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# FINAL DEGREE PROJECT

**TITLE OF FDP:** Experimental investigation of phase equilibria in the Zr-Cu-Al system at 500° C

**TITULATIONS:** Bachelor's degree in Airports Engineering, Bachelor's degree in Air Navigation Engineering

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**SUPERVISOR:** Yee-Wen Yen

**DATE:** June 22<sup>nd</sup> 2016



**Título:** Investigación experimental del equilibrio de fases en el Sistema Zr-Cu-Al a 500° C

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**Fecha:** 22 de junio de 2016

## Resumen

El peso es uno de los factores que más influyentes en el rendimiento de un aeroplano. Para la mejorar los aviones del presente es crucial encontrar nuevos materiales para los elementos estructurales de los aeroplanos y reducir el peso. Las aleaciones de Al son comúnmente utilizadas dado que son aleaciones con relativa baja densidad y buenas propiedades mecánicas. Por este hecho en este estudio se ha elegido el sistema ternario Zr-Cu-Al. Para este sistema no existe acuerdo sobre la forma de su diagrama de fases isotérmico. Por eso el objetivo de este estudio es el de tratar de añadir un poco de luz en esta materia, encontrando otra solución del sistema y ayudándonos a entender mejor el propio sistema.

En este estudio se determina la sección isotérmica del sistema Zr-Cu-Al a 500°C.

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## Overview

Weight is of a fundamental importance in the performance of aircraft. Finding new materials for the structural elements of an aircraft that are lighter while giving the performance needed is crucial. Al alloys are commonly utilized materials because of their relatively low density and good mechanical properties. This is why the Zr-Cu-Al ternary system has been chosen in this study. There is no agreement on the shape of the isothermal phase diagram of this system. This study has the goal of adding some light on this matter, by finding yet another result that can help us understand better this system.

In this study the isothermal section of the Zr-Cu-Al system at 500 °C is experimentally determined.

I would like to thank the help, the dedication and the tutory of prof. Yee-Wen Yen, as well as his welcome with open arms in his laboratory. Thanks to all our labmates for making of our stay on the laboratory a more complete and satisfactory experience, since without them we could not present such a complete project. To all our friends in Taipei for distracting us in our down times. And lastly but not of least importance to all my loved ones who have supported me unconditionally from home, being the pillars that hold me in the distance.

Thank you everybody

Eduard Esquerdo Estalella

This work would not have been possible without the help of many people. It is impossible to mention them all, but I will try anyway. Firstly, prof. Yee-Wen Yen with his supervision and help has been crucial, but above all I would like to thank him his somewhat flexible attitude towards our plans to visit Taiwan. Thank you from one globetrotter to another. Without the help of Yung-Chin, Gita, Dave and the rest of our labmates we would without a doubt never been able to perform the experiment, and for that and your friendship I thank you. Irene, both from home and Taiwan has been the pillar that has kept my spirit up in the blue days. Without her everything would have been much more difficult. Finally, a great thanks to all my friends in Taipei and in Spain, and to my beloved ones for their support.

Thank you very very much

Joaquim Poncet Manso

*“Heaven for climate, Hell for society.” – Mark Twain*

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## CHAPTER 1. INTRODUCTION

The aim of this study is the experimental determination of an isothermal section of the phase diagram at 500° C for the Zr-Cu-Al system. This system has been selected because of its potential use in aircraft manufacturing, given its relatively low density and potentially good mechanical properties.

Weight is a critical factor on the selection of the materials when designing an aircraft, because every gram of weight will need a gram of lifting force in order to fly. On the other hand, the chosen materials also need to have a very specific mechanical performance, both to tension and compression, and be resistant to fatigue, among other requirements. Satisfying this two important conditions at the same time is not easy, and often compromises have to be taken when either performance or payload requirements are high. Because of this, the need for suitable light materials is great in order to improve the performance of the next generation of aircraft.

On the first chapter of this study the introduction is laid out, and the motivation of the authors, the environment in which this work took place, the background information used throughout the process and a brief explanation of the physical principles at game.

On the second chapter the experimental procedure that is followed can be found, that is, the weighing of the pure materials, the melting of the samples, the encapsulation of the samples, annealing for six weeks in the furnace, the cutting, mounting and polishing, and finally the analysis using XRD, SEM and EDS to obtain the results of this study.

On the third chapter the results obtained from experimentation can be found, as well as its pertinent discussion, the phase analysis, and the isothermal section computed from the obtained data.

On the fourth chapter we explain the conclusions of our investigation and the whole final degree project (TFG from now on, for its Spanish name). And our point of view about this topic, the results and the experience. Because we understand that this is not only a material investigation, as half of this TFG is the experience to work in a laboratory, in another culture, with other methods of work, with different goals. And all together make this TFG a really interesting thing for us.

### 1.1. Motivation

Materials Science is a very interesting topic, especially when studying the materials that may be used in the future to build amazing feats of engineering, such as aircraft. This has had a great weight on our choice of topic. The results that we obtain may be useful for future researchers in order to find materials fit for aeronautical applications, and that thought is very rewarding.

Another reason that pointed us to this research topic was the possibility of performing this study in Taiwan. We were very interested in the experience of studying abroad, and this seemed to us as the perfect opportunity to do so.

However, one of the most important points was our supervisor Yee-Wen Yen because since the first contact with him, he was open and interested with us. His support was the final push that we needed to take the decision of choosing this topic.

## 1.2. NTUST

The National Taiwan University of Science and Technology (NTUST or Taiwan Tech) is a public technological university established in 1974 in Taipei, Taiwan. It is ranked as Asia's 10<sup>th</sup> best institute in science and technology by the *CNN's* special report *AsiaNow*. NTUST is actively engaged in various kinds of exchange programs, and has signed cooperative relationship agreements with 181 academic institutions on five continents throughout the world.

Taiwan Tech enrolled about 10,000 students (graduate and undergraduate), and employed about 400 full-time faculties and about 300 staff members in 2013. The university's 14 departments and 24 graduate programs are divided into the following 7 colleges, College of Engineering, College of Electrical Engineering and Computer Science, School of Management, College of Design, College of Liberal Arts and Social Sciences, College of Intellectual Property Studies, and Honors College.

Because of its privileged location in Taipei, and its renowned reputation as a technology institute, when we were given the option to study in Taiwan Tech, we quickly realized that we should take advantage from this opportunity and started the procedures in order to perform there our exchange program. We received a lot of support from the different bodies of NTUST, and with their help we have been able to learn from them, for what we are very thankful.

## 1.3. Background

In this section we want to explain all the information we used as a part of our initial data to start to computing our own results or as reference from previous studies. We have two different types; binary phase diagrams and isothermal sections result of previous investigation. We use the result of isothermal section as a reference. So we get an idea about how should our results look and this is useful because we can work faster knowing what we need to obtain.

We use the three binary phase diagram that make the three combinations of our elements. We use them because the phases at 500° C that appears in that diagrams will be the same as the walls of our diagram.



### 1.3.1 Binary Phase Diagrams

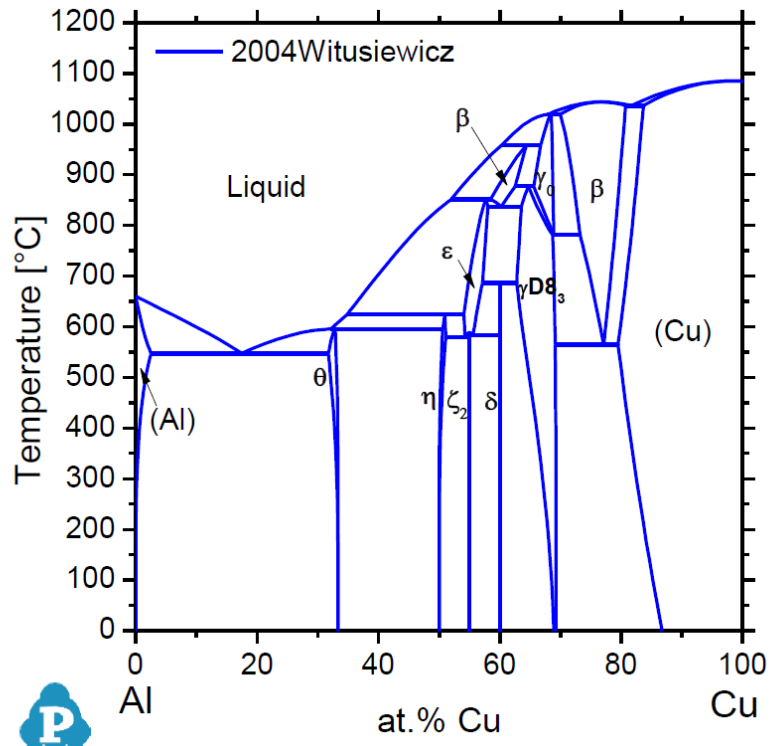


Fig. 1.1 Al-Cu binary phase diagram published by Witusiewicz in 2004 [9]

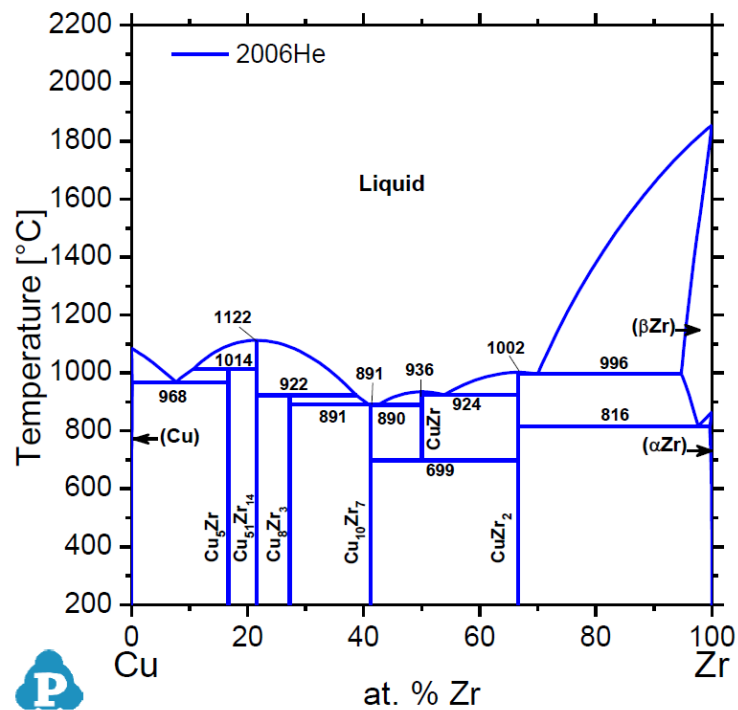
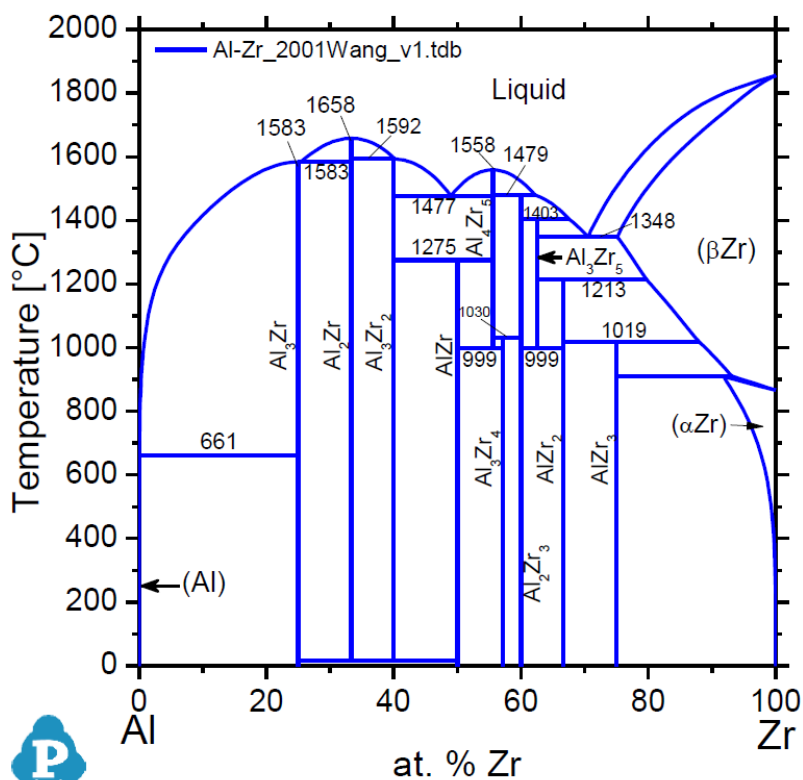


Fig. 1.2 Cu-Zr binary phase diagram published by He et al. [10]



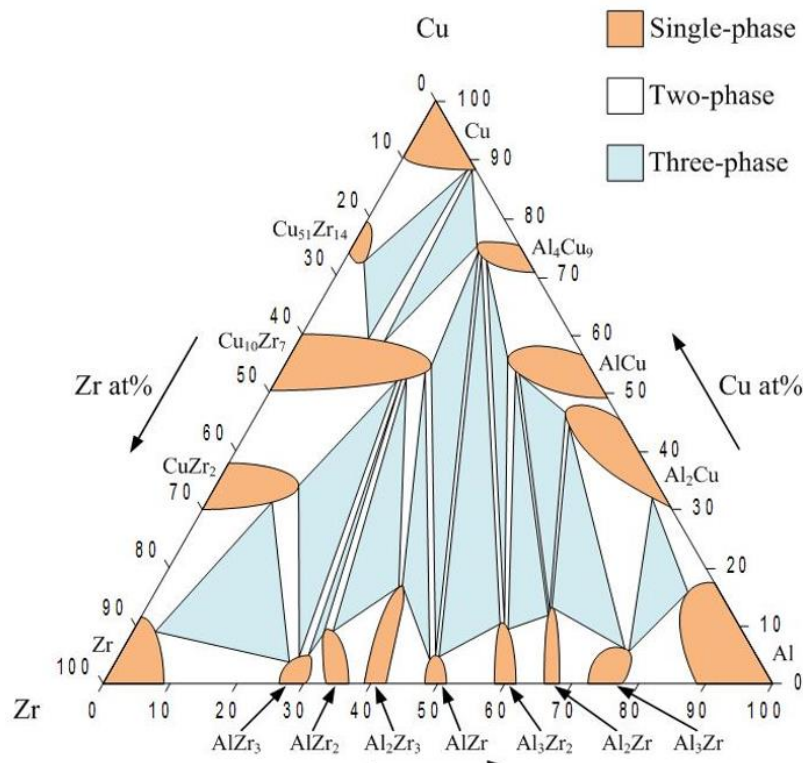
**Fig. 1.3** Al-Zr binary phase diagram published by Wang in 2001 [11]

The binary phase diagrams used were selected after reading the reference documentation, especially that of Hsiao under Yen [2], and assessing for each of the pairs of elements which phase diagram was the one that fit us more. In the case of Cu-Al, all the reference agreed greatly on the shape of the diagram, and there was little doubt on which one to use. On the other hand, the Cu-Zr diagram took a much greater process, since as many as 8 different diagrams were found in disagreement with one another. In the end, the one used was chosen after finding the results of this system, and then choosing the one that best agreed with the found phases. The same is true for the Al-Zr binary system.

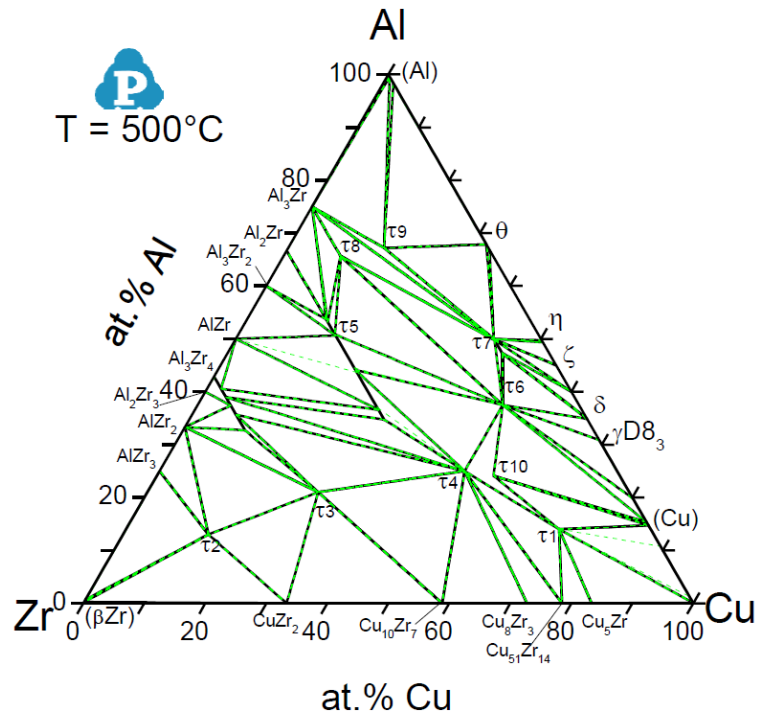
### 1.3.2 Previous Isothermal Sections at 500° C

The reference isothermal sections used in this work were obtained from both previous publications and previous studies performed at professor Yen's lab. Also, the study published by Tretyachenko [1] is a review and addition of a number of other studies, and because of that it was particularly useful. Many other documents were used as reference, but the ones showed below were those that displayed a full isothermal section at 500° C for the Cu-Zr-Al system.

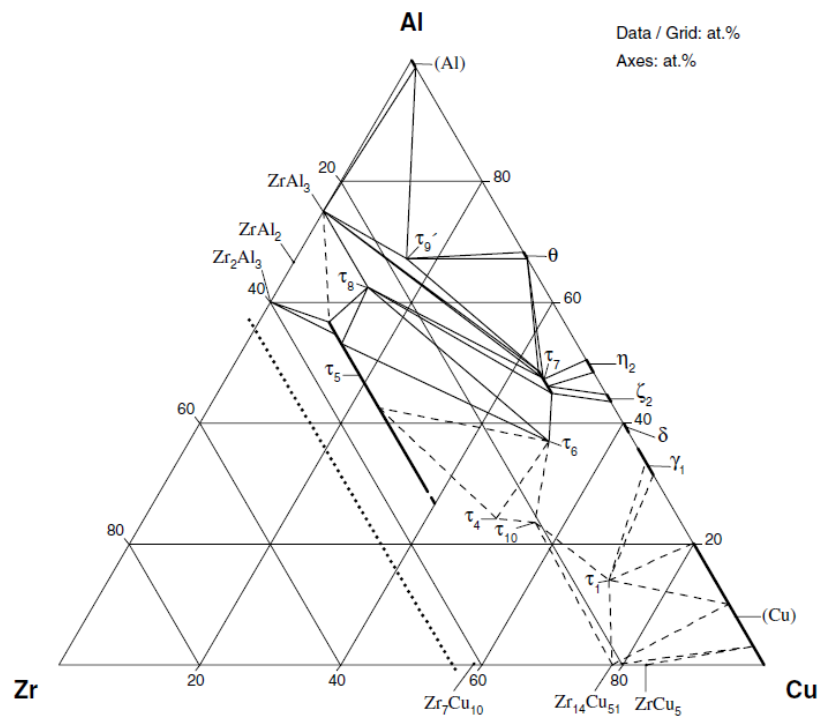
It is notable to mention that our reference showed contradiction on the existence of ternary phases. Because of that, we were particularly careful when assessing their existence. However, most of the publications we had access to confirmed the existence of the *Tau* phases.



**Fig. 1.4** Al-Cu-Zr isothermal section phase equilibria system at 500° C experimentally found by Chen in NTUST under the supervision of professor Yen in 2015 [4]



**Fig. 1.5** Al-Cu-Zr isothermal section phase equilibria system at 500° C computed by Hsiao using CALPHAD in NTUST under the supervision of professor Yen in 2015 [2]



**Fig. 1.6** Al-Cu-Zr isothermal section phase equilibria system at 500° C published by Tret'yachenko in 2004 [1]

## 1.4. Physical Principles

In this section we explain and understand the physics behind our experiment. The most important things to understand perfectly why and how all the phenomena happens will be explained.

First of all we need to know which type of system we are dealing with. The system is a meta-stable. The system gets to the meta-stable point when we quickly cool down the samples after the annealing, and enters a stable point, but not the lowest-energy stable position. That's why the system is meta-stable. This implies that care should be taken with the external supplies of energy because if this supplies are bigger than the activation energy the system will get to the lower energetic stable position and change the results.

The alloys can have a really different atomic structure, every different atomic structure is a different phase. For every composition and temperature the alloy will derive to the most stable phase or keep the same if the previous phase is the most stable. This structures make crystal alloys. Every single crystal alloy has its own mechanical properties. However some alloys do not have a structure, this type of alloys have the name of amorphous or bulk metallic glass. This type of atomic "structure" doesn't have any type of structure so the bonding of the atoms is practically random. This disorder implies different mechanical properties, and some of some of them make this type of materials very interesting.

After explaining this we need to explain how to obtain the crystal and glass alloys. To explain the process we first have to introduce the T-T-T diagram. This diagram show the relation between *Temperature*, *Time* and *Transformation* during an a continuous cooling starting on the melting temperature. If the cooling rate is fast enough the alloy will never enter the crystal region and will therefore stay a glass. Otherwise, if the rate is too slow, the alloy will enter the crystal region and start to move the atoms to the most stable structure. Our case is an example of the latter, as we cool the samples slowly, so we obtain a crystal alloys.

Now we know that the samples present structures of mixed composition. But after the melting and the cooling process the structure is the most stable structure at room temperature. However, for the experiment we want to find the stable structures at 500° C. To achieve that state we put the samples in a furnace at 500° C enough time for all the samples to finish the diffusion process, because the phases at room temperature and 500° C are different so the atoms move to the new lowest-energy phase. This annealing process needs time, so to ensure that all the samples are in the stable state at 500° C the furnace time needs to be long enough.

After this we want to explain why we cool down fast our samples after the annealing process. This was done because we want to learn about the stable phases at 500° C. So if we do not cool the system quickly, the atoms will have energy and time to move and organize to the most stable point at all

temperatures until arriving at atmospheric temperature. So doing this we keep the phases at the 500° C equilibria state.

Another important matter is the Gibbs' phase rule. This rule was proposed by Josiah Willard Gibbs in 1875, and explains the relationship between the number of elements ( $C$ ), the number of phases in the sample ( $P$ ), how many freedom degrees does the sample have ( $F$ ), pressure and temperature. This rule is important in our study because it shows us how many phases should appear in each sample. We need to explain that we put all the samples in the same conditions, this conditions were the same temperature and pressure. So all the samples have been under the same temperature and pressure during all the process so we can ignore this two variables and therefore make 0 the 2 in the formula. Therefore, we have  $C$ , which is 3 all time so the only variable is  $P$ , or how many phases appear on the sample, in order to determine the number of freedom degree existant in the region.

$$F = C - P + 2 \quad (1.1)$$

## CHAPTER 2. EXPERIMENTAL

In this chapter the complete experimental procedure that has been performed will be thoroughly explained. During the whole process, a number of steps were followed, and several tools and machines were used in order to achieve the results. All of this procedures were new to us, and because of that, every new tool and every new step needed a learning process until its proper implementation.

From the separated pure elements to the analyzed samples, a long process has taken place, and it will be broken down in three main sections; Sample Preparation, Furnace Annealing and Sample Analysis. This division makes sense in a double basis: it separates both the different phases of the procedure in a natural way and in a chronological way.

### 2.1 Sample Preparation

In this first section, the process from the separated pure materials to the encapsulated samples ready for the furnace will be explained, including the weighing, melting and encapsulation of every sample.

#### 2.1.1 Preliminar Calculations

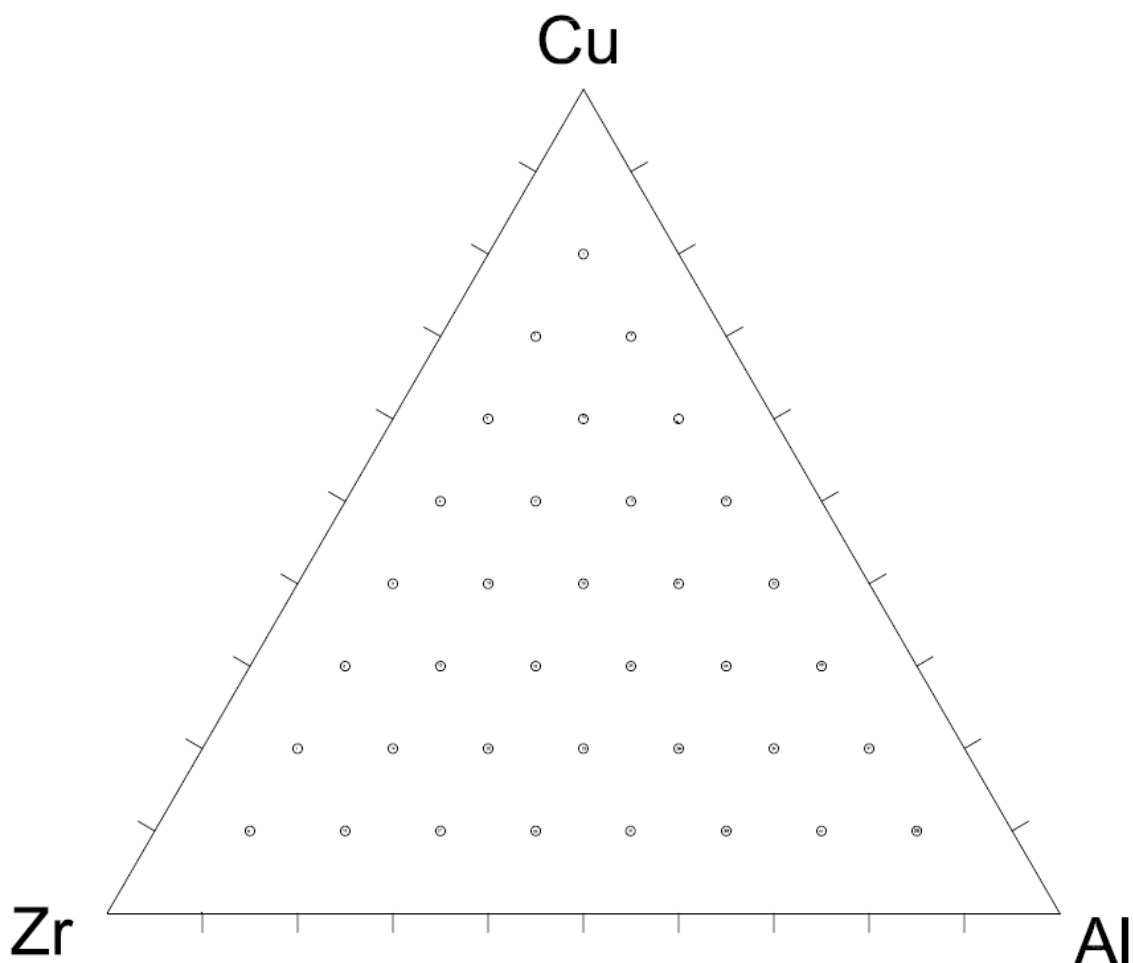
Before starting the experimental procedure, we needed to know exactly how much of every material would be needed for every sample. It was decided that samples would weight 1 gram each, because it is a big enough amount of material for analysis, and small enough for it to be easy to treat and process.

A table with the atomic ratios of the 36 samples was provided by Professor Yee-Wen Yen (see **Appendix I**), and from that table and knowing the total mass of every sample it was possible to compute the weight percentage (and therefore the mass) of each material in every sample. This were the formulas used for calculating the copper weight ratio of a certain sample given the atomic ratios of said sample:

$$wt\%Cu = 100 \frac{P_{Cu}}{P_{Cu} + P_{Zr} + P_{Al}} \quad (2.1)$$

Where  $P_{Cu}$  is a constant and  $A_{Cu}$  is the atomic mass of copper. The same process was followed for the three components in all samples, and a table was produced with all the results (see Appendix I). Because the total weight of every sample in grams was 1, the numerical value of the weight ratio and the mass of

an element in a sample are the same. This is why this table was used without further calculations to weigh the pure materials that would be used for every sample.



**Fig. 2.1** Sample disposition on the isothermal section

### 2.1.2 Pure Materials Weighing

Once the weight of each material needed for each sample was known, it was possible to proceed to the weighing. This was done using a Shimadzu AUX 220 analytical balance, and with a tolerance of +0.05 g and -0.01 g. The source pure materials had 99.9% of purity at least.

In order to achieve this level of precision pieces of pure materials often had to be cut with manual tools, because the pieces were otherwise too big. This took more time and effort, meaning that the whole weighing process took place in a one-week period, and after that we could proceed to the melting of the samples in a single piece of material.



### 2.1.3 Arc Melting

The melting procedure is one of the most important parts, because in this phase of the process, it is very easy to make a small mistake that could render the sample unusable. This is probably the most complex part of the whole procedure, and as such thorough care was needed.

The following will be a description of the procedure followed in order to melt a single sample:

The first step was to clean the pure materials to get them rid of any possible residue such as oxide or grease. In order to do that, they were dipped first in acetone ( $(\text{CH}_3)_2\text{CO}$ ), that would remove any trace of grease proceeding from hands. After the acetone bath, the pieces were dipped in hydrochloric acid (HCl) with the aim of eliminating all oxide traces from them, and finally they went through an alcohol bath in order to eliminate traces of acetone and hydrochloric acid. Every 6 samples, the bath substances had to be renewed in order to keep them clean, especially in the case of HCl and Alcohol.

On addition to cleaning the pure materials the copper crucible also needed to be cleaned. To that purpose it was grinded with several sandpapers of different grain, starting at 600 and going down to 4000. Once it was grinded and all possible remains of previous uses had been eliminated, it was polished using industrial metal polish and a paper wipe. Finally, alcohol was used to eliminate the metal polish and only then the crucible was used. This complete procedure was performed after every 3 samples, and between every other sample only the polishing and alcohol part was performed.

Once both the pure materials that were to be melted together and the crucible were this would be done were clean, the pure materials were placed on the crucible. This was done in such a way that the first material the arc would touch, and therefore melt, was the one with the highest melting point, with the aim of preventing the possibility of a solid core. In this fashion, the Al was the material that was placed in a central position, followed by the Cu and finally all of this was covered with the pieces of Zr.

With the pieces of materials placed on the crucible in this manner, the crucible was mounted on the arc melter, and the chamber was then hermetically isolated from the environment. Then the air in the chamber had to be replaced with Ar, in order to be able to melt the metals in a non-reactive atmosphere. In order to replace air with Ar, a vacuum pump was used to extract the air while Ar was pumped into the chamber at a low pressure. This ensured that after some minutes the pressure in the chamber was really low, and when then the pump was shut down, the argon pumped in the chamber slowly raised again the pressure. In order to prevent air from entering the chamber due to joint imperfections, the argon pressure in the chamber was kept low but higher than that on the environment. A small one-way valve allowed Ar to exit the chamber so that pressure inside would not rise beyond control.

With a non-reactive atmosphere, and the pure elements properly placed, the arc was finally applied, at a current setup of about 180 A. Once the sample was melted one time, it became an amalgam of several pieces and was in no way homogeneous. Because of that, this amalgam was turned upside down and melted again, and this process was repeated some 5 times over for every sample. After the 5<sup>th</sup> melting, the sample was ready, and the crucible cleaned for the next sample.

It is important to mention a phenomenon that took place during this phase of the process. All samples were melted following the above explained procedure, but at the time when the last samples were to be melted, it happened that it was only possible to melt them 2 times over, as at the 3<sup>rd</sup> melting they would shred into pieces, thus rendering them non-usable. This happened only when the at% of aluminum was between 40 and 50. The samples that were melted twice only are 24, 25, 27, 28 and 30.

#### 2.1.4 Quartz Encapsulating

Once all samples were melted into a single piece weighing 1g +- 5% it was time to encapsulate them all at the same pressure so that the thermal process that would take place during the furnace annealing would affect them all equally. Also, it was intended to reduce the possible effects of oxidation, and therefore the obvious choice was to encapsulate them at the minimum possible pressure, thus minimizing the amount of oxygen that remained inside the capsule and making all samples at the same pressure. The selected pressure was  $10^{-3}$  Torr (0.133 Pa). The encapsulating procedure was performed as follows.

In order to make the encapsulation easier, choosing the smallest quartz tube diameter was the best. With that in mind, a tube with 10 mm outer diameter and 1 mm wall thickness was selected. The tubes were sealed in one end and 1 m in length, and therefore needed to be cut in half in order to be handled properly.

The encapsulation procedure started by placing the sample inside the tube. Then the tube was fixed in a holder that allowed a vacuum pump to suck air from inside the tube. Then both ends of the tube were protected using wet paper tissues, in order to prevent the heat to damage the sealing of the holder or the sample. Once the pressure inside the tube was the desired  $10^{-3}$  Torr, everything was ready to heat the quartz with the blowtorch.

The blowtorch, which was fed with both gas and oxygen, was used to heat the quartz slowly, being very careful not to make a hole on it that would allow external pressure to get in the tube. Once the glass was hot enough to make it malleable, it was possible to twist the tube and separate the capsule from the rest of the tube, thus obtaining a sealed capsule, resistant to high temperatures, and at the desired pressure.

Such was the procedure followed to seal all the samples, but there were a couple incidents that we need to mention. The first was that the last few

samples, due to their high content in aluminum, were significantly bigger than the others, and as a result were too big to fit in the 8 mm internal diameter tubes that had been used so far. Instead, 15 mm outer diameter and 1 mm width tubes were used for such samples. The other incident was that the vacuum pump malfunctioned and had to be replaced, and this delayed our procedure some three weeks. Nevertheless, all samples were eventually successfully encapsulated and were ready for the furnace annealing.

## 2.2 Furnace Annealing

The second phase of the sample preparations was annealing the samples in a furnace at 500° C enough time to allow the equilibria state to be reached. We were advised to leave the samples at least 6 weeks in the furnace, and up to 8 weeks. As we had been delayed some weeks already by the pump malfunction, it was decided that the samples were to remain 6 weeks in the furnace.

Therefore, all samples (each inside their capsule) were placed in a holder in such a way that it was easy to know the number of each sample in case the heat would erase the permanent marker used to number them, and put inside a furnace, which was set to 500° C and adjusted during the next hours using a thermal sound. In the end, the setting was 518°C and the internal reading read exactly 500° C. After this, the furnace was checked every week and seen working properly every time. Thus, six weeks later, the samples were at their equilibria state and ready to be quenched.

After the six weeks, it was critical to quench the samples in icy water in order to prevent them to slowly cool and change their state, as they might reach an equilibria stat at a lower temperature otherwise. Therefore, just as the door of the furnace was opened, the samples were submerged in icy water, thus cooling them quickly enough as not to allow any change in their phase equilibria. However, some problems happened during the quenching. First, the samples that had been encapsulated in the larger tube happened to be less dense than water, and therefore floated in in, thus moving from their position and greatly hindering their identification. Also, one capsule broke from thermal shock and sample 20 appeared carbonized. We do not know if this was due a particularly weak capsule or because of an undetected hole on the capsule that allowed air to go in it during the annealing process. Notwithstanding this, it was analyzed as any other sample.

## 2.3 Analysis

The final and most important phase of the experiment was the analysis in order to obtain data from the samples that would allow us to extract conclusions. Two main analysis tools have been used in this work: **X-Ray Diffusion (XRD)** on one side, and **Scanning Electron Microscope (SEM)** and its function **Energy Dispersive X-Ray Spectroscopy (EDS)**. XRD allowed us to identify which

phases are present on each sample, and SEM and EDS allows us to actually see them and assess their composition. Before the samples could be analyzed, though, some preparation was needed. All the steps followed are explained as follows.

### 2.3.1 Sample Cutting, Mounting and Polishing

After quenching, all samples were taken out of the capsules by breaking them. In order to analyze them, it was needed to cut each sample in at least two pieces, one thin and flat for XRD analysis and another flat and thick enough to polish for SEM and EDS analysis. It was decided to add a third piece to prevent possible situations where a replacement could be needed. In order to cut the samples, it was needed to mount them on a piece that could be fixed while cutting. This was done by gluing the samples to M5 bolts with Cyanoacrylate adhesive. Once the samples were fixed to the bolts, they were cut.

The samples were cut using a radial diamond-coated saw 13 cm in diameter, set up at 2000 rpm and a feed movement of 0.005 mm/s, using a *Struers Secotom-10* machine.

During this phase many samples broke before the cut was complete. In order to solve this, slower and faster rotation speeds were tested, and also slower feed velocities. However, the only solution that proved effective in the preventing of the brittle samples to break during the cutting was the use of the slow cutting machine, that allowed a much less aggressive cutting speed of 6 rpm. The slow cutting machine used was a *Buehler IsoMet Low Speed Saw*.

As said, one of the pieces obtained from each sample was intended for its observation under the SEM. These pieces needed to be thoroughly polished in order to give good results when observed. With this aim, they were grouped according to the smoothness of their flat surface and mounted in groups of three or four into cylindrical mountings. These were done using *KonductoMet Conductive Filled Phenolic Mounting Compound* and a *Buehler SimpliMet 1000* machine. These mountings were numbered and mapped in order to keep track of every sample.

The mountings were then grinded using sandpaper of progressive grit, each of them for at least 3 minutes starting at 800, then 1200, 2400 and finally 4000. After the grinding, the mountings were polished using 1  $\mu\text{m}$  polishing fluid, followed by 0.3  $\mu\text{m}$  fluid, and finally using water only. After this procedure, the mounted samples were ready for the SEM.

After some days and troubles, all samples had been cut as best as possible, and polished, and they were finally ready for the analysis using XRD and SEM.

### 2.3.2 XRD

The first analysis performed was the XRD test, as it needed to be booked in advance, and had been therefore scheduled beforehand. This procedure consists on bombarding the sample with X-Ray waves, and recording the resultant reflection. This reflection is affected by the diffraction coefficient of the sample, and by changing the angle of incidence and recording the reflection intensity during an angle interval it is possible to identify the phase composition of the sample.

In order to collect this data, the piece of the sample needed present a flat surface and be 1 mm in thickness or less. It is important to mention that not all samples complied with these requirements, due to cutting difficulties. This probably led to some distortion on the results obtained from said samples. However, most were within parameters, and in general, the results of the XRD were satisfactory. The machine used in this testing was a *Bruker D2 Phaser*.

Once all the files with the XRD patterns had been obtained, each one of them was analyzed and compared with a *Joint Committee on Powder Diffraction Standards (JCPDS) Powder Diffraction File (PDF)* [12] provided database in order to identify the present phases on each of the samples. This was done using the *Bruker AXS DIFFRAC.EVA V3.0* software. For each of the samples, a list of the matching phases was generated, even if these phases made little sense, as they were to be compared later with the EDS data. It is remarkable that for some samples, even if the diffraction pattern showed some clear peaks, there were no phases on the database that matched with those peaks. This was key on the conclusions that were obtained later.

### 2.3.3 SEM & EDS

After the XRD data had been collected, the next step (and last on the experimental procedure) was to study the samples under the SEM, and asses the composition of the different observed phases using the EDS tool. In order to see them properly, the samples had been polished in a very thorough procedure. Prior to observation, the mountings were cleaned with alcohol in an ultrasonic vibration machine for some 10 minutes, in order to remove remains of polishing fluids on their surface. After this last step, they were finally ready for observation.

The SEM device used was a *Hitachi TM3000 Tabletop Microscope*. The samples were observed with an augmentation range between 3000 and 5000 times its real size. Once a good image of the different phases present on the sample was obtained, a picture was saved, and the analysis with the EDS began. This analysis was done three times per phase, at different regions of the same phase in order to average the composition of said phase. The EDS used was a *Bruker XFLASH MIN SVE* and *Bruker Scan Generator*. The data

collected this way was summed in a table that is included as the **Appendix II**. For every measure, a *.docx* file was saved with an image of the measured area, the specter obtained and the resulting composition. It has to be remarked that not all samples presented three clearly differentiated phases, and therefore, not all the table could be completed. Some of the images obtained from the SEM imaging can be found in the **Appendix III**.

Once all the samples had been observed and analyzed with the SEM and the composition of the phases assessed with the EDS, the analysis of the samples was completed. The next and final task was to process the obtained data into a phase diagram.

## CHAPTER 3. RESULTS AND DISCUSSION

After obtaining all the data from the EDS and XRD analysis, it was time to extract results from that information. This meant matching the phases observed with the EDS with the candidates that had been selected from the assessment of the XRD pattern. Also, when looking for possible phases and to help us decide whether the obtained results made sense or not in a given sample, we used the above shown previous studies on the same system.

### 3.1 Results

In this section, the data processing and the obtained results will be explained, from the raw data obtained with the XRD and EDS to the isothermal section of the ternary phase diagram.

#### 3.1.1 XRD & EDS results comparison

The first thing to do after obtaining the EDS results was to compare them with the XRD candidate phases. To do this, the candidate phases were first compared with the reference documentation, and discarded if this documentation showed that they were impossible. For instance, in sample **#18** the XRD pattern showed that it was possible that the Cu rich phase was present. With a simple glance at the reference one can see that such phase in a centric region is not found in any of the previous studies. Because of that, this candidate phase was discarded and others were selected instead. Also, the candidate phases found with the XRD were compared with the results of the EDS, and if a phase matched (a phase with a similar composition was listed on the EDS results of that sample) then it was selected.

When performing this assessment, it was seen that sometimes all of the candidate phases found with XRD made no sense whatsoever. After some discussion it was found that the ternary phases were not listed on the diffraction pattern database. Because of that, when no candidate phases were in accordance with the reference and this reference showed ternary phases that matched with our EDS results, it was concluded that the said ternary phases had been found. However, in the previous studies 10 ternary phases had been found, and in our study it was impossible to find them all. Only if the above mentioned conditions took place (no viable candidates in XRD pattern, ternary phases found in previous studies and similar composition to said ternary phases) a ternary phase was identified.

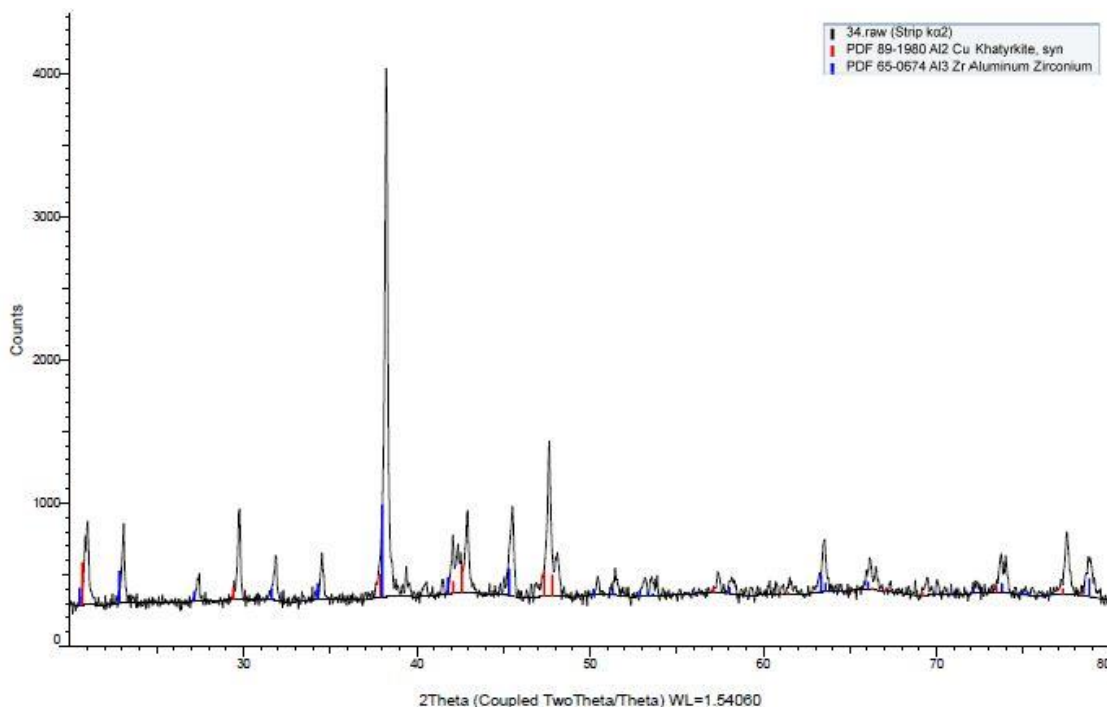
For example, the samples **#32** and **#36** describe the same region in the ternary phase diagram at 500° C. The composition of this two samples is (Cu - 10 at%Zr - 70 at%Al) for the sample **#32** and (Cu - 10 at%Zr - 80 at%Al) for the sample **#36**. They show three regions with different brightness in the SEM

images. Determining the composition of those phases and comparing the results with the XRD pattern we obtain the next result.

The dark color region has a uniform composition of (Cu - 2.63 at%Zr - 89.98 at%Al) for the sample **#32** and (Cu - 2.05at% Zr - 95.11 at%Al) for the sample **#36**. This phase is likely to be the (Al) phase, which is the Alumina rich phase.

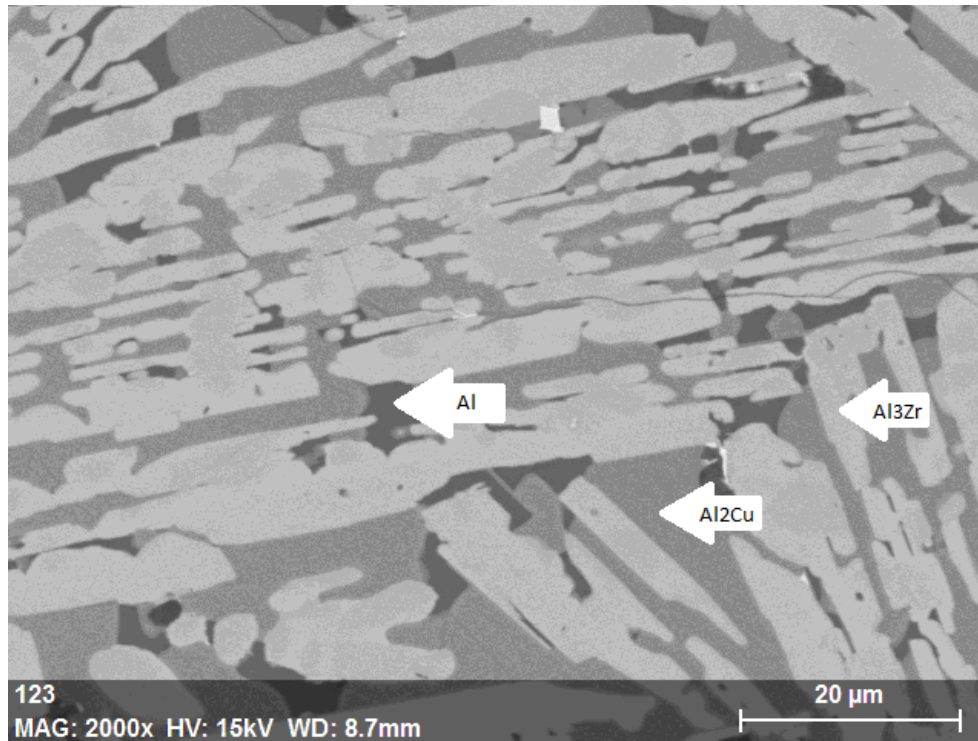
The gray color region has a uniform composition of (Cu-2.04at%Zr-71.17at%Al) for the sample **#32** and the composition (Cu - 2.58 at%Zr - 72.23 at%Al) for the sample **#36** it is likely to be the  $\text{Al}_2\text{Cu}$  phase, which is the richer phase in Copper.

And the bright region has a uniform composition of (Cu - 14.73 at%Zr - 80.82 at%Al) for the sample **#32** and (Cu - 20.59 at%Zr - 76.18 at%Al) for sample **#36** describe the  $\text{Al}_3\text{Zr}$  phase.

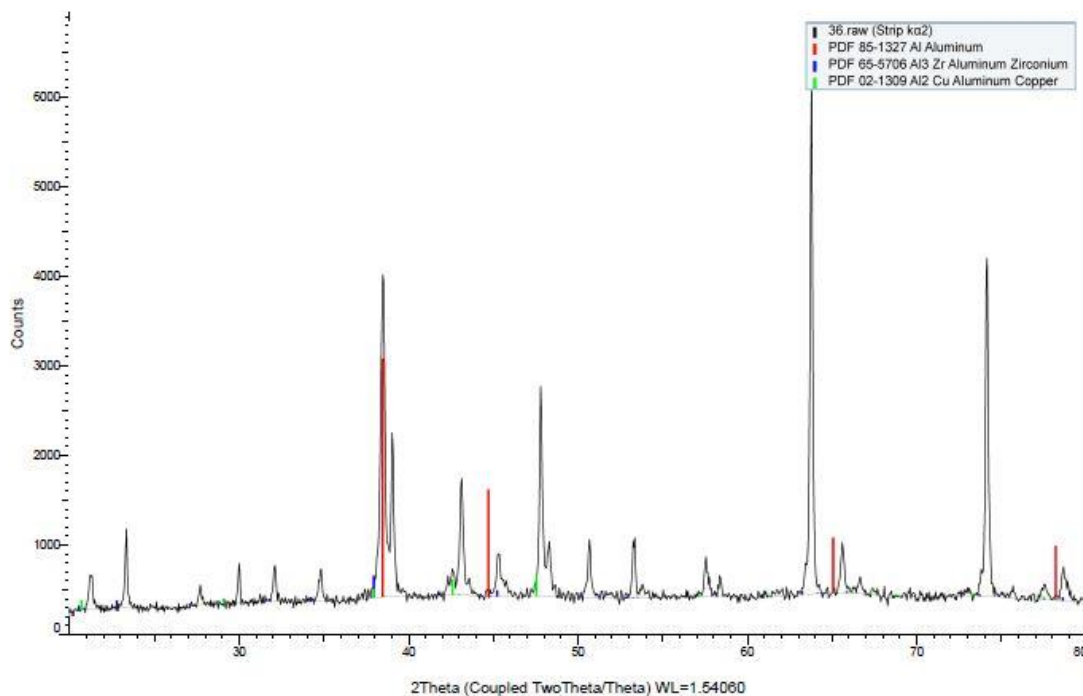


**Fig. 3.1** XRD pattern of sample **#32** analyzed with *Bruker AXS DIFFRAC.EVA V3.0*

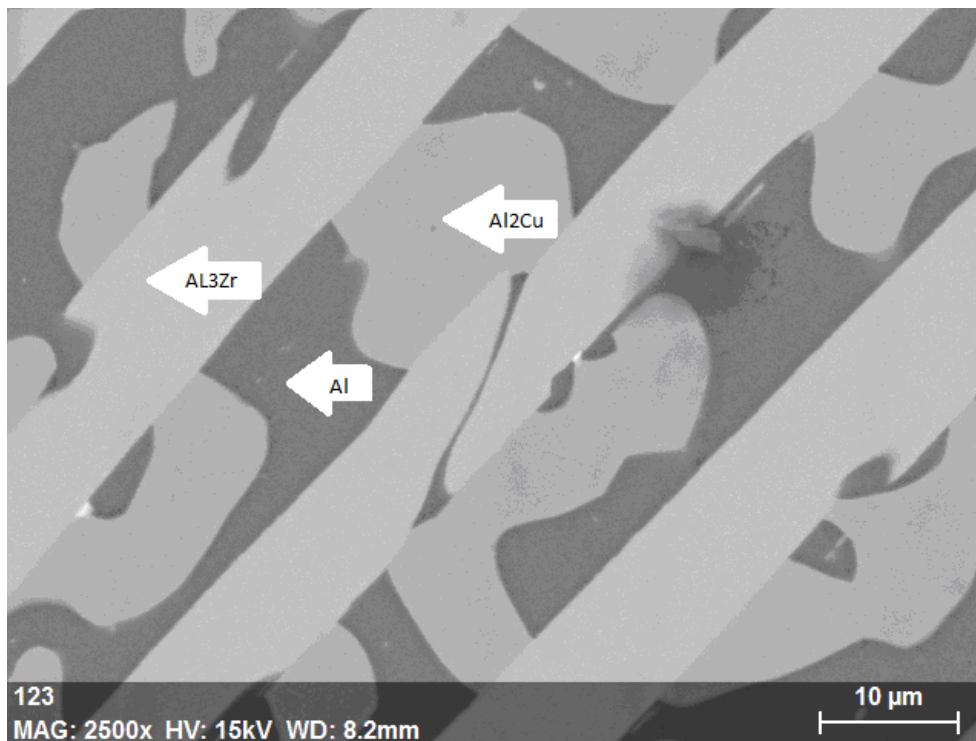




**Fig. 3.2** SEM micrograph of sample **#32** done with *Hitachi TM3000 Tabletop Microscope*



**Fig. 3.3** XRD pattern of sample **#36** analyzed with *Bruker AXS DIFFRAC.EVA V3.0*

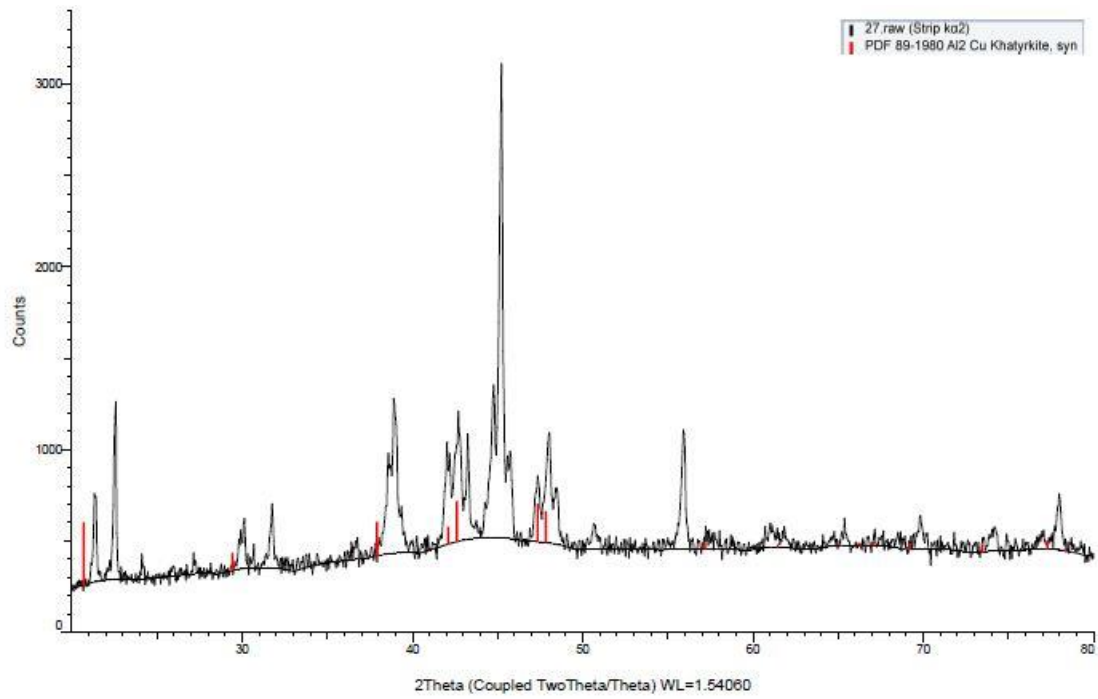


**Fig. 3.4** SEM micrograph of sample **#36** done with *Hitachi TM3000 Tabletop Microscope*

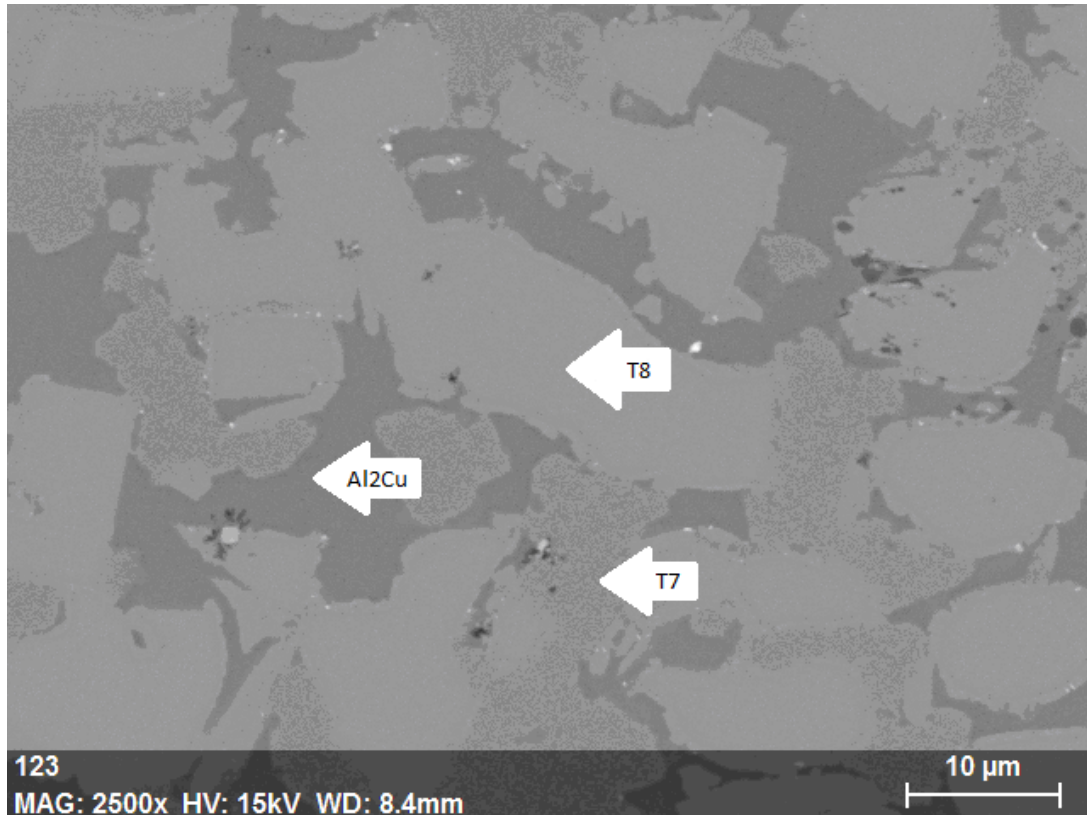
Sample **#27** will allow the explanation of a more complex (and usual) situation. As mentioned, ternary phases do not appear in the used database of XRD patterns. However, we clearly see three different regions in the SEM, where the black region is the  $\text{Al}_2\text{Cu}$  phase. We know this because we can identify it with the XRD. No other (reasonable) candidate phase shows in the database, so comparing the EDS-found composition (Cu - 2.65 at%Zr - 66.02 at%Al) we make the double check and conclude that the dark region is indeed the  $\text{Al}_2\text{Cu}$  phase.

But to identify the other two phases we only have the composition information and the previous studies. So comparing our EDS-found compositions with the previous results we can identify the gray region which has the uniform composition (Cu - 3.02 at%Zr - 55.3 at%Al) as the phase  $\tau_7$  and the bright region which has the uniform composition (Cu - 21.49 at%Zr - 62.57 at%Al) phase  $\tau_8$ .

After assessing every phase found in every sample, the majority had been identified. The list of identified phases can be found in **Appendix IV**.

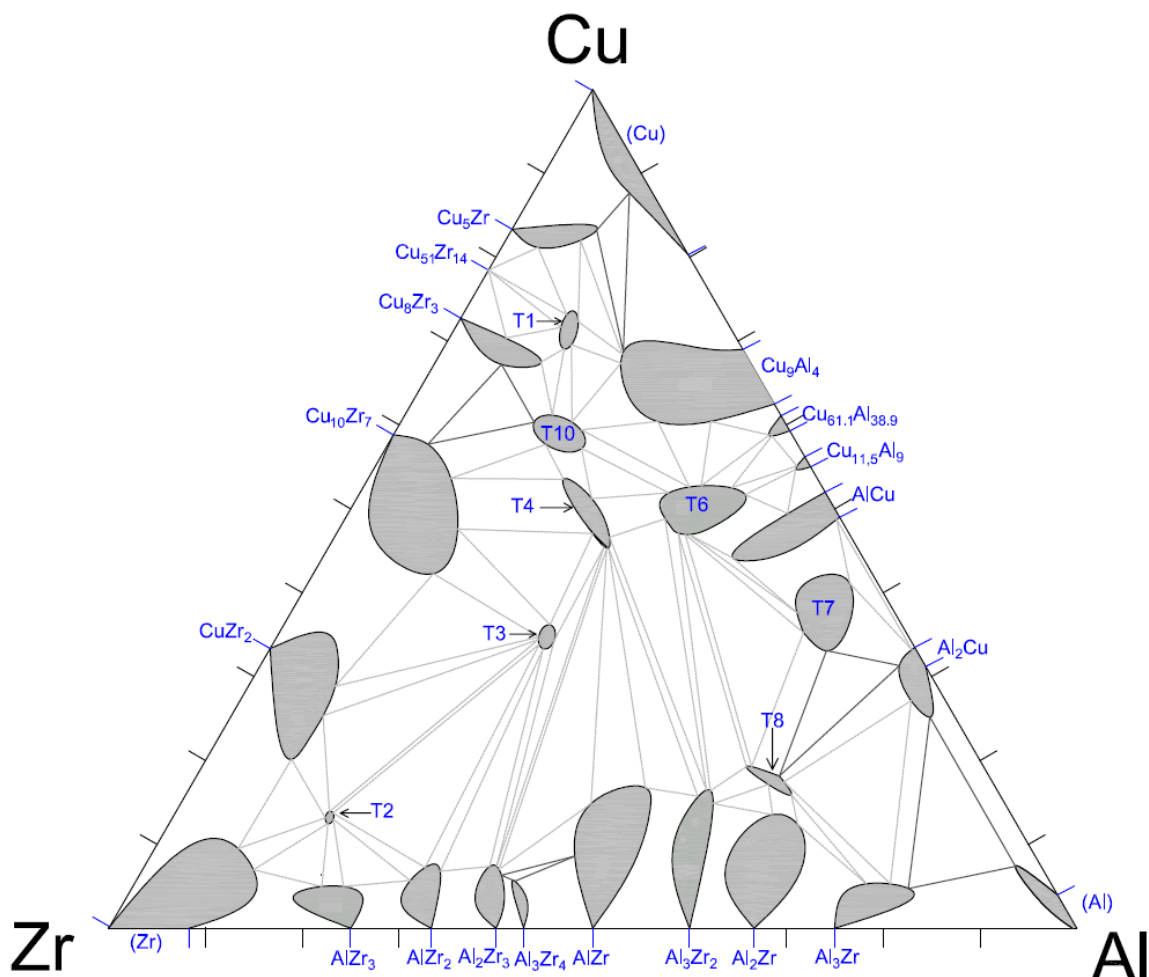


**Fig. 3.5** XRD pattern of sample #27 analyzed with *Bruker AXS DIFFRAC.EVA V3.0*



**Fig. 3.6** SEM micrograph of sample #27 done with *Hitachi TM3000 Tabletop Microscope*

### 3.1.2 500° C Isothermal Section



**Fig. 3.3** Al-Cu-Zr isothermal section phase equilibria system at 500° C experimentally found in this work

After computing all the samples with the same procedures shown in the previous examples, we can finally draw the isothermal section of the phase diagram at 500° C. The regions experimentally found that agree with the reference documentation were drawn in continuous black lines. The rest of the triangles are gray indicating that for those regions the results did not match the results of previous studies. Therefore, these regions were assumed following Gibbs' phase rule and combining our results with the previous studies.

On the walls of the diagram, as can be seen, solubilities of the binary phases are obtained. The shape of these regions has been experimentally found. If in the binary phase diagram there is an intermetallic compound, in the isothermal section it shows as a point in the walls and then its corresponding solubility until including all the points of the same phase. If in the binary phase diagram there is a region, the solubility has its limits on region boundaries in the binary phase diagram.

## CHAPTER 4. CONCLUSIONS

After all the study the isothermal section of the Cu-Zr-Al ternary phase diagram at 500° C has been determined experimentally. Fifteen binary phases have been found and three assumed, and seven ternary phases have been found. That makes up for a total of 28 single-phase regions. Between them 63 two-phase regions have been found and 35 three-phase regions. The most relevant knowledge we obtain from all the experiment is the ratification of the existence of ternary phases. Since it completely contradicts this, we therefore conclude that the last experiment performed in this laboratory got wrong conclusions.

Another important conclusion we draw is that for this particular system, the temperature is too low in some regions to find good results. Because the melting point of Zr is 1852° C, 500° C do not add enough energy to the system to occasion diffusion in the atoms and create good phase equilibria. That explains why Zr rich part of the diagram shows assumed regions only. The results obtained from our samples did not match those found in previous studies. We therefore understand that in the following investigations a good way to improve the results is to find the isothermal section of a higher temperature than 500, for example 800° C.

We have enjoyed a lot our time working in the laboratory, learning about the interesting topic of material science, of crucial importance since the most primitive humans and for sure nowadays. Selecting the appropriate material for each application makes it easier at the very least and often possible, and finding new combinations of them with better proprieties is a huge advance for the technology.

But we didn't learn about materials only, as another important skill for us it was working in a laboratory. This is our first time doing so, and therefore it was new and valuable experience. The precision, the equipment and the thorough care with which everything is taken was for us a really valuable thing to learn as we can apply this work culture in our future jobs and thus obtain better results.

However, working with in these conditions has led us to discover that the experimental studies will never turn out as planned. For example, when we were melting the samples some of them broke spontaneously and we needed to start over again with 5 of the samples several times. Another trouble was that when we needed the vacuum machine it malfunctioned so we lost 2 weeks. When we arrive to the cutting step many of the samples shred into pieces, and we needed to figure out the appropriate cutting settings for each sample. Also, ternary phases never showed in the XRD pattern, thus greatly hindering the task of phase identification. But for every trouble we eventually found a solution so in the end we are glad to have lived through all this experiences because they made us better engineers.

Finally, living this semester in Taiwan has been a life-changing experience. We have had the privilege of learning from the kindest, more honest and more

helpful people in the world their way of living. Taiwan is an example of coexistence that should be mimicked in most countries where multiculturalism leads to unease. Here religions, cultures, ethnicities and languages all share spaces, friendships, love and even temples. Summing up, studying in such a spectacular country, so far away from our homes, with such a different and beautiful culture, different way to work and different point of view on life, has greatly opened our minds, making us better persons by marking forever the good parts of Taiwan in our hearts.

## BIBLIOGRAPHY

- [1] Tretyachenko, L., *Al-Cu-Zr Ternary Phase Diagram Evaluation*. 2004, MSI, Materials Science International Services GmbH: Stuttgart, Germany.
- [2] Hsiao, H.M., *Prediction of the Metallic Glass Formation Regions for the Ag-Al-Cu-Zr Quaternary System by the Calculation of Phase Diagram (CALPHAD) Method*. 2015, Department of Materials Science and Engineering, NTUST: Taipei, Taiwan
- [3] Wang, C.P. et al., *Experimental investigation of phase equilibria in the Zr-Cu-Al system*. 2012, Intermetallics: Xiamen, China
- [4] Chen, *Phase Equilibria of Cu-Zr-Al Ternary Systems at 500° C*. 2013, Department of Materials Science and Engineering, NTUST: Taipei, Taiwan
- [5] Yen, Y.W. et al., "Phase equilibria of the Fe-Cr-Ni ternary systems and interfacial reactions in Fe-Cr alloys with Ni substrate", *Journal of Alloys and Compounds* 457, 270-278 (2008)
- [6] Bo, H., Wang, J., Jin, S., Qi, H.Y., Yuan, X.L., Liu, L.B., and Jin, Z.P., *Thermodynamic analysis of the Al-Cu-Zr bulk metallic glass system*. Intermetallics, 2010. 18(12): p. 2322-2327.
- [7] Shin, H.S., Park, J.S., Jung, Y.C., Ahn, J.H., Yokoyama, Y., and Inoue, A., *Similar and dissimilar friction welding of Zr-Cu-Al bulk glassy alloys*. Journal of Alloys and Compounds, 2009. 483(1-2): p. 182-185.
- [8] Wang, X., Cao, Q.P., Chen, Y.M., Hono, K., Zhong, C., Jiang, Q.K., Nie, X.P., Chen, L.Y., Wang, X.D., and Jiang, J.Z., *A plastic Zr-Cu-Ag-Al bulk metallic glass*. Acta Materialia, 2011. 59(3): p.1037-1047.
- [9] Witusiewicz, V.T., Hecht, U., Fries, S.G., and Rex, S., *The Ag-Al-Cu system: Part I: Reassessment of the constituent binaries on the basis of new experimental data*. Journal of Alloys and Compounds, 2004. 385(1-2): p. 133-143.
- [10] He, X.C., Wang, H., Liu, H.S., and Jin, Z.P., *Thermodynamic description of the Cu-Ag-Zr system*. Calphad, 2006. 30(4): p. 367-374.
- [11] Wang, T., Jin, Z., and Zhao, J.C., *Thermodynamic assessment of the Al-Zr binary system*. Journal of Phase Equilibria, 2001. 22(5): p. 544-551.
- [12] American Ceramic Society, JCPDS-International Centre for Diffraction Data, Swarthmore, PA, 2003

## Appendix I – Sample Composition

No.	at% Cu	at% Zr	at% Al	pTot	wt% Cu	wt% Zr	wt% Al
1	80	10	10	62.657	0.811	0.146	0.043
2	70	20	10	65.425	0.680	0.279	0.041
3	60	30	10	68.193	0.559	0.401	0.040
4	50	40	10	70.961	0.448	0.514	0.038
5	40	50	10	73.729	0.345	0.619	0.037
6	30	60	10	76.496	0.249	0.716	0.035
7	20	70	10	79.264	0.160	0.806	0.034
8	10	80	10	82.032	0.077	0.890	0.033
9	60	10	30	55.344	0.689	0.165	0.146
10	60	20	20	61.769	0.617	0.295	0.087
11	50	30	20	64.537	0.492	0.424	0.084
12	40	40	20	67.304	0.378	0.542	0.080
13	30	50	20	70.072	0.272	0.651	0.077
14	20	60	20	72.840	0.174	0.751	0.074
15	10	70	20	75.608	0.084	0.845	0.071
16	70	10	20	59.001	0.754	0.155	0.091
17	50	20	30	58.112	0.547	0.314	0.139
18	40	30	30	60.880	0.418	0.450	0.133
19	30	40	30	63.648	0.300	0.573	0.127
20	20	50	30	66.416	0.191	0.687	0.122
21	10	60	30	69.183	0.092	0.791	0.117
22	50	10	40	51.688	0.615	0.176	0.209
23	40	20	40	54.456	0.467	0.335	0.198
24	30	30	40	57.224	0.333	0.478	0.189
25	20	40	40	59.991	0.212	0.608	0.180
26	10	50	40	62.759	0.101	0.727	0.172
27	10	20	70	43.486	0.146	0.420	0.434
28	30	20	50	50.799	0.375	0.359	0.266
29	20	30	50	53.567	0.237	0.511	0.252
30	10	40	50	56.335	0.113	0.648	0.239
31	20	10	70	40.719	0.312	0.224	0.464
32	40	10	50	48.032	0.529	0.190	0.281
33	10	30	60	49.911	0.127	0.548	0.324
34	20	20	60	47.143	0.270	0.387	0.343
35	30	10	60	44.375	0.430	0.206	0.365
36	10	10	80	37.062	0.171	0.246	0.582



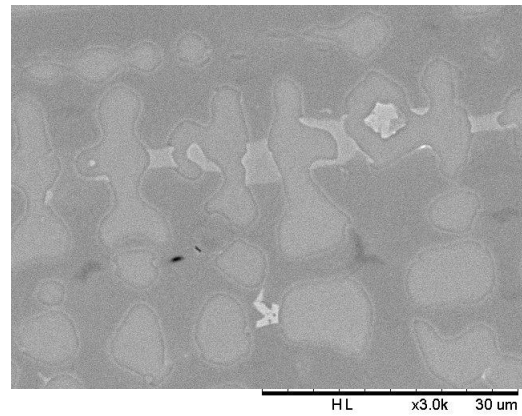
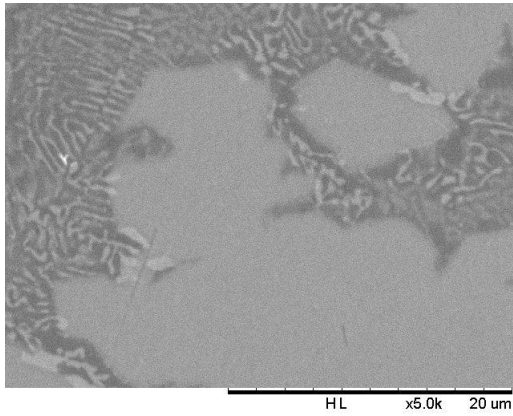
## Appendix II – EDS-Found Phase Composition

Sample	Phase	%at Cu	%at Zr	%at Al	Total
#1	#1	73.48	15.37	11.15	100
#1	#2	89.15	2.84	8.00	100
#1	#3	81.28	15.43	3.29	100
#2	#1	67.13	22.11	10.76	100
#2	#2	45.33	49.25	5.43	100
#2	#3	69.07	18.40	12.53	100
#3	#1	60.32	25.89	13.79	100
#3	#2	67.21	25.81	6.98	100
#3	#3	57.69	38.18	4.13	100
#4	#1	0.00	0.00	0.00	0
#4	#2	0.00	0.00	0.00	0
#4	#3	0.00	0.00	0.00	0
#5	#1	49.71	39.42	10.88	100
#5	#2	0.00	0.00	0.00	0
#5	#3	0.00	0.00	0.00	0
#6	#1	26.25	65.76	7.98	100
#6	#2	34.82	54.64	10.54	100
#6	#3	0.00	0.00	0.00	0
#7	#1	22.34	62.90	14.76	100
#7	#2	9.61	81.92	8.48	100
#7	#3	20.67	70.12	9.21	100
#8	#1	12.48	71.04	16.48	100
#8	#2	5.39	81.98	12.63	100
#8	#3	0.00	0.00	0.00	0
#9	#1	32.70	59.98	7.32	100
#9	#2	57.63	22.03	20.34	100
#9	#3	67.01	11.54	21.45	100
#10	#1	36.14	36.33	27.53	100
#10	#2	46.66	43.13	10.21	100
#10	#3	29.37	47.83	22.80	100
#11	#1	68.95	2.73	28.32	100
#11	#2	34.33	59.52	6.14	100
#11	#3	63.35	14.61	22.04	100
#12	#1	42.31	45.20	12.49	100
#12	#2	53.52	26.27	20.20	100
#12	#3	27.79	64.23	7.97	100
#13	#1	33.31	38.44	28.25	100
#13	#2	33.57	52.40	14.03	100
#13	#3	27.61	49.52	22.87	100

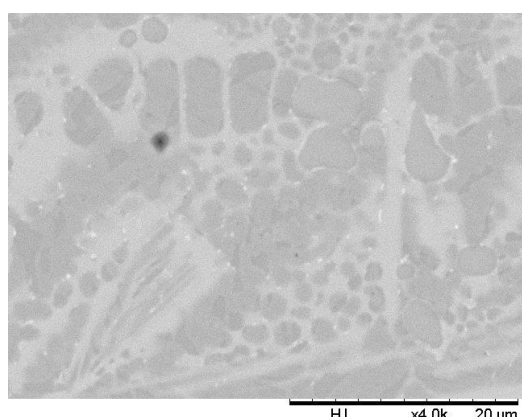
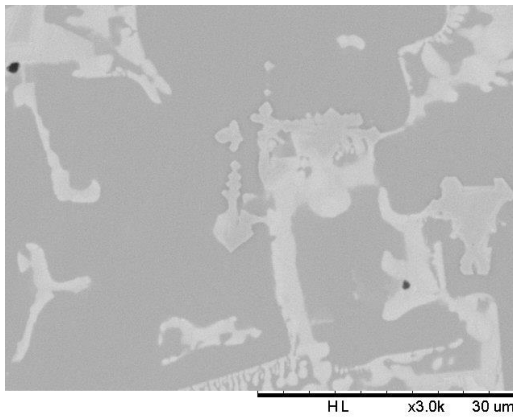
Sample	Phase	%at Cu	%at Zr	%at Al	Total
#14	#1	16.80	58.12	25.08	100
#14	#2	22.99	64.64	12.37	100
#14	#3	7.65	62.65	29.70	100
#15	#1	22.17	68.44	9.38	100
#15	#2	3.45	68.08	28.47	100
#15	#3	0.00	0.00	0.00	0
#16	#1	68.72	12.47	18.81	100
#16	#2	83.22	7.98	8.80	100
#16	#3	87.67	2.39	9.94	100
#17	#1	49.19	24.36	26.45	100
#17	#2	50.80	17.65	31.55	100
#17	#3	32.89	29.49	37.62	100
#18	#1	27.63	33.21	39.16	100
#18	#2	48.07	26.62	25.31	100
#18	#3	15.00	24.06	60.95	100
#19	#1	11.96	35.16	52.88	100
#19	#2	4.50	57.99	37.51	100
#19	#3	7.53	56.45	36.03	100
#20	#1	22.89	38.18	38.92	100
#20	#2	14.67	54.46	30.87	100
#20	#3	0	0	0	0
#21	#1	5.06	58.08	36.86	100
#21	#2	3.75	65.18	31.07	100
#21	#3	20.06	63.89	16.04	100
#22	#1	51.41	8.46	40.14	100
#22	#2	23.80	27.48	48.73	100
#22	#3	28.89	22.63	48.48	100
#23	#1	47.38	17.93	34.69	100
#23	#2	22.50	30.75	46.75	100
#23	#3	50.58	13.49	35.92	100
#24	#1	26.75	31.69	41.56	100
#24	#2	45.31	25.75	28.94	100
#24	#3	13.94	70.07	15.99	100
#25	#1	16.21	36.01	47.78	100
#25	#2	17.09	48.39	34.52	100
#25	#3	14.40	55.00	30.60	100
#26	#1	14.25	36.93	48.82	100
#26	#2	5.62	55.22	39.16	100
#26	#3	3.64	60.33	36.03	100
#27	#1	31.33	2.65	66.02	100
#27	#2	15.95	21.49	62.57	100
#27	#3	41.68	3.02	55.30	100

Sample	Phase	%at Cu	%at Zr	%at Al	Total
#28	#1	16.21	30.54	53.25	100
#28	#2	43.84	11.46	44.69	100
#28	#3	19.24	24.52	56.24	100
#29	#1	12.66	33.06	54.28	100
#29	#2	43.83	12.84	43.33	100
#29	#3	24.21	26.30	49.50	100
#30	#1	10.59	35.37	54.03	100
#30	#2	3.27	57.51	39.22	100
#30	#3	3.99	78.82	17.19	100
#31	#1	13.41	23.31	63.28	100
#31	#2	35.24	10.61	54.16	100
#31	#3	9.07	23.54	67.39	100
#32	#1	26.79	2.04	71.17	100
#32	#2	4.45	14.73	80.82	100
#32	#3	7.39	2.63	89.98	100
#33	#1	7.24	32.65	60.11	100
#33	#2	10.32	26.41	63.27	100
#33	#3	11.84	22.58	65.58	100
#34	#1	30.23	2.42	67.35	100
#34	#2	4.73	21.68	73.59	100
#34	#3	35.65	8.90	55.46	100
#35	#1	40.44	8.40	51.16	100
#35	#2	18.16	21.64	60.20	100
#35	#3	33.08	9.26	57.67	100
#36	#1	3.23	20.59	76.18	100
#36	#2	25.19	2.58	72.23	100
#36	#3	2.84	2.05	95.11	100

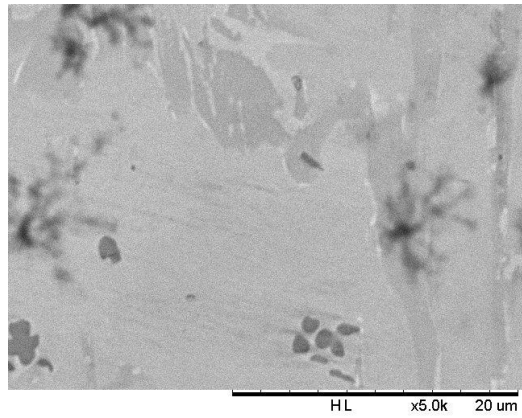
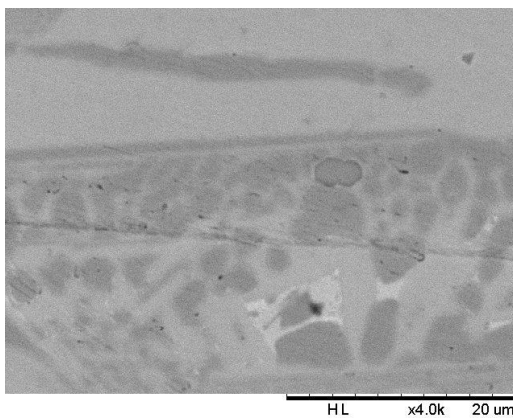
## Appendix III – SEM Images



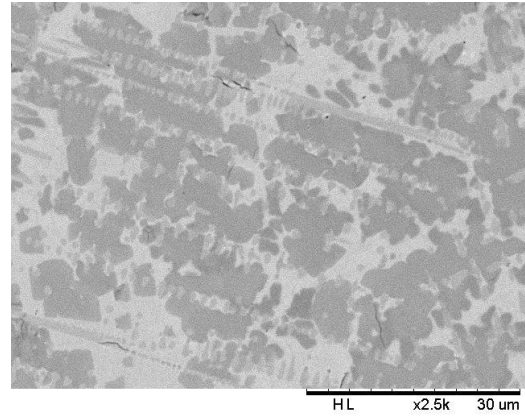
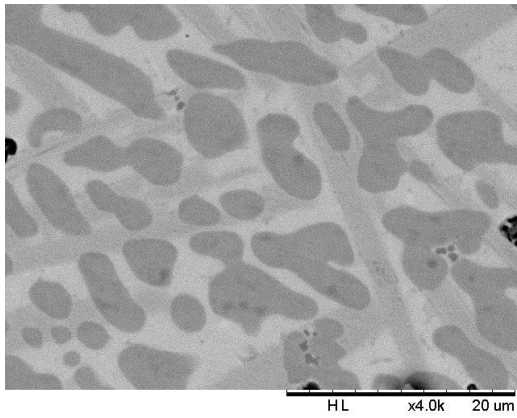
**Fig App3.1 Left: SEM image of sample #16. Right: SEM image of sample #23.**



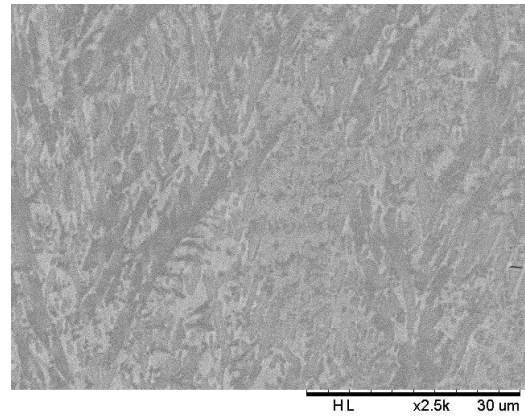
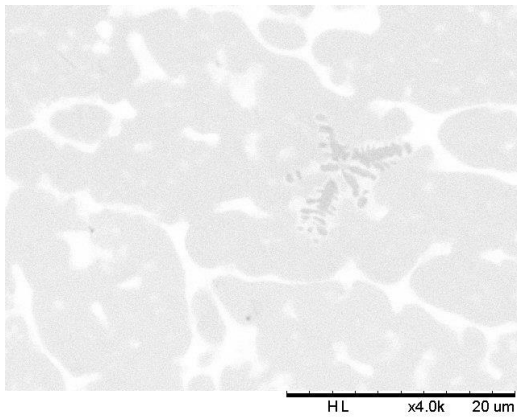
**Fig App3.2 Left: SEM image of sample #30. Right: SEM image of sample #11.**



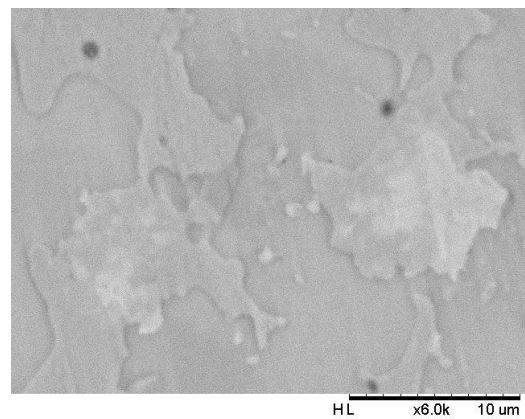
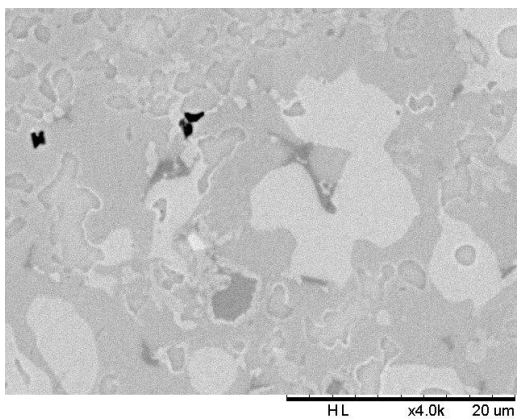
**Fig App3.3 Left: SEM image of sample #1. Right: SEM image of sample #2.**



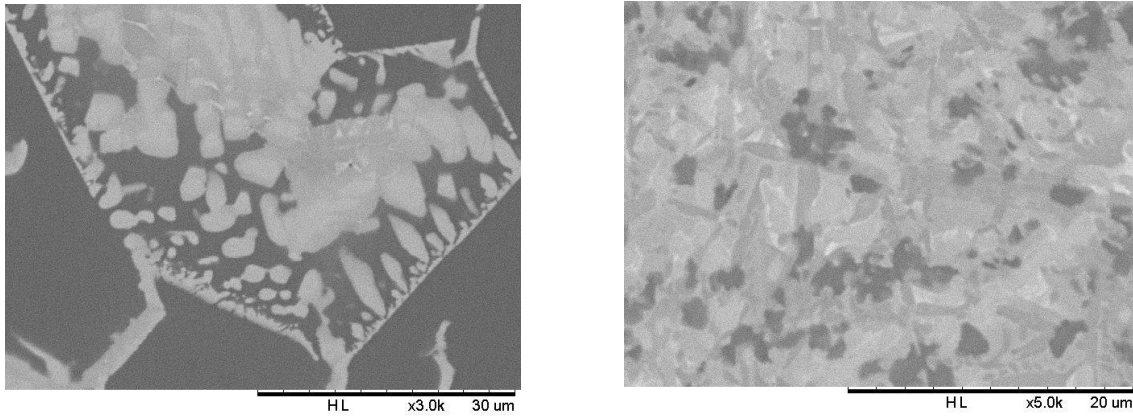
**Fig App3.4 Left: SEM image of sample #3. Right: SEM image of sample #10.**



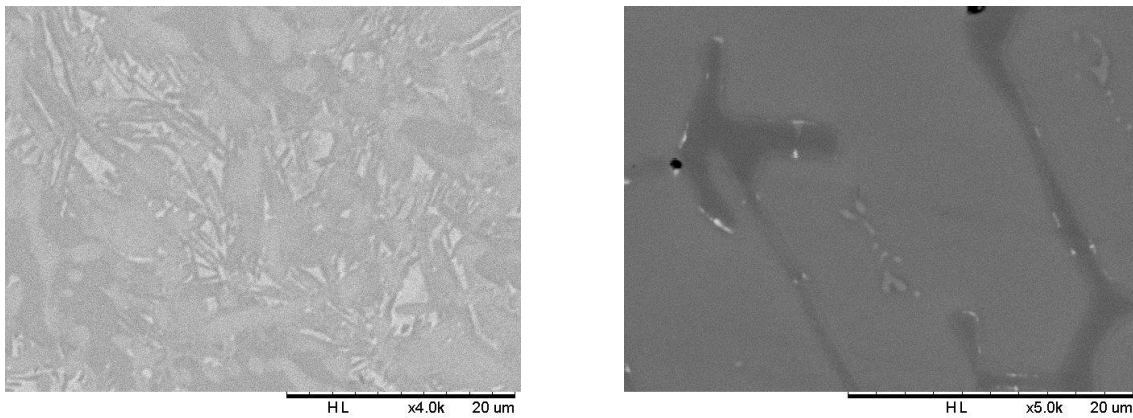
**Fig App3.5 Left: SEM image of sample #12. Right: SEM image of sample #13.**



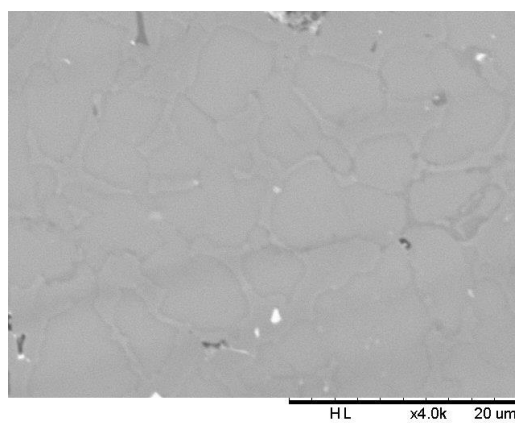
**Fig App3.6 Left: SEM image of sample #17. Right: SEM image of sample #18.**



**Fig App3.7 Left: SEM image of sample #19. Right: SEM image of sample #20.**



**Fig App3.8 Left: SEM image of sample #21. Right: SEM image of sample #29.**



**Fig App3.9 SEM image of sample #31**

## Appendix IV – Identified Phases

Sample	Phase Nº	Phase Name
32	#3	Al
36	#3	Al
27	#1	Al <sub>2</sub> Cu
32	#1	Al <sub>2</sub> Cu
34	#1	Al <sub>2</sub> Cu
36	#2	Al <sub>2</sub> Cu
31	#1	Al <sub>2</sub> Zr
31	#3	Al <sub>2</sub> Zr
33	#3	Al <sub>2</sub> Zr
33	#2	Al <sub>2</sub> Zr
33	#1	Al <sub>2</sub> Zr
19	#2	Al <sub>2</sub> Zr <sub>3</sub>
19	#3	Al <sub>2</sub> Zr <sub>3</sub>
21	#1	Al <sub>2</sub> Zr <sub>3</sub>
26	#3	Al <sub>2</sub> Zr <sub>3</sub>
30	#2	Al <sub>2</sub> Zr <sub>3</sub>
32	#2	Al <sub>3</sub> Zr
34	#2	Al <sub>3</sub> Zr
36	#1	Al <sub>3</sub> Zr
19	#1	Al <sub>3</sub> Zr <sub>2</sub>
28	#1	Al <sub>3</sub> Zr <sub>2</sub>
29	#1	Al <sub>3</sub> Zr <sub>2</sub>
30	#1	Al <sub>3</sub> Zr <sub>2</sub>
26	#2	Al <sub>3</sub> Zr <sub>4</sub>
28	#2	AlCu
29	#2	AlCu
18	#1	AlZr
25	#1	AlZr
26	#1	AlZr
14	#3	AlZr <sub>2</sub>
15	#2	AlZr <sub>2</sub>
21	#2	AlZr <sub>2</sub>
30	#3	AlZr <sub>3</sub>
1	#2	Cu
16	#3	Cu
2	#2	Cu <sub>10</sub> Zr <sub>7</sub>
3	#3	Cu <sub>10</sub> Zr <sub>7</sub>
10	#2	Cu <sub>10</sub> Zr <sub>7</sub>
12	#1	Cu <sub>10</sub> Zr <sub>7</sub>

1	#3	Cu <sub>5</sub> Zr
16	#2	Cu <sub>5</sub> Zr
2	#1	Cu <sub>8</sub> Zr <sub>3</sub>
3	#2	Cu <sub>8</sub> Zr <sub>3</sub>
6	#1	CuZr <sub>2</sub>
7	#3	CuZr <sub>2</sub>
9	#1	CuZr <sub>2</sub>
11	#2	CuZr <sub>2</sub>
12	#3	CuZr <sub>2</sub>
15	#1	CuZr <sub>2</sub>
9	#3	gamma
11	#1	gamma
11	#3	gamma
16	#1	gamma
1	#1	tau <sub>1</sub>
2	#3	tau <sub>1</sub>
3	#1	tau <sub>10</sub>
9	#2	tau <sub>10</sub>
8	#1	tau <sub>2</sub>
24	#3	tau <sub>2</sub>
10	#3	tau <sub>3</sub>
13	#3	tau <sub>3</sub>
12	#2	tau <sub>4</sub>
17	#1	tau <sub>4</sub>
18	#2	tau <sub>4</sub>
24	#2	tau <sub>4</sub>
17	#2	tau <sub>6</sub>
22	#1	tau <sub>6</sub>
23	#3	tau <sub>6</sub>
23	#1	tau <sub>6</sub>
27	#3	tau <sub>7</sub>
31	#2	tau <sub>7</sub>
34	#3	tau <sub>7</sub>
35	#3	tau <sub>7</sub>
35	#1	tau <sub>7</sub>
27	#2	tau <sub>8</sub>
28	#3	tau <sub>8</sub>
35	#2	tau <sub>8</sub>
7	#2	Zr
8	#2	Zr

