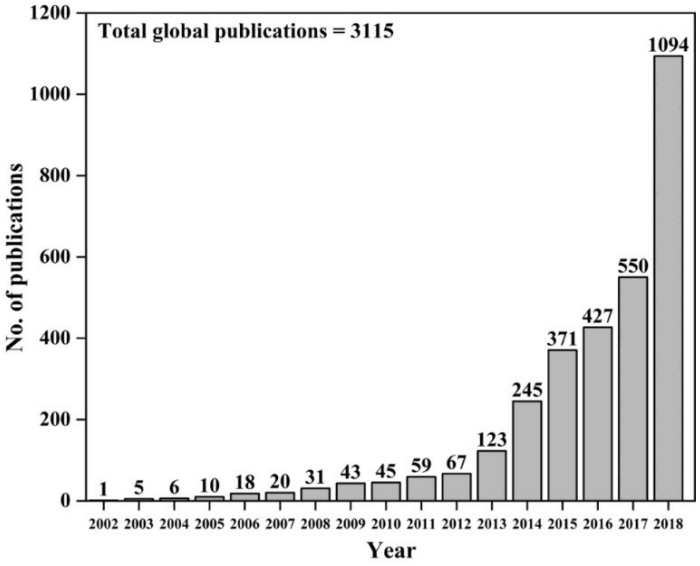

Figure 1: Publication chart for high entropy alloy scientific papers [1]

in terms of processing and materials used, the fundamental theory of lattice distortion maintains relevance.

High entropy aluminum alloys are a very versatile material field that is already used all over the engineering market and is championed for its lightweight attributes, resistance to corrosion, cheap material cost, optical qualities, bond capabilities and more. However, casting is a fickle and expansive field and based on the alloy in use, strong, definitive results are difficult to acquire. This may be due to a variety of possible material properties and handling choices which became a main focus of this project. The tensile test is an important method used to look into the strengths and ductility of materials and is an important indicator of the characteristics of an alloy. The project found that certain alloys while capable of forming into the mold had no good way to test their mechanical properties and this project looks to address that challenge.

To gain a better understanding of the properties of less castable materials that would face defects and diminished results should they be cast through our conventional testing methods the project team developed a new form of tensile bar in an attempt to make less castable materials more studiable. The project attempted to gain a method of testing tensile bars through CNC machining smaller samples allowing us to test materials that otherwise would be too difficult to create. This had the potential to increase the scope of the research and increase the range of element possibilities that could be added to aluminum as well as present an alterior testing method for the present alloys that may be able to perform better under the new testing platform. This paper will focus on the development of the new sample design and constraints as well as the relationship to previous tensile bar strengths and their correlation with the added variable of heat treatment schedules.

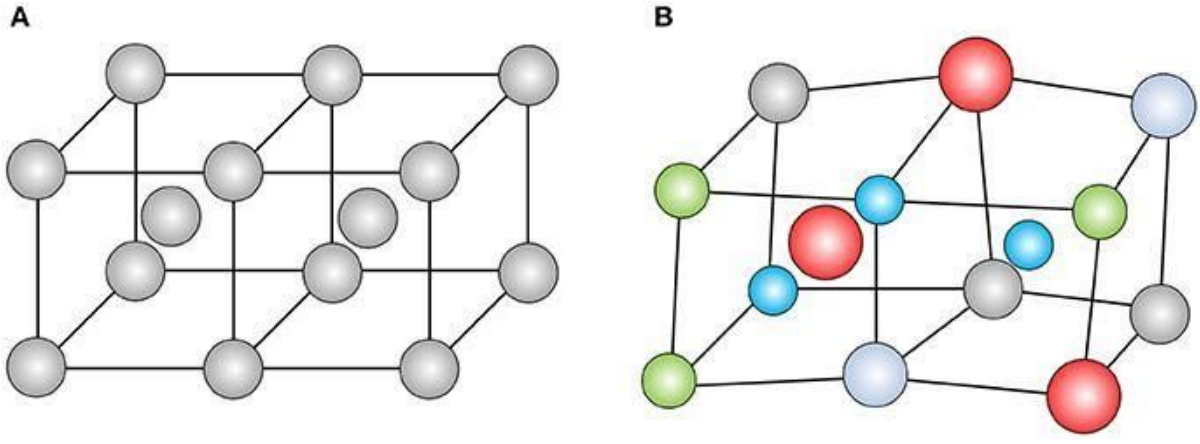

Figure 2: Body-Centered Cubic structure(A) Compared to lattice distortion visualization(B) [3]

2.0. Background

Throughout this section, the background of aluminum casting and the potential for alloy improvements through different compositions will be explored. This section will cover the effects of different materials on the aluminum crystal structure, the effects, and mechanical properties. This portion will also discuss past studies conducted that align with the direction of the high entropy alloy project.

2.1. Pure Aluminum

Aluminum in its pure form alone is a highly desirable material due to its many applications and is considered pure if its composition is above 99%. It is relatively cheap, according to Infomine.com, aluminum is currently priced at about 80 cents per pound where a material such as copper is priced at $2.64 per pound. By comparison with other structural materials such as steel, aluminum has a relatively low density at 2.7 g/cm^3 compared to steel's average of 7.8g/cm^3, showing that steel is more than twice as dense as aluminum. As can be seen in the image below structural aluminum is becoming highly desirable for applications such as the automotive industry to replace some of the cars' major body components. Aluminum can also be manufactured to be highly ductile and elastic such as food preservation foil and as a structural material, it is used second in frequency only to steel [4]. This ductility allows it to be more malleable and can be formed into more shapes with higher precision than its competitors. It is an important material consideration when comparing its lightweight to strength ratio and manufacturability giving it many vehicle applications from aircraft parts to land and water vehicle applications that are making it replace composites as well [5, 6]. This is strengthened by its natural corrosion resistance that can be attributed to the oxide layer that forms on the surface of the material. This

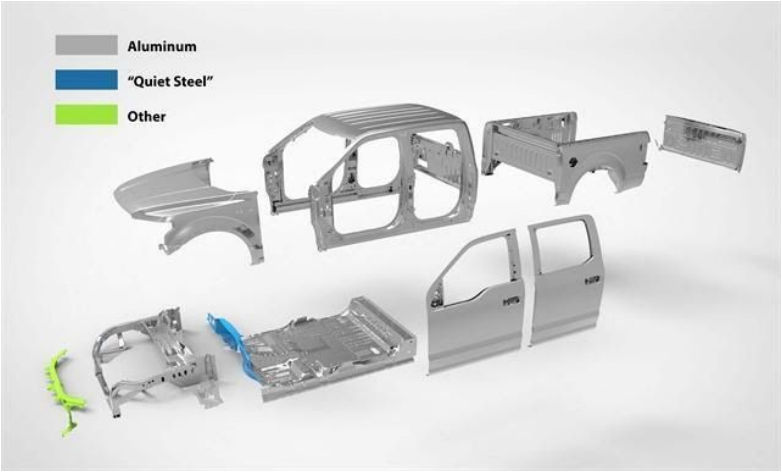

Figure 3: Breakdown of increased aluminum use in automobiles [5]

oxide layer is highly desirable and at roughly 5 nm it can reform and seal itself upon being torn or damaged making Aluminum highly resistant to corrosion from chemical or environmental factors. Chemically the oxide will remain stable from the oxide pH range of 4-9 having only minimal effects [4]. Aluminum has a Face-Centered Cubic (FCC) crystalline structure in its pure solid phase. Aluminum also holds considerable optical properties and its surface can vary in color and shine based on the needs of the design. Aluminum can conveniently be split between two categories: wrought and casting. As an example, Aluminum can be cold worked, a wrought process, using accumulative back extrusion to reach strengths of 300 MPa reached through grain refinement and dynamic recrystallization methods [7]. This project worked solely in casting, so the remainder will include possibilities related to this form of material processing.

2.2. Casting Aluminum

Cast aluminum can be manipulated through different thermal treatments including quenching, heat treatment, and precipitation hardening. These thermal treatments affect the crystalline structures of the material. However, it is possible for casts to not need thermal treatment and these are called as-cast or otherwise known as F-state. Starting with the casting process alone it is important to mind the melting temperature, the pouring method of the material and the cooling rate of the cast inside the mold. Starting with the temperature if the material is too cold it will not be fluid enough to enter the mold and may prematurely begin the nucleation of certain phases besides liquid. This is bad because the proper and predictable formation of certain phases is what gives a material its strength [8]. Issues specific to fluidity include not forming to the proper shape of the mold or having a surface tension that prevents flow into necessary pockets of space. Fluidity also needs to be laminar when it is flowing into the mold otherwise when it is cooling this may affect the formation of grain boundaries. Turbulent flow can also degrade the

Figure 4: Active crucible with aluminum melt

quality of surface finish or create cracks upon solidification. Delving into cooling rates, consideration for hot tearing and shrinkage were the main concerns for our aluminum alloys. Hot tearing occurs when two sections of a cast cool at separate rates and the solidification causes shear forces to occur at the final cooling locations making cracks form. Hot tearing is most likely to occur in locations where dimensions vary, or heat transfer will occur at a different rate than other locations on the cast. Shrinkage happens when the material cools and forms into its crystalline structure, its organized form takes up less space than the liquid form, so the final part is smaller than the poured melt was when it entered the mold. Shrinkage may cause the part to decrease in size to the point it falls outside of tolerable limits and may not be used [8].

Another factor in cooling is the sublimation of secondary phases. When cooling Austenite into Martensite for steel the metal must be quenched, and the heat is transferred at an extremely high rate to promote nucleation of the correct phase. If the cooling rate does not meet the requirements, secondary phases will form and the strength of the steel will not be that of Martensite but a weaker secondary phase. Aluminum is also capable of the creation of non-ideal secondary phases when the cooling rate is not controlled [9]. These are just a few of the considerations and based on different compositions an aluminum alloy can have vastly different properties even if only trace amounts are present in the material.

2.3. Alloying Aluminum and the possible Applications

Metallic alloys dominate the market of materials when it comes to many different applications such as conductivity and tensile strength also being highly promising in fields requiring ductility and optical properties. During this project, the main considerations for aluminum alloy combinations were restrained by the investigative focus of using cheap materials and easy to replicate casting techniques. Through this mindset, the final alloy product would be more marketable in the industry. This also allowed us to be less conservative with experimental combinations as there was not too much financial stake in any individual cast having desired results. The combinations that were settled on involved using Thermo-Calc® and material modeling systems to narrow the near-infinite

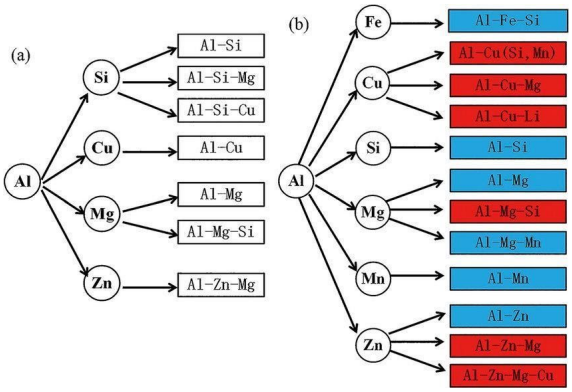

Figure 5: Secondary alloy (A) Ternary alloy (B) [10]

possibilities to a feasible and experimental number. This experiment saw the utilization of the elements magnesium, zinc, copper, lithium and silicon. Although the focus of this paper looks at the alloy relationship between aluminum and zinc-magnesium combinations. Alloying is an important method of improving material properties by combining desirable characteristics of materials or characteristics developed from elemental and bonding interactions. Although compositions and base elements and bonding principles vary drastically based on application or desired result a family of metallic alloys are typically based around a single element's structure with other things added interstitially [4]. The aluminum alloys developed by this project were from this family. The aluminum composition for most of the alloys experimented with was over 80% and saw extreme differences in properties.

2.4. High Entropy Alloys and the Core Effects

By including multiple elements in a single material lattice, distortion of the crystalline structure can act to strengthen the physical properties of a material. Although there is no formal definition of what a high entropy alloy is it is largely accepted that alloys must consist of at least five elements and make up 5-35% of the alloy's composition [11]. The advantage of having more elements in an alloy is the resulting greater configured entropy which can act to stabilize and strengthen the solid phase of an alloy to produce enhanced material characteristics. There have been various tests done to prove the effectiveness of high entropy alloys including a study conducted by North Carolina State University which was able to produce an alloy with an, especially high strength to weight ratio that outperformed any existing alloy made through traditional processes [12, 13]. The interactions that are responsible for the high entropy alloys increased properties are referred to as the "Core Effects". The four Core Effects are labeled in the diagram above and are as follows: the High Entropy Effect, the Sluggish Effect, the Severe Lattice Distortion Effect and the Cocktail Effect [13].

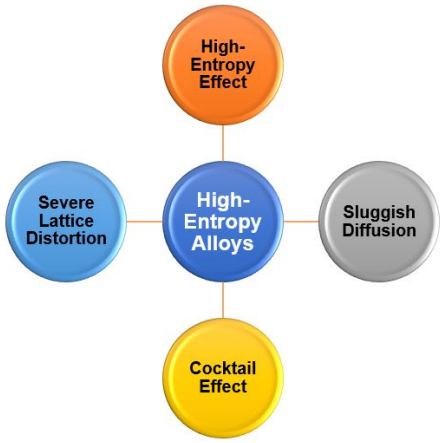

Figure 6: High entropy alloy "Core Effects" diagram

Before discussing the impacts that the Core effects have it is important to understand crystalline structures. The main three single solid phase microstructures for metals are

Face-Centered Cubic (FCC), Body-Centered Cubic (BCC) and Hexagonal Close Packed (HCP). These three structures are depicted below and can be described as the building blocks that make up alloys. The alignment of atoms is due to the bonding between individual atoms finding

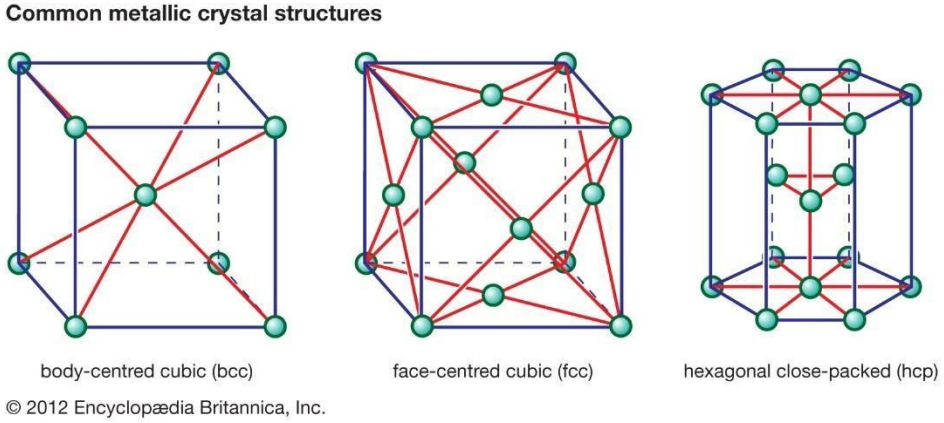

Figure 7: Crystalline structures common in metals [14]

a balance in this state; the lines between the atoms represent their bond. As illustrated BCC has a cubic structure with eight atoms at the corners and one in the middle. Since the atoms at the corners are each theoretically in 8 other structures, technically only $1/8^{th}$ of the corner atoms are represented in the image [14]. This means that if you do the math 2 atoms are present in this structure counting the atom at the center of the structure. FCC still has that cubic structure however now some atoms lie at the center of each face half in the structure and half out. Following the pattern from before this means that 4 atoms are present in each structure and a similar calculation

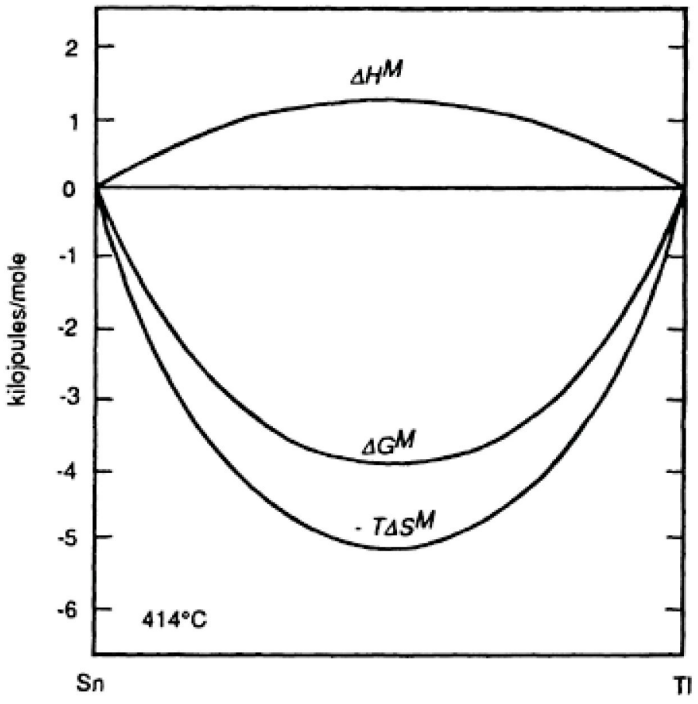

Figure 8: The molar enthalpy, entropy and Gibbs free energy mixing of thallium and tin at 414 degrees Celsius [15]

can be done for the HCP structure. This understanding is important when looking at the individual structures to understand the atom's impact in the system and how these building blocks fit into the larger lattice.

The High Entropy Effect is a main principle of high entropy alloys and has to do with the interactions between atoms in a crystalline structure [16]. This effect relies on the idea that because the alloying elements exist in more equal proportions than previously thought the interactions between the elements are still capable of forming the crystalline structures discussed above [13]. The High Entropy Effect is based on the Gibbs Free Energy of the solid phase. By comparing the Gibbs Free Energy of different phases, it is possible to deduce which phase is more likely to occur at certain temperatures. In the diagram above, it is possible to observe the Gibbs Free Energy diagram of mixing Thallium and Tin at 414 degrees Celsius [15]. Gibbs Free Energy is the thermodynamic potential of the work necessary for a material to achieve a certain state.

Gibbs Free Energy is expressed by the following equation 1:

$$G = H_{mix} - TS_{mix} \qquad (1)$$

In the above equation, G stands for the change in Gibbs free energy, the lower this value is the more likely it is to occur, H_{mix} is the change in enthalpy of the whole mixture, while T is the absolute temperature of the mixture and S_{mix} is the change in entropy of the mixture. This equation states that as Entropy increases the Gibbs Free Energy will decrease meaning that a stable single solid solution is more likely to occur [15, 16].

Severe Lattice Distortion is another Core Effect that is responsible for the enhanced properties found in high entropy alloys [13]. Severe lattice distortion in principle is the idea that the crystalline structure is deformed at the introduction of other materials to its lattice [17]. This distortion is present due to the effect of the different bond energies and sizes of the elements which cause different areas to be in tension and compression. These points of tension and compression act to strengthen the material [17].

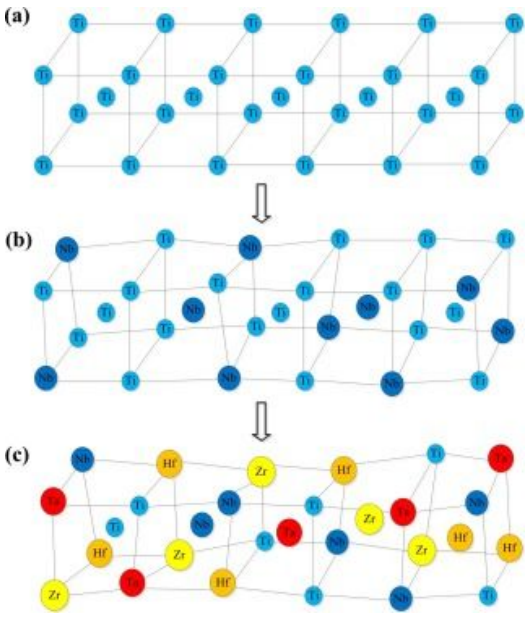

Figure 9: Severe lattice distortion visual representation [2]

Sluggish Diffusion is the observation that kinematic transformations are far slower in high entropy alloys when compared to conventional alloys. This is related to the bonding relationships between the atoms and the higher activation energies. The theory states that because of this transformation phenomenon the high entropy alloys have greater fracture resistance, hardness, and increased thermodynamic properties compared to their conventional alloy counterparts.

Finally, the last Core Effect is the Cocktail effect which states that the strength of the overall alloy is stronger than the average strength of the elements present in its composition. The forces present in high entropy alloys between the elements are caused by interactions that are not a factor in standard alloys. These interactions result in the increased strength of the high entropy alloys [13].

3.0. Methodology

3.1. The State of the Tensile Bars and Challenges before the Major Qualifying Project

Previous to the start of this major qualifying project the project team had already begun testing several different high entropy combinations and had already found success with several iterations of the aluminum alloys being tested in terms of desired mechanical properties. However, Some material combinations proved difficult to test due to casting and property constraints that meant new testing avenues had to be explored. Enter the development of this project's ultimate goal of tensile bar development that made casting difficult materials more feasible. The elements that were in question were copper and lithium. Although copper was capable of being cast to make it easier a new sample testing method would have proved helpful. The main purpose though was for the samples that contained lithium which is highly reactive and can even be considered dangerous if proper precautions are not taken. The lithium pours were having a lot of trouble just filling molds and to avoid this issue in the future and increase future testing possibilities the development of smaller machined tensile bars was greenlit for experimentation.

The manufacturing of tensile bars was a major aspect of this project and this section will cover the need for their creation as well as the manufacturing process that resulted in their development. Then the results will delve into the procedure following the manufacturing and the results of the tensile bars that went through heat treatments versus as-cast. This will also be compared to the results of the tensile bars for alloys that did not have casting issues and constraints.

3.2. CNC Experimental procedure for the development of small tensile bars

The start of the project saw the use of standard circular tensile bars which have a .505 inch diameter at the intended point of fracture and a length of 8 inches being the only method of tensile testing that could be relied on. However, there were a few issues when looking at the accuracy of the tests due to the limitations of the bars that lead to the development of the new

tensile bars. The main problem was that the bars were so large that they had a tendency towards producing poor samples when the alloy had low castability. The small tensile bar plates also had a much faster cooling rate which results in a much finer grain structure making it highly desirable. Another issue was even when cast properly, surface defects in the cast that were within casting tolerances were causing premature failures in samples. This was theorized to

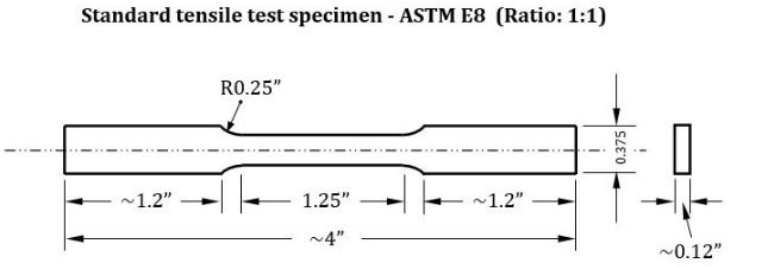

Figure 10: Standard Tensile Test Specimen Specifications

occur because it would fracture at the surface defect location meaning that defect was the point of low strength in the bar. To get a better idea of what the alloys were capable of it became necessary to manufacture new tensile bars. The design depicted here is the ASTM industry standard we decided to use because it allowed for thickness changes and was much smaller making it easier to avoid hot tearing and increase cooling rates. Its small size was also a huge save in materials weighing a fraction of the previous tensile bars and producing far less waste upon post-processing. To manufacture the tensile bars, we had to cast thin plates and then CNC those plates into the bars that we would then test. The bars took several iterations to properly manufacture them.

Casting the plates presented its difficulties in our efforts to use the small plates certain alloys ran into castability issues with fluidity. The accelerated cooling rate also resulted in the need for cleaner faster pours, however, if the pour was too quick the flow of the melt would be turbulent which would result in decreased properties. Once the plates were cast they would have to be checked for cracks or surface defects. The advantage of the plate is that there was the potential to get five tensile bars from each plate so even if crippling defects were present if a large enough section was still good the sample was usable for at least one tensile bar. Since the original large bars were so much bigger there was no room for error and if they had any defects they had to be deemed unusable. Following the tensile bar design in SOLIDWORKS, we transferred the file into the computer-aided machining software Esprit. Below is an image of the basic SOLIDWORKS design downloaded into the Esprit software. Initial design parameters

required the project to solve for tooling feed and speed rates. Since we were working with experimental aluminum alloys we set the parameters for the highest setting for aluminum to make sure we did not create the potential for overloading the tool to the point of fracture [18].

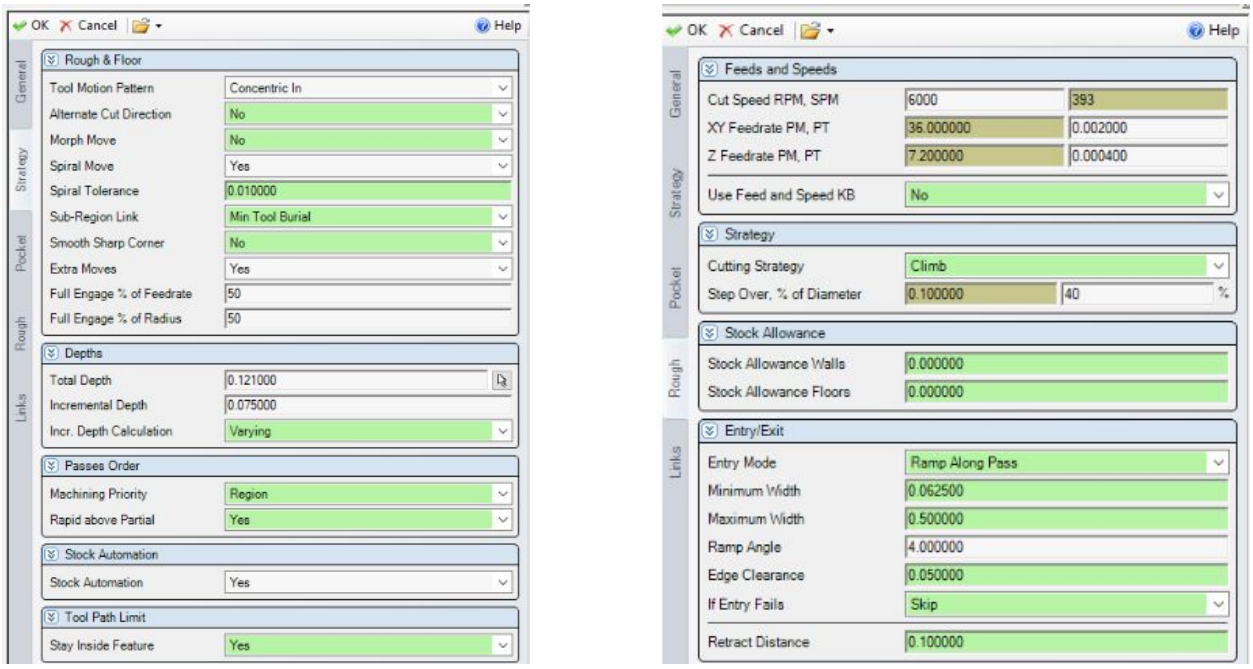

Figure 11: Manufacturing specifications in the ESPRIT program for tensile bar development

The major issue in manufacturing the tensile bars was the low tolerances and thinness of the final product. It was not an option to machine into the vice jaws, made of a structural aluminum, holding the plates in place or even worse accidentally machining the vice. We needed to develop a process that would machine the plate and give us our product without any damage to the vice. The project started with the goal of getting 3 bars from each plate, once we were able to prove our method worked we would then move towards manufacturing more bars per plate. The first issue was properly mounting the sample so that it was perfectly flat to be machined. The cast samples had a rough surface finish and in some places burrs and deformities that kept it from being properly secured. Any form of jiggling or vibration would result in deformed products that were not the same. This led to the first CNC operation of facing off a single side longways to

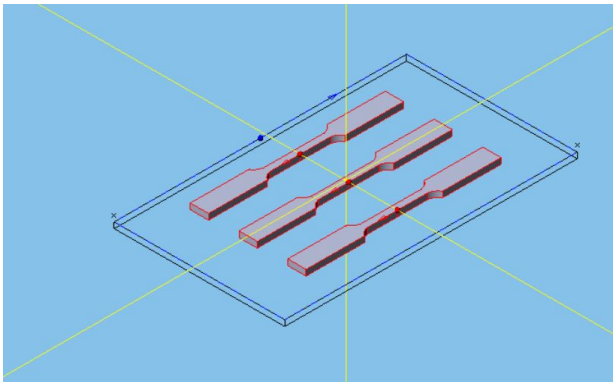

Figure 12: ESPRIT isometric view of the first tool path consideration

give the surface finish needed to manufacture the bars. Following the facing operation, we had to solve the issue of the thinness of the bars, it was hard to have the plate in the vice and safely machine the excess. Manufacturing this way also didn't make sense for getting multiple samples at once because as soon as the parts were finished the tool would have to separate them causing our current fixture method to collapse. It was possible to simply post-process them but that would take too much time and defeat part of the purpose of having them finished in the CNC machine [19].

We settled on fixturing by getting a sacrificial block and fixturing the block to the plate using a high strength tape on the surfaces of the plate and sacrificial block then using a high strength industrial glue on the non-sticky side of the tape to combine our two components. This would then allow for the tool to pass into the sacrificial block and make the three desired tensile bars. Following the manufacturing, the operator could then just remove the bar from the tape, and reface the sacrificial block before they continue with another plate. However, this method was flawed for a few reasons. The glue and tape needed 10 minutes to set and even then it was liable to come off due to the high speeds of the tools and lubrication of the coolant constantly spraying the part. Then there was the issue of always having to resurface the sacrificial block which took more time.

This setback forced us to move back into ESPRIT and re-evaluate our problem. One of the main issues was that the time spent machining especially with the coolant loosening the current fixture method it was not possible to machine three tensile bars at a time. By cutting the plates into fifths we could increase the yield per bar and decrease the amount of time each bar was being machined, however, we would be machining one bar at a time. This could be done

Figure 13: Processing and cutting out tensile plates to be machined in a CNC machine

using a bandsaw to accurately manufacture our bar block. This added step so the use of a sacrificial block had to be cut to save time and instead we developed a parallel bar configuration that satisfied supporting our blocks. Through initial tests with parallel bars, we knew that our piece had to be protruding from the vice .14 inches to clear enough room for the .12 inch -z-direction pocketing operation that shaped the bar.

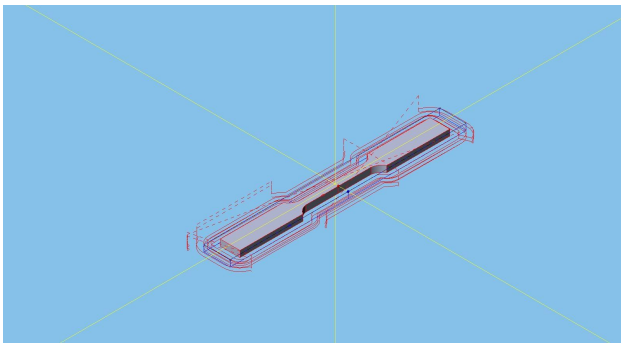

Figure 14: Final tool path guidelines viewed in ESPRIT

By configuring the parallels in the same way we could guarantee its clearance and we didn't have to measure using calipers every time. Although by using the parallel bars the vice configuration would often get filled with metal shavings and would have to be sprayed with the air hose to fulfill the flush-fitting necessary to machine the tensile bars. Then the other issue became that the bandsaw cuts were not always perfectly straight so it became difficult to fixture them even with the bottom face being perfectly flat from the initial facing operation. This led to the conclusion that the sides of the bars would benefit more from being faced as opposed to the back to give the vice flat sides to grip.

This led to the development of the operation side-facer which would see one side of the tensile bar block machined flat which significantly helped in the vice grip on the unfinished part. We were able to develop a tensile bar that only needed the back, that was in the vice during the pocketing operation, faced off. This problem could be solved again with the parallel bar configuration however now the tolerance in the z-direction was .01 inches and required several minutes with the calipers to confirm the correct setup. Following this operation, we had completed tensile bars that could be tested, however, setup time and machining time led to the production of a single tensile bar taking 35-40 minutes to manufacture. The CNC machines could only be rented from 3-4 hours per day meaning through this method only 4-5 bars could be made a day. The project had the

Figure 15: 3/8 inch endmill during manufacturing

potential to create over 200 tensile bars from the plates that had already been cast and as previously mentioned the limitations of the larger tensile bars meant experimentation depending on quicker manufacturing of the tensile bars.

The set up was a large limiting factor on tensile bar development so the project led towards custom soft jaw development. The soft jaws would be screwed into the vice and we could machine them into the shape needed to manufacture the bars by having them held

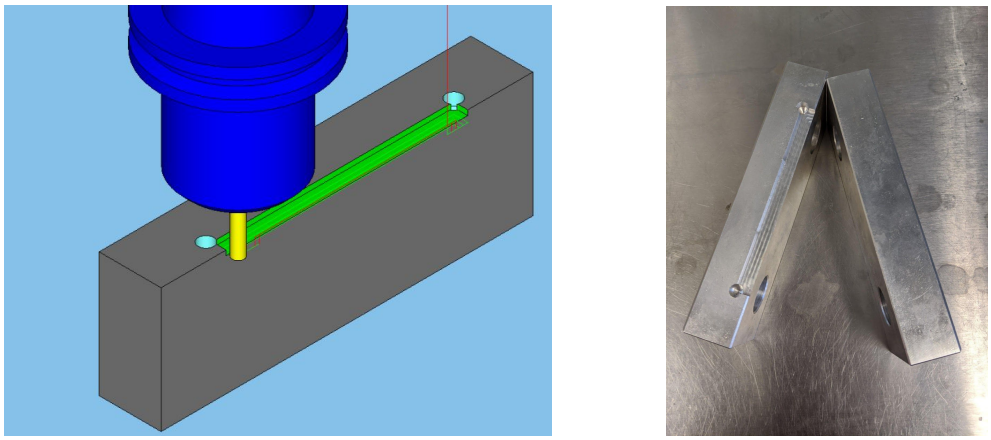

Figure 16: Left: ESPRIT image of the soft jaws simulation being manufactured Right: Finished machined soft jaws

however we wanted. A second advantage is that due to the design of the soft jaws we could guarantee the coordinates of each sample placed in the vice. This meant that we could skip the manual probing of each operation after the first bar cut. Following the design of the soft jaws, the tools for the other operations were changed to increase speed. This included changing the pocketing operation from a Facemill to a 3/8th endmill to decrease the shear forces applied while machining the surface. Now the project had three main operations: the side-facer operation, the pocketing operation, and the rear-facer operation. These three operations now brought the total manufacturing time down to roughly 10 minutes per tensile bar.

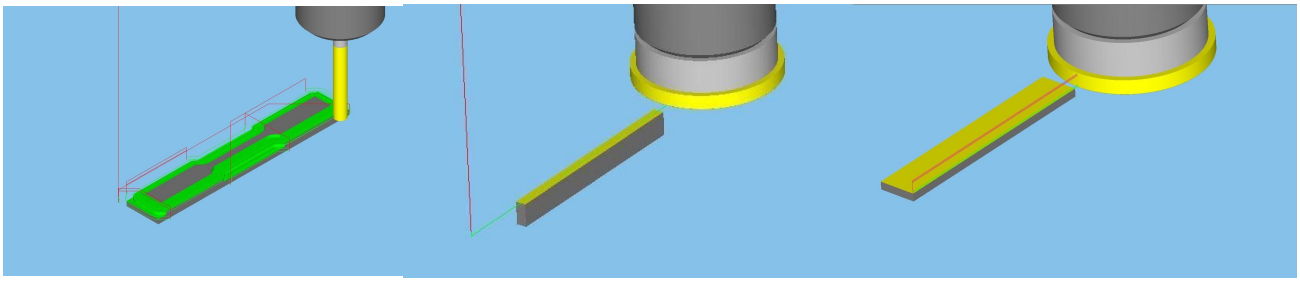

Figure 17: Tensile bar operations (left to right): Pocket Operation, Side Facer, and Rear Facer

4.0. Results

Experimental results following the creation of the small tensile bars in relation to the large. This article will discuss the treatment that the samples underwent post-machine processing before being tested. The details of their compositions and microstructure evolution are also discussed.

4.1. Composition and Casting of a known Ternary Alloy

Following the manufacturing of the smaller tensile bars the project needed to be able to prove that both tensile bars were capable of yielding the same results as the larger tensile bars when they were performing optimally. If the project could prove that the manufactured smaller bars could produce statistically similar results to the larger tensile bars then we could trust the results when testing alloys that could not be cast in the large bar form. Although the development of the five-element aluminum alloy and other compositional alloys did employ the development of the small tensile bars this paper will focus on the heat treatment and experimentation conducted on the ternary alloy dubbed P2. Below are the two composition tests from two separate casts which can be denoted as P2Alpha and P2Alpha1. The composition of the ternary alloy sees twice as much zinc than magnesium in terms of weight percent however in terms of molar percent they are much closer seen as Al-4Zn-4Mg (mol%).

Table 1: Composition test of P2Alpha

P2Alpha	Aluminum	Zinc	Magnesium
No.	(wt%)	(wt%)	(wt%)
1	87.2	9.18	3.49
2	87.4	9.07	3.44
3	87.3	9.12	3.45
4	87.1	9.28	3.51
5	87.1	9.31	3.53
$\bar{x}$	87.22	9.19	3.48

The composition tests were conducted on the OES Composition Testing Machine and share very similar results as can be seen in the two tables [20]. The gas used in the OES composition testing was argon gas. The materials listed here account for over 98.5% of the overall alloy the remainder being trace amounts of various elements including iron and silicon. These trace elements are due to impurity in the ingots the project cast with and is not a negative aspect. This is due to the fact that in the industry the less exact measurements need to be or the less impure ingots affect the desired material properties the more advantageous the material. So low levels of impurity are a necessary part of our compositions. Each row signifies a separate test with an average at the bottom of each table. The repeatability over these two casts was imperative to maintain assumptions while conducting the heat treatments.

Table 2: Composition test of P2Alpha1

P2Alpha1	Aluminum	Zinc	Magnesium
No.	(wt%)	(wt%)	(wt%)
1	87.0	9.4	3.48
2	87.2	9.25	3.42
3	87.1	9.31	3.45
4	87.0	9.4	3.5
$\bar{x}$	87.08	9.34	3.46

4.2. Alloy Development of High Entropy Aluminum Alloys Post-Processing through Heat-Treatment Schedules

The heat treatment schedules for the two casts include no heat treatment otherwise known as as-cast, one-step solutionization and two-step solutionization. The one versus two-step solutionization is simply the difference between being solutionized at a single temperature over a specified duration of time as opposed to two temperatures for different amounts of time. While the effects of precipitation hardening were experimented with in terms of temperature levels and durations the focus of the report will analyze the optimized system of treatment for each schedule. Heat treatments allow for the nucleation of proper phases if manipulated properly and are commonly used in industry to eliminate detrimental phases and features in an alloy. The large presence of secondary phases in differentiating quantities greatly

weakened the strength of the alloys being developed. Using Thermo-Calc® to develop the temperatures to be used and the duration of time at each stage the one-step solutionization saw a significant increase in ductility. While this was impressive it became necessary to follow up the one-step solutionization with two-step solutionization. This again saw the physical properties of the alloy drastically increase. The significance of this discovery in terms of the tensile bars was that regardless of which tensile bar was undergoing the treatment the increase in properties was

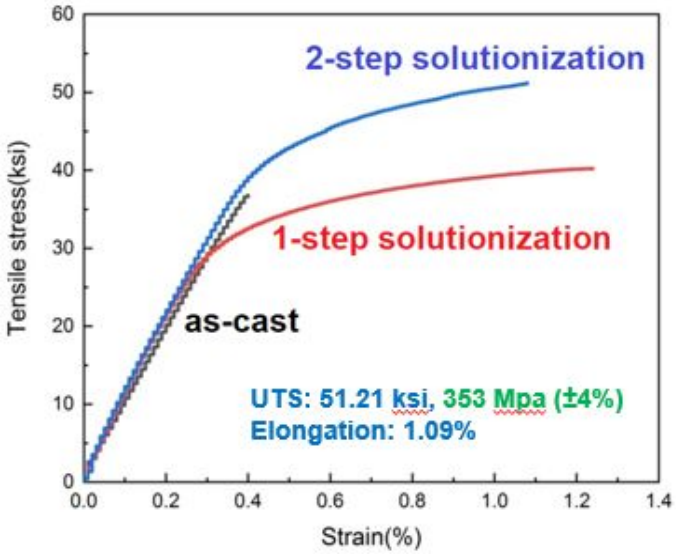

Figure 18: Tensile-Strain graph comparison of three treatment schedules

evident through the tensile tests. In the diagram above we can see the effects of each change. The first step of solutionization sees a massive increase in elongation stretching to three times the elongation in the as-cast sample. However, with this increase in elongation, we see the yield strength decreases slightly and the ultimate tensile strength is very similar. The major change occurs when we observe the results of the two-step solutionization where we can see that ultimate tensile strength, yield strength, and elongation form the greatest results. The transformation of the alloy can even be observed on the microscopic level. Following the fracture of the tensile bars, the results were analyzed. Certain tensile bars could be discarded due to surface defects or heavy deposits of impurities that led to premature failure. The successful tests were taken to have their surface analyzed using high powered optical microscopy, the pictures taken were at 100μm. Upon comparing the as-cast surface with the surface of the two-step solutionization it is plain to see that the two-step solutionization has a far more homogenized appearance. This demonstrates the importance of observation of the nucleation and diffusion of secondary phases in the lattice and the effects of this relationship on

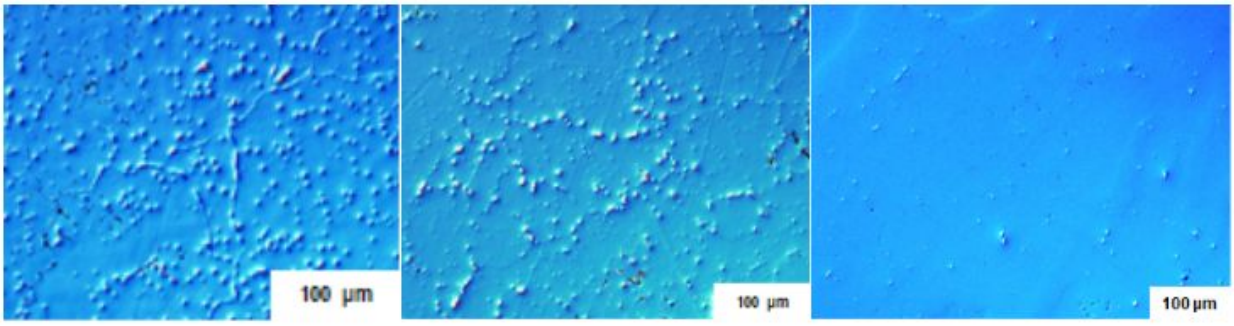

Figure 19: Microscopic view of three samples at 100µm that underwent three separate treatments Left: As-cast, Middle: one-step solutionization, Right: two-step solutionization

the material properties. The difference can even be observed in the results between one and two-step solutionization. Following the manufacturing process the smaller tensile bars needed to perform as well or demonstrate the same improvements and reactions to heat treatments that the larger bars experienced. Below are images of the as-cast small tensile bar test versus the two-step solutionization small tensile bar test. Upon immediate comparison to the above images, it is clear that the small tensile bars do not perform at the same stresses and elongations that the large bars provide. However, the reaction to heat treatment and solutionization follows a similar trend. We can observe that the ductility does increase along with ultimate tensile stress. Possible reasoning for these results will be discussed in the conclusion.

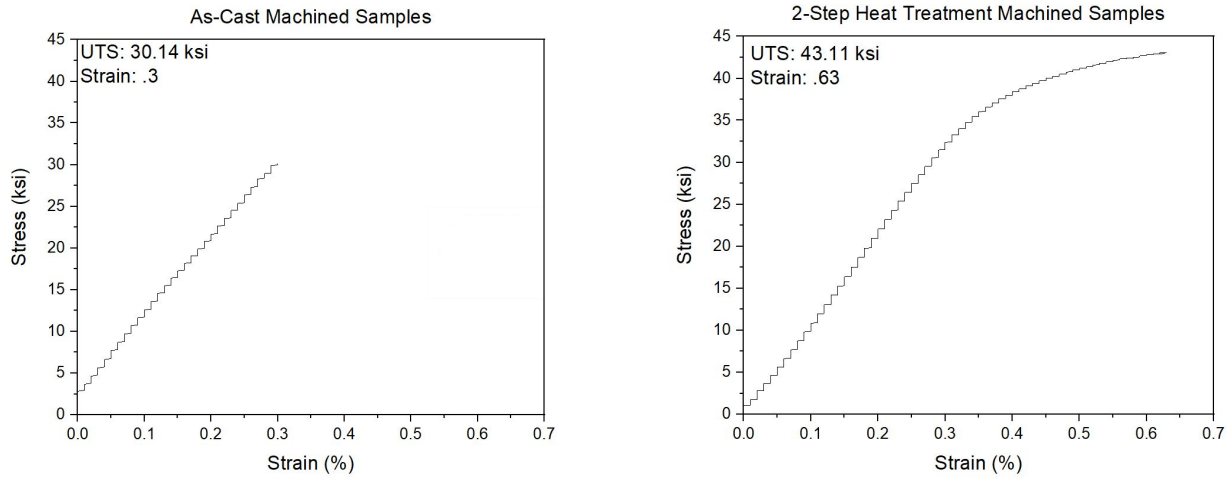

Figure 20: Left: As-cast machined sample graphed on a Stress-Strain graph Right: Two-step solutionization machined sample on a Stress-Strain graph

5.0. Conclusions

The development of the small tensile bars saw several successes that promote it as a possible testing platform that can be used under several parameters depending on the constraints of the tests. The material needed to manufacture the smaller tensile bars is far less than the original bars. The original bars weigh roughly 120 grams each, while 20 of the smaller bars weigh 110 grams. The length of the smaller bars is half the length of the large bars at four

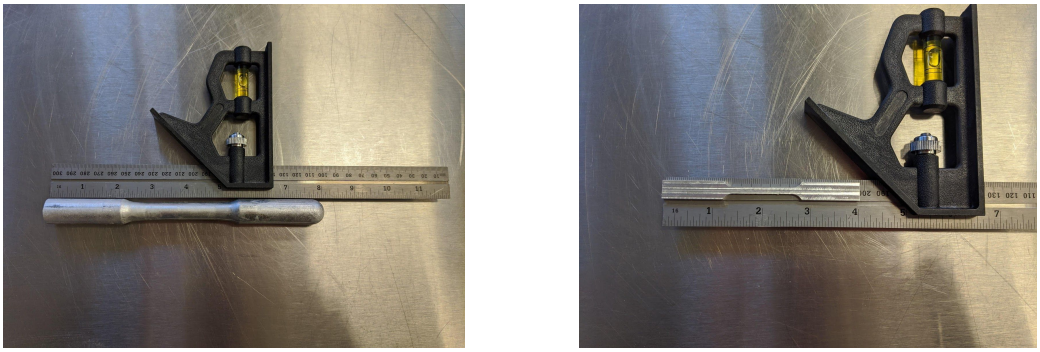

Figure 21: Left: Large tensile bar length Right: Small tensile bar length

inches. Besides the material saving, there is also the increased castability of the plates versus the large bars. The increased cooling rates and small size of the plates means that refined grain structures are formed which is highly desirable and always increases strength. However, none of this would matter if experimentally they did not have similar results to the larger tensile bars. After all the premise of the experiment was to prove with the Al-Zn-Mg ternary alloy that after undergoing the same heat treatment schedule the bars would be capable of pulling at similar strengths and elongations. This would then allow us to forgo attempting to cast the larger bars when castability was in question for a particularly fickle alloy. The results between the two tensile bars are different showing different tensile strengths and elongation. This is a negative aspect of the small bars showing that they cannot pull at equal strengths. This is not a fatal flaw for the small bars because they still show a similar relationship to heat treatments that would allow them to be valuable for experimentation. From their experimental strength, it would be possible to extrapolate the theoretical strength of the material, though this would require further testing to narrow down the correlation between the two tensile bar results. Another important consideration is the small tensile bars have a far higher rate of premature fracture so when considering successful test yield in the future it is important to consider possible failure numbers

and understand that in small batches the small tensile bars may not be accurate enough to justify manufacturing.

Finally, the reason for the small tensile bars lower results is most likely the machining process. The process of manufacturing bars developed to make them stronger may be causing microcracks and defects on the surface of the tensile bar that could be held responsible for their fracture. In order to improve the feeds and speeds will need to be edited going forward to produce cleaner cutting and reducing the chance of failure. Another possible method of weakening could be hot tearing microcracks forming due to the faster cooling rate. These microcracks would directly affect the strength of the microstructure and possibly weaken the sample strength. For alloys that have strong castability, it would be advantageous to rely on the larger bars to avoid the manufacturing process. Although the smaller bars took less material they took a lot more processing before the tensile test could take place. At the very least the inclusion of the smaller tensile bar allows for flexibility in testing a wider range of alloys when the large bars are incapable. This new form of the tensile bar has great potential to increase the range of testing various experimental alloys but its limitations need to be studied and experimented with to optimize its potential as a high entropy alloy testing platform.

6.0. References

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7.0. Appendix:

7.1. Appendix A: Casting Aluminum in steps (Procedure)

7.1.1. Safety

Due to the dangers of working with such high temperatures and molten metal, it was necessary to wear the proper safety gear when operating the foundry. This included making sure not to wear any polyester clothing due to the fabrics melting properties; cotton was the only

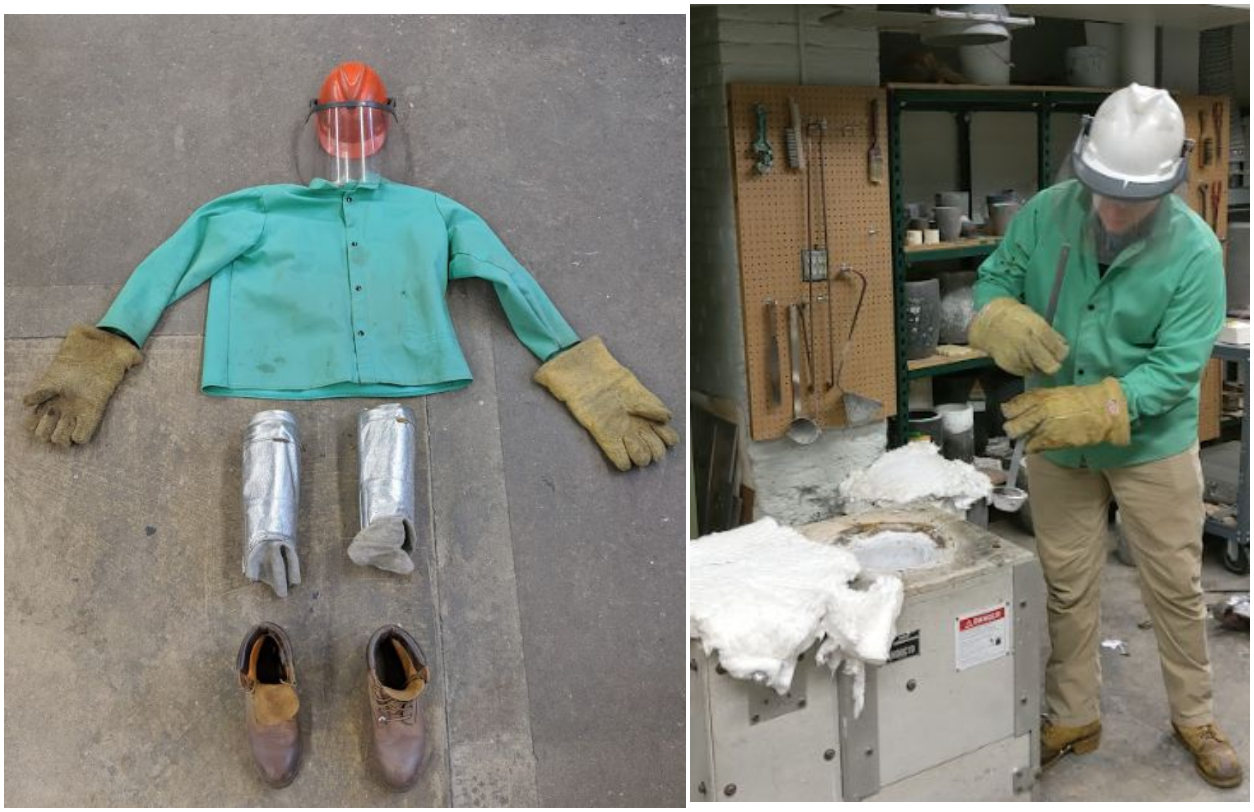

Figure 22: Left: Proper personal protection equipment Right: An operator cleaning impurities from the melt

acceptable fabric for the upper body and pants with jean like fabric. As safe as the lab was made to be, closed-toe steel boots were mandatory because of the heavy machinery present and tripping hazards. Polyester clothing is especially dangerous because it doesn't burn, it will

melt onto the wearer's skin, worsening the potential burns. Even with precautions, if molten metal were to for whatever reason come in contact with the clothing it would only leave half a second for the person to get the clothing or footwear off before being burned. This made it necessary to implement Flame retardant shin guards and jackets for those tasked with the handling of the crucible. Safety glasses and full-face shields were used by all attendants of the cast to protect against potential facial hazards.

7.1.2. Crucible Preparation

The first step in preparation for the cast was cleaning the workspace in the foundry. Crucible preparation is important because any debris left in the crucible may be reactive upon heating or at the very least cause impurity in the cast. Typically, there would be solidified alloys at the bottom of the crucible from the last cast that would need to be scraped up. This remainder is there because there was not enough to continue the previous experiment. The induction furnace, the heating generator for the crucible, does not need to be turned on at this time. The scrap can simply be scraped out of the crucible and recycled. Next, a Boron Nitride spray is painted onto the crucible walls, this will form a non-stick layer with the future melt, so it does not bond to the walls. The heating elements, copper coils, that lie around the crucible are then checked for defects and insulation is stuffed between. Everything must also be completely dry because aluminum is highly reactive to water. The metals necessary for the cast are measured out in weight percent and held on standby. The base metal is then put in its solid state at the desired weight inside the crucible signaling the end to the preparatory stage of the casting process.

Figure 23: Boron Nitride spray

7.1.3. Starting and Managing the Cast

The induction furnace in principle is a high voltage electrical source from a primary coil that induces a low voltage high current in the metal otherwise referred to as the secondary coil. This is the simple explanation for the transfer of energy into the metal. The secondary coil is what surrounds the crucible; this method allows for a wide variety of alloying possibilities with minimal melt losses but is limited in its metal refinement [21, 22]. The type of induction furnace

used in our experiments was a coreless induction furnace capable of working with a 35-40lb melt. The basics of its operation and a picture of the one used in experiments are depicted below. To cast the desired alloy with accuracy, calculations are made using the following equation set 2:

$$\sum_{n}^{0} p * at\% = p_{total} \qquad \frac{\rho * at\%}{p_{total}} = w \qquad \frac{w}{100} = wt\% \qquad (2)$$

To figure out the necessary amount of each element to add to the melt the following equation 3 is used:

$$Total\ mass\ of\ melt * wt\% = desired\ mass\ of\ element \qquad (3)$$

When the induction furnace is first turned on only the base element is inside the crucible in our case the 99.9% aluminum alloy.

When the induction furnace is turned on and the melt has become liquid, we would operate between 760-780 degrees Celsius. This temperature is important to keep the aluminum

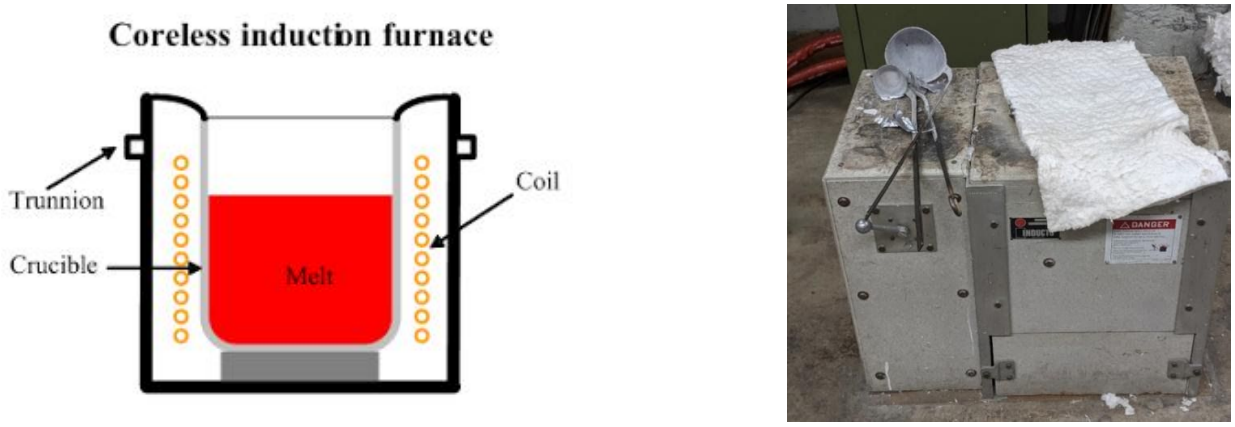

Figure 24: Left: Diagram of a coreless induction furnace [21] Right: The crucible used in experimental casts

liquid and manageable state. If the melt gets too cold its fluidity will be poor making it difficult to pour into the molds and if it's too hot the chemical and physical properties would be altered, and we would not reach the cooling specifications required.

After the melt is completely liquid the other metals are added to the melt, when these materials have been sufficiently melted into the cast a composition test is necessary. The composition test lets us know how close our estimates were during our initial measure. Even though we measured out what we added to the melt because we are testing unknown alloys this second measurement allows us to guarantee more absolute precision. Following the composition tests if the components are found to deviate from expected values after 4-6 composition tests it becomes necessary to add in the missing elements in percentages that will give the desired result. Upon a successful composition test, the melt must then be cleaned. The

WPI Foundry uses argon gas to get rid of potential porosity within the alloys. Porosity is highly crippling to an alloy's strength by pumping argon gas, a non-reactive element into the melt to give any stuck gas bubbles a method of escape. Once the bubbles are cleansed from the melt the alloy is ready to be poured, this is when the mold preparation process will be explained.

7.1.4. Mold Preparation and Pouring

The molds used in this alloy project were permanent molds that were preheated. Although the project desired was to promote fast cooling it would not be advantageous to leave

Figure 25: Left: The large tensile bar mold Right: The furnace where the molds are preheated

the molds at room temperature because if the alloy cools too fast the speed of the shrinkage would cause hot tearing. As such the molds are heated to temperatures lower than the melt temperature to promote a specified cooling rate. The heated mold is placed in the lab space near the crucible and the pouring process can begin. Our operation occurred using three roles: a pourer, a second and a standby to ensure safety and precise pouring.

The pourer has the job of managing the melt temperature with a thermometer, skimming impurities and pouring the molten alloy into the mold. The second helps the pourer manage the mold and detach the cast from the mold to prepare for the next pour. Both positions need to act quickly and precisely under high heat, so a standby is necessary to switch with either position to help battle

Figure 26: Two operators checking melt temperature

fatigue and keep the experiment running smoothly. In the case of multiple molds being used at once, the standby can act as a second or a pourer depending on the demand of the experiment. After the pourer has lowered the crucible melt to a level that can no longer sustain the demand of a test sample then the induction furnace is turned off and the cleaning process commences.

7.2. Appendix B: Sample Preparation for Microstructure Study

Sample preparation for high powered microscopy was exceedingly precise because of the high standard of the machines required to achieve accurate results. First, a broken test sample is taken and cut into a smaller cylinder at the point of break using the Buehler machine. Then the small cylinder-shaped sample is placed with the flat side down in the resin molded and sealed with a plastic powder. The resin molder heats forms and applies pressure to the plastic coating around the sample. The resin molder makes a manageable plastic covering around the sample so that the operator can avoid touching the sample face potentially smudging or scratching it. Finally, the sample must be polished and is placed on the wheel below on the

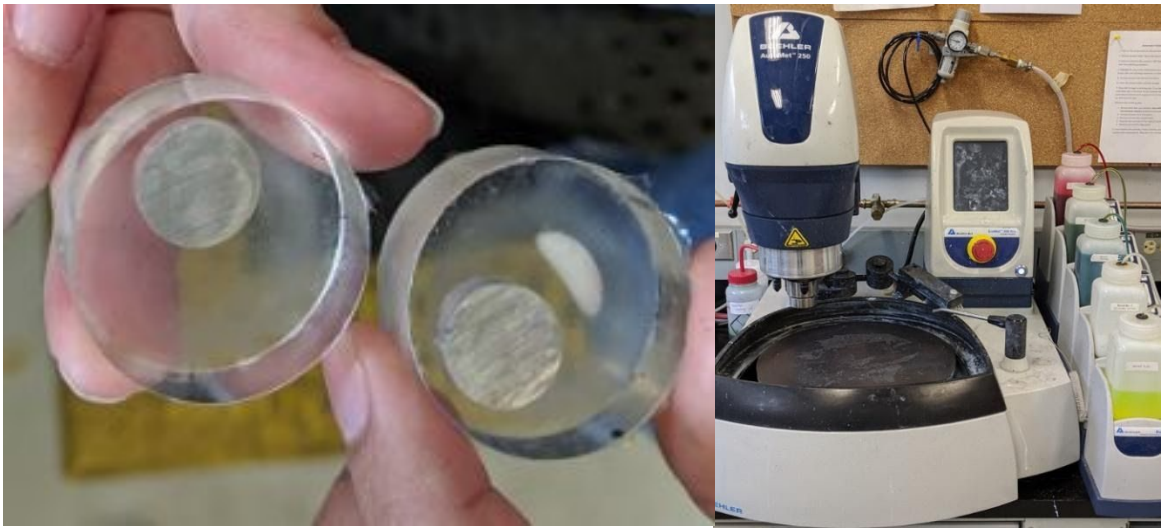

Figure 27: Left: Polished samples ready for microscopy imaging Right: Buehler Ecomet 300 Pro

Buehler Ecomet 300 Pro. The black wheel then has a grinding mat placed on it and the lubricants on the right then grind the sample's surface to finer and finer tolerances. The red lubricant grinds down scratches to the length of nine microns to the white lubricant that grinds the scratches down to less than one micron. Each lubricant must be used with its grinding mat

to continue the refining process. If a lubricant from a higher grade is used on a finer mat that mat can no longer be used. After each lubricant is used the wheel and sample must be washed with water and the mat must be replaced with the next grade to be used. Once the sample has been ground with the lowest lubricant it is washed with acetone to keep it from getting smudges or watermarks. The sample is then brought to the high powered optical microscope and the optical sample analysis can commence.

7.3. Appendix C: Tensile Testing

7.3.1. Safety

When operating the tensile testing Instron Machine it is important to be cognizant of the potential danger upon the fracture of the dog bone samples. Although the environment is controlled and that most of the time it can be observed that there is a clean break into two pieces when experimenting with unknown alloys all safety precautions must be considered. Due to this potential danger, all operators were required to wear safety goggles when operating the Instron machine regardless of what stage the testing was in.

Figure 28: Safety glasses

7.3.2. Tensile Testing Machine

Tensile testing was the only method this project used for evaluating the tensile strength of the experimental high entropy alloys. The experiment saw the use of a few different types of tensile bars with different post-processing and heat-treatments. The tensile testing machine that we used in this experiment was the Instron 5500R. This particular model is capable of pulling up to 50,000 lbs of force between the two clamps shown in the image to the right. The bottom arm stays in a static position and holds the sample in place while the top arm slowly increases the force of the pulling motion until the part fractures. When operating, the

Figure 29: Instron 5500R tensile testing machine

process begins at a computer monitor setting the parameters of the test such as test restrictions and sample dimensions. The Sample is then loaded into the machine being inserted into the top clamp first. Although, the operating speed is a slow continuous pull when setting the sample the clamps are set to move at a higher speed to save time. The top clamp is then lowered until the sample can then be locked into the bottom clamp and a strain gauge is attached to the neck, or thin band, of the tensile bar. The clamp speed is then set to a much lower setting, followed by a zeroing of the strain gauges sensors and a safety check to make sure the operation of the machine is ready to commence. Once the test has begun the machine automatically tightens its grip on the bar as it begins to apply low tensile loads, once the bar has been sufficiently clamped the machine will be increasing tension at a steady rate.

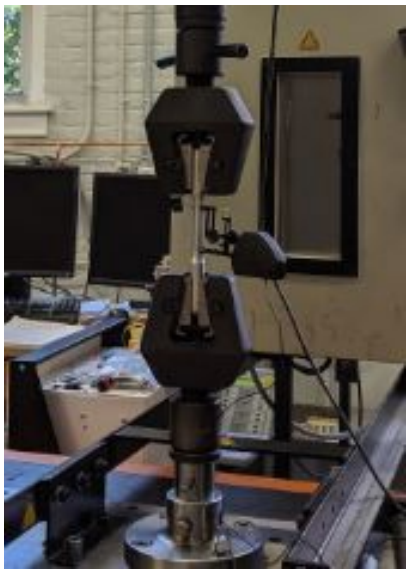

Figure 30: A readied tensile bar sample with a strain gauge at the predicted point of fracture

The advantage of our machine was it was capable of showing data in real-time and the point was the yield strength was reached on the graph and could be seen by the operator during the experiment. After the point of fracture, the Intron stops itself and the operator clips the irregular points in the data where the strain gauge reacted to the fracture. If the fracture was outside of the necking area that means the sample was defective because the tensile bar is designed to have its weakest point at the neck. Following the strain gauge check, the operator manually measures the modulus of Elasticity and compares it to the program generated solution. The data for each pull is then saved and graphed for interpretation with other pulls.

7.4. Appendix D: Optical Emission Spectroscopy (OES) Composition Testing

When casting composition needs to be nearly exact to weigh the benefits of the cast alloy accurately and accurately analyze the scientific results. Even trace amounts of elements can have drastic impacts on the alloy's properties. When the initial cast is weighed out the operator is working with large ingots that may be hard to cut into exact weights, so it becomes somewhat of an estimate on the first try. In our case when you add the secondary materials, we

do it in small pellets and shards and then measure after the melt has become significantly liquid. The induction furnace takes care of most of the stirring and mixing itself due to its heating properties, so it is only necessary to wait for the melt roughly 15 minutes before the first composition test. A small pour is then conducted into a permanent mold that forms the alloy into an optimal testing shape. The composition sample must then have its bottom ground in a belt sander to ensure that it is sufficiently flat. The sample is then taken to the OES composition

Figure 31: Optical Emission Spectroscopy machine used in composition testing

testing machine to analyze the alloy's composition. The OES composition machine uses an Argon laser and shoots a spark that vaporizes a small amount of the material sample. The discharge from the sample gives off a unique chemical signature that can then be interpreted and an elemental breakdown becomes possible. Above the OES composition machine can be seen.It is important that the point where the sparking occurs is cleaned after each firing and the sample is placed flush against the firing location to avoid outside contaminants or

Figure 32: Composition sample after spark testing has occurred

particulates from corrupting the data. The tools used to clean the laser are specific to aluminum alloys and cannot be used with any other alloy to help prevent contamination. 4-6 tests are conducted and an average across the findings is found because at the level of specificity the OES machine is operating at there may be deposits of slight bias towards certain results. If the composition is way off from estimated values, it may be necessary to cast a new composition sample which could happen if not enough time was given for the melt to homogenize. After the results are acceptable any deviation from the desired weight percent is accounted for by adding more material to the crucible and re-testing the composition with another sample. It is important not to add the tested composition samples back to the melt to avoid the contamination of the melt due to the sample's exposure to other materials from its pre-testing processing.

7.5. Appendix E: Computer Numerical Control (CNC) Machining

7.5.1 Safety

When operating with the high velocities and rotational speeds of the CNC machines it is important to follow dress and safety protocols. Tight but operational long sleeve shirts and pants are recommended for operation. Closed-toe shoes are mandatory and laces must be tied at all times in the machine shop area. Safety glasses are provided and necessary for all in the shop even if the person in question may not be operating anything. Necklaces and neckties are not allowed in the shop because of the potential for it to get caught and drag the operator into the machine. If clothing does get caught and the person is at risk there are safety scissors around the shop that can be used to cut the caught person free. All hair must be tied up and out of the eyes of the operator. The CNC door should remain closed during the duration of its program if the door is opened the operation will stop however if something is going wrong this should not function as an emergency stop. There is an emergency stop button on the Haas if the operator sees some sort of malfunction or potential hazard the button can be pressed to shut down the whole operation.

7.5.2. Operating the Haas CNC machine and Procedure

Figure 33: Operator manually inputting facemill into CNC machine

CNC machining was a large part of the experimental process for the tensile bar manufacturing. This section will cover the operation of the Haas CNC machine used to manufacture the tensile bars. The machining area is first inspected and cleaned of previous material and debris that could be sticking to or piled up in the tool operation area using the air hose or coolant hose. The coolant levels are then checked and replenished if necessary. Following the cleaning of the tool operation area, the Haas is booted up and the vice is screwed into place. The tools can then be entered into the machine by hand and the tool path program can be loaded into the HAAS. The calibration of the tools must then commence which entails all of the tools being individually tested on a sensor to make sure they are operating properly and the machine knows exactly how they are fixtured. The tooling program is then simulated on the operating screen to make sure there are no crashes or defects in the program. The raw material that will be machined can then be measured and fixtured into the vice. It is important to make sure that the program operation does not run deeper or farther than the part of the material that is exposed by the vice. The feeds and speeds of the tools during each operation must then be checked cross-referencing the material properties with the machining capabilities to avoid tool breakages and sample destruction. The probe tool is then loaded into the spindle head. The operator then selects a program and enters the offsets to best measure the dimensions of the sample. Even if the same program is being run on multiple samples, each sample must be probed before each operation as a safety precaution unless it can be guaranteed that the sample has the same dimensions and is fixtured in the same coordinates.

After the probe has finished its operation the tooling operation can commence. On the first tool pass before the material is touched the operation is halted and the distance to go coordinates are looked at and verified as reasonable before resuming the operation. If the face mill is being used unless the operation is very long the coolant is turned off, with every other tool the coolant is running for the duration of their use to ensure the tool doesn't overheat and either deform or fracture. Following the last operation after the spindle head returns the tool to the

tooling rack and the machine has returned to the home position the door to the machine can be opened and the machined sample can be retrieved from the vice. Post-processing of the sample may include sanding or deburring parts that the CNC machine creates to get a better surface finish. Following the use of the machine, the inside must be cleaned and shavings that have been caught need to be scraped out of the coolant area into a waste bin. The Haas can then be powered down and the vice can be returned to storage.

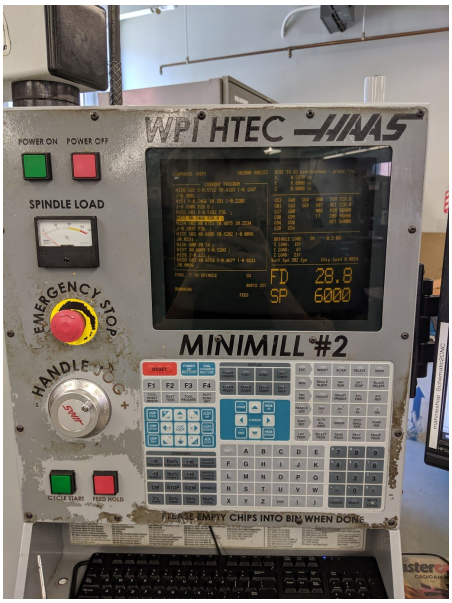

Figure 34: HAAS minimill operation display during tensile bar manufacturing