# INTERNSHIP REPORT

# Single Crystal Growth of Constantan by Vertical Bridgman Method

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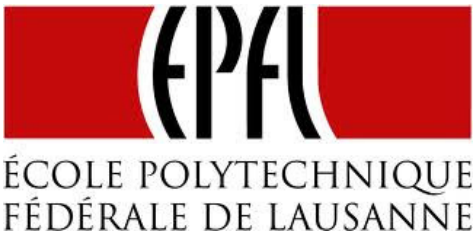
Laboratory for Quantum Magnetism (LQM)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# INTRODUCTION

This project deals with aspects involved in the growth of single-crystals of Constantan.

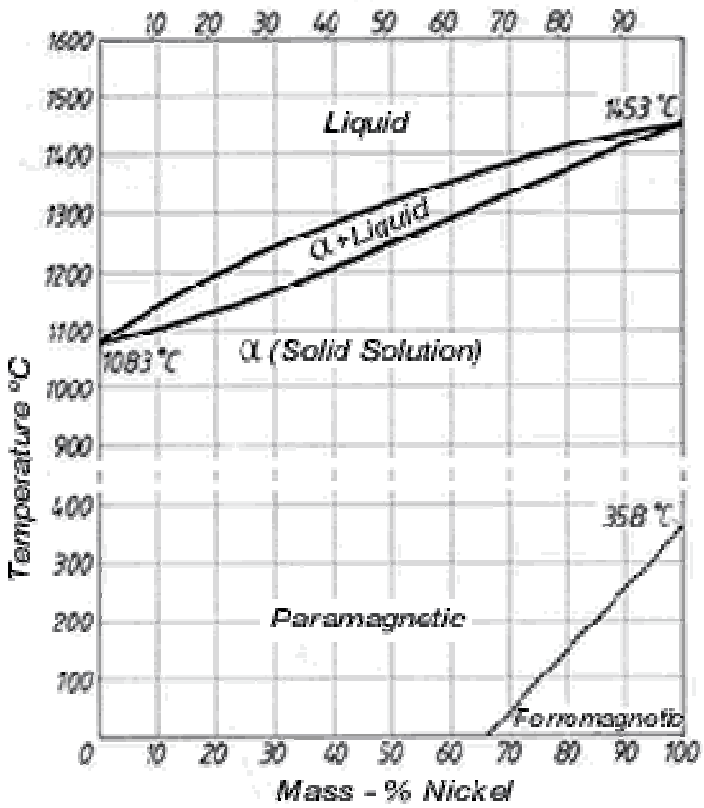
**Constantan is an alloy of Nickel in Copper, whose technological interest is that resistance is independent of temperature over a very large range of temperatures** (hence the name Constantan). This, along with other suitable properties such as high strain sensitivity, high resistivity and low coefficient of thermal expansion makes it the principal component of all modern strain gauges used.

However, Constantan also represents exactly **the critical composition of Nickel in Copper (45% by weight Ni in Cu), which is the border between ferromagnetism and paramagnetism at low temperature. Such a transition in magnetic states at low (zero) temperature is called a quantum phase transition**, and results in a uniquely scaling excitation spectrum.

The eventual purpose of growing these single crystals is to validate our hypothesis that in fact the technologically relevant properties of Constantan are the result of quantum critical fluctuations. This can be investigated by a technique called inelastic neutron scattering.

It is presumed that many aspects of the magnetism in Cu-Ni alloys can be best explained in terms of localised moments. These moments are associated with Ni rich regions on an atomic scale, which due to statistical fluctuations are over-stoichiometric in Ni. They are best described as polarization clouds or spin clusters and their interaction leads to long range ferromagnetic order. The order–disorder of these cluster moments leads to the transition from ferromagnetism to paramagnetism and vice versa. It is believed that at the critical composition, the localised moments freeze into a state without long range magnetic order, called a spin glass [1].

We endeavour to carry out magnetic characterization of single crystals of Constantan alloy and nearby compositions of Cu-Ni at different temperatures and values of field.




*<<**phase diagram of Ni-Cu** and the transition from paramagnetism to ferromagnetism with increasing Ni wt% and decreasing temperature at a given composition. The experimental line runs almost straight to very low temperatures; on extrapolation yields the critical composition between 44-46 wt % Ni* [2].

# REQUIREMENTS OF THE SAMPLE

NATURE: Single crystalline

SIZE: Neutron scattering measurements require large crystals (>1 cubic cm) to achieve a sufficiently intense signal.

COMPOSITIONS: Approximate critical composition= 45wt% Ni in Cu and samples varying by 2wt% over-stoichiometric in Ni to provide data for plotting transition temperature ($T_c$) with composition allowing for extrapolation to determine the actual critical temperature.

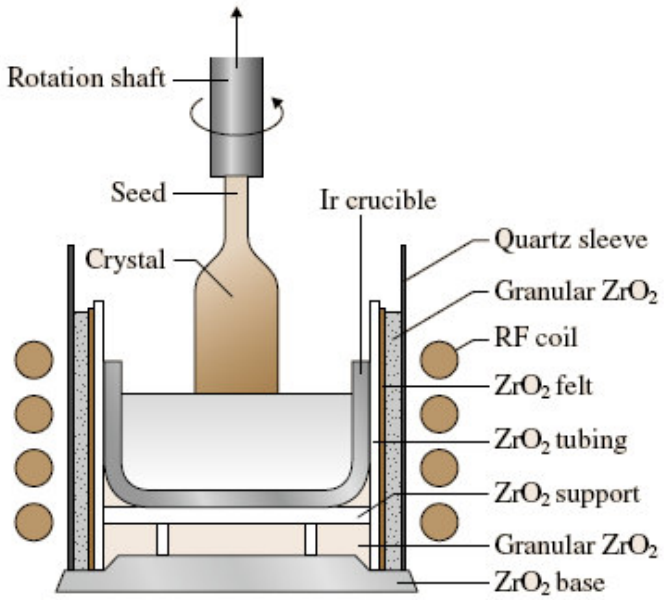
ORIENTATION: specifically oriented crystals are not required.

Hence, our requirement is to **grow "thumb" sized single crystals of Copper-Nickel of varying compositions around the critical composition where the ferromagnetic-paramagnetic transition occurs**. Of the various methods to grow single crystals, the vertical Bridgman is the most suitable for a variety of reasons.

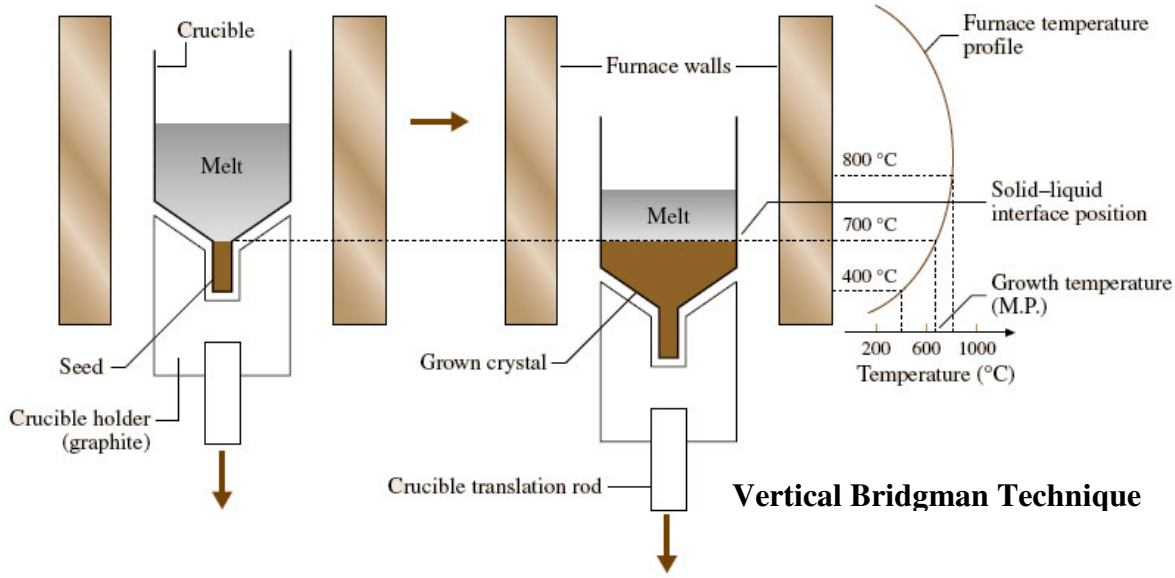
# SOME METHODS TO GROW SINGLE CRYSTALS

A very brief description of basic methods and their ability or inability to allow growth of Cu-Ni single crystals is now provided. Selection of a particular melt growth technique is done on the basis of the physical and chemical characteristics of the crystal to be grown. Generally, metal single crystals with melting point < 1800'C are grown by Bridgman-Stockbarger method, and those with melting point > 1800'C by zone melting. Semiconducting crystals are grown chiefly by Czochralski method, and by zone melting. Single crystals of dielectrics with melting point < 1800'C are usually grown by the Bridgman-Stockbarger or Czochralski methods, while higher-melting materials are produced by flame fusion (Verneuil method).

**CZOCHRALSKI**: *The setup is as shown below*. It consists of a **rod-mounted seed crystal is dipped into the molten melt. The seed crystal's rod is slowly pulled upwards and rotated**. This provides a virtually constant growth rate for the crystal. By controlling the temperature gradients, rate of pulling and speed of rotation, it is possible to extract a large, cylindrical, single-crystal ingot from the melt. Czochralski is normally performed in an inert atmosphere (Argon) and in an inert chamber (quartz). Since the growing crystal is not in contact with a crucible there is lesser contamination however heating and cooling times are slow. The melt can also be magnetically levitated.

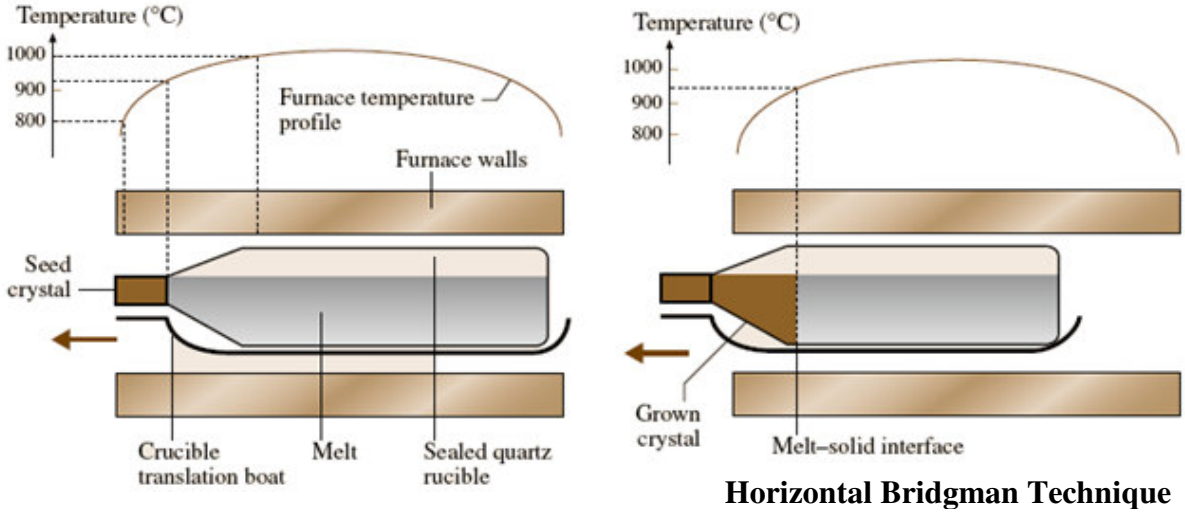


**BRIDGMAN (vertical and horizontal):** is characterized by the relative translation of the crucible containing the melt to the axial temperature gradient in a vertical/horizontal furnace.




**Vertical Bridgman Technique**

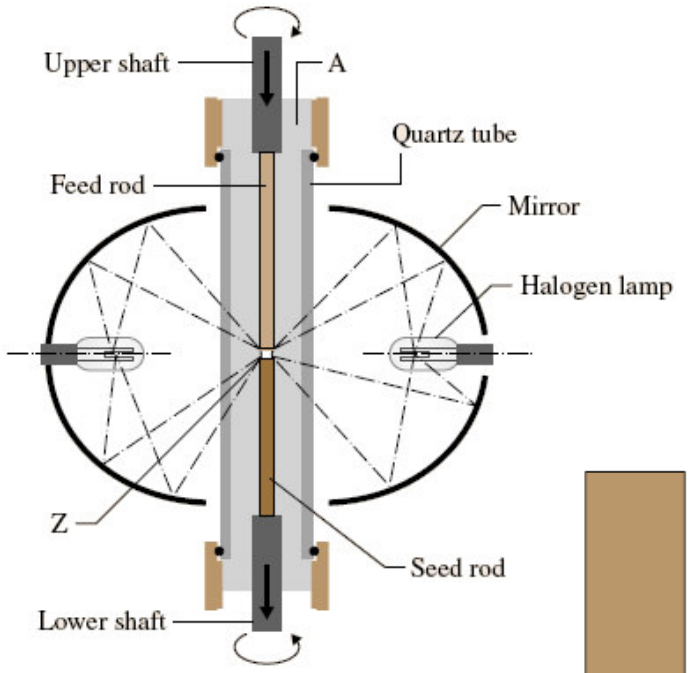
The principle of crystal growth using Bridgman technique is based on **directional solidification by translating a molten charge (melt) from the hot to the cold zone** of the furnace. The presence of a seed at the end of the crucible ensures single-crystal growth along specific crystallographic orientation. At the beginning of the experiment, the crucible with the polycrystalline charge and seed is placed inside the growth chamber. The chamber is evacuated by a vacuum pump and refilled with inert gas. The temperature of the furnace is then raised. The homogenization of the melt can also occur by natural convection and diffusion in the melt without any forced convection.



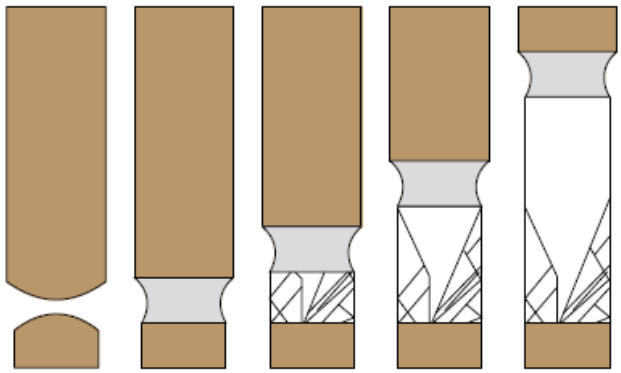

**Horizontal Bridgman Technique**

The vertical and horizontal arrangements have their own advantages and disadvantages. The wafers extracted from vertical Bridgman grown crystals are perfectly circular in shape, unlike the D-shaped wafers from horizontal Bridgman grown crystals. For large-scale epitaxial growth on the substrates and device fabrication, circular wafers are certainly beneficial. The primary advantages of the horizontal Bridgman grown crystals are the high crystalline quality and low defect densities. The crystal experiences lower stress due to the free surface on the top of the melt. The solid does not touch the crucible on the top and hence is free to expand. Another advantage is the enhanced mixing in the melt due to thermal convection in the melt along the growth direction [3].

**FLOATING ZONE:** It is essentially the same as Zone Refining which is used for purification of crystals based on the principle that the segregation coefficient, which is defined as the ratio of an impurity in the solid phase to that in the liquid phase, is usually <1. At the solid-liquid interface, the impurity atoms diffuse to the liquid region. **The crystal is passed through a very thin section of furnace very slowly such that only a small region is molten at any time, the impurities are segregated at the end of the crystal as the furnace travels upward** (or the crystal downward). Heating up a thin slice is achieved by a method suitable to the material of the single crystal. It can be heated by a thin Induction Coil (RF heating) or in an image furnace by optical means. In an image furnace, light from a lamp is comcentrated on a ring of rod by means of parabolic mirrors. Another method recently used is melting by lasers and electron beams. Because of the lack of impurities in the leftover regions which solidify, the boule can grow as a perfect single crystal if a seed crystal is placed at the base to initiate a preferred direction. Finally, the impure end is cut off.




**^ Optical floating zone setup**



*>> Stages for nucleation of single crystals during growth by floating zone methods.*

The above mentioned three techniques are described as techniques where the crystal is "Grown from the Melt". Other types of techniques include Solution growth, Vapour Phase Deposition and Solid Growth.

**The first step of attempting to grow a single crystal of a binary compound is to study its phase diagram.** The system we are currently looking at is a binary alloy of Copper and Nickel with complete solubility in the solid and liquid phases. Although it is one of the simplest phase diagrams encountered, it poses definite challenges during single crystal growth due to the fact that it melts incongruently and poses a problem of Solute Segregation which I shall explain in a more detailed fashion later.

For a congruently melting alloy, one in which the composition of the solid and liquid phases doesn't change on cooling, the best method to grow crystals is the Czochralski. Large boules of relatively good purity, as much as 300kgs, can be grown by this method. Hence, it is the most preferred and widely used method used to grow single crystal Silicon.

Both, **Directional Solidification methods (Bridgman) and Floating Zone have an advantage while growing crystals of incongruently melting compounds**. Floating zone and its variations generally prove more useful but in this case it is not possible to grow crystals of Cu-Ni as the **thermal conductivity of the alloy being high, a narrow melted zone is not achieved** which is crucial for growth by this method. Generally, a melted zone should not exceed 5 mm but in this case at least 10 mm or more becomes mushy. The liquid would have a tendency to flow away as it is held between the two solid rods due to surface tension and other forces.
Thus we attempt to grow single crystals using Vertical Bridgman.

# TESTING THE SAMPLES

**POLISH and ETCH:** The samples were first cut using a wire cutter and then ground using successively fine grades of emery paper (100, 200, 400, 600, 1000, 2400, 4200) and (in some cases) polished on the polishing wheel with diamond paste on particle size 5micron, 3micron and 1.5 micron to give it a mirror finish. It was subsequently etched with an appropriate etchant which revealed its grain boundaries and grain structure.

Choice of Etchant: Several etchants are used for copper alloy systems but only a few of them give a good result with Copper Nickel alloys. Among those which are probables include []:

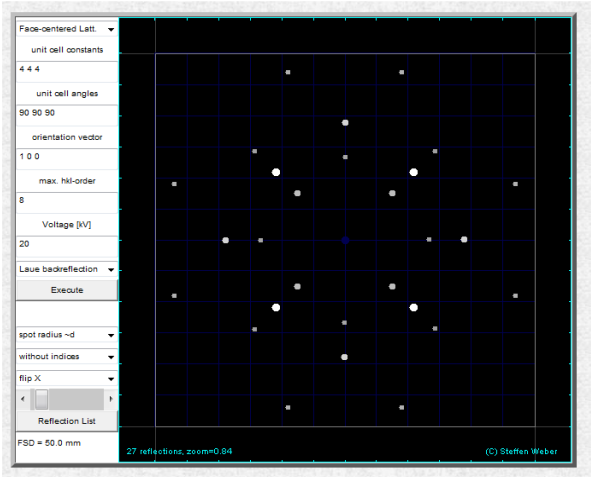
- Chromic acid with a few drops of HCl
- $(NH_4)_2S_2O_8$ 10% in water, KCN (this one doesn't work)
- Aq soln of Copper Ammonium Chloride with Ammonium Hydroxide to control pH
- $FeCl_3$, Ethanol, HCl
- Aq soln of Acetic Acid, Nitric Acid

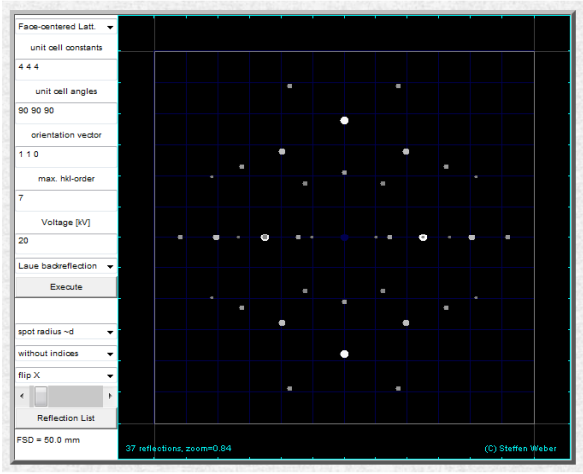
Of these, the one which was used was **(for 100 ml etchant),**
**50ml $HNO_3$ (1.4 kg/lit, ~65%)**
**25ml $CH_3COOH$ (100%) i.e. glacial Acetic Acid.**
**25ml water**
Etching can be done by swabbing or dipping in solution or electrolytically. We swabbed the specimen for 2 minutes with the etchant and washed it with ethanol and water. It was dried so as not to leave stains and observed under the optical microscope and images of its microstructure taken. Grain Boundaries are clearly visible establishing its single/poly crystalline nature.

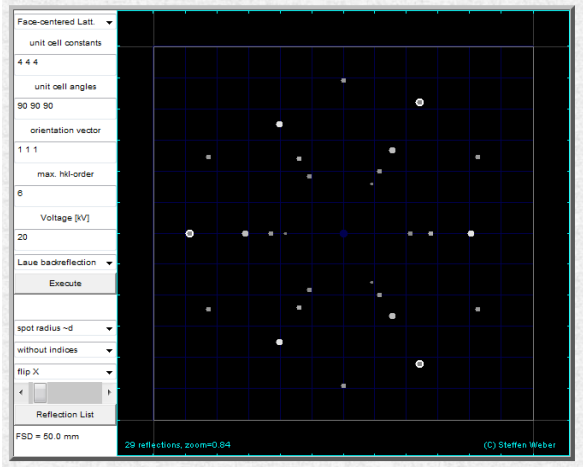
**X RAY DIFFRACTION**: X ray diffraction was performed only on the first sample as it provides no other information other than its composition. We did not perform powder diffraction. In single crystal XRD, no intense peak is generally expected as the probability for the X-rays to reflect off directly into the detector from a high symmetry plane is very low. If, coincidently it is so oriented that reflection takes place off a high symmetry plane, an intense peak is observed which overshadows other peaks. *Standard peaks for Ni and Cu:*

| ***plane*** | ***Ni*** | ***Cu*** |
|---|---|---|
| *111* | *44.53* | *43.35* |
| *002* | *51.89* | *50.49* |
| *022* | *76.45* | *74.20* |
| *113* | *93.03* | *90.03* |
| *222* | *98.55* | *95.25* |
| *004* | *122.11* | *117.09* |

**LAUE METHOD:** The Laue method in back reflection mode is immensely useful as it gives a degree of freedom above the XRD. By providing the hkl values and other parameters, the observed pattern can be compared to simulated patterns. By translating along the length of the crystal, by observing that the patter of dots doesn't change, it can be verified that the crystal is single crystalline. >>*Alongside is the simulated laue pattern for an FCC lattice in particular orientations (high symmetry planes) The 4 bright dots in the first in the form of a square, and the 3 in the third were commonly observed with our specimen but did not persist when translated, implying a small grain size* [4].



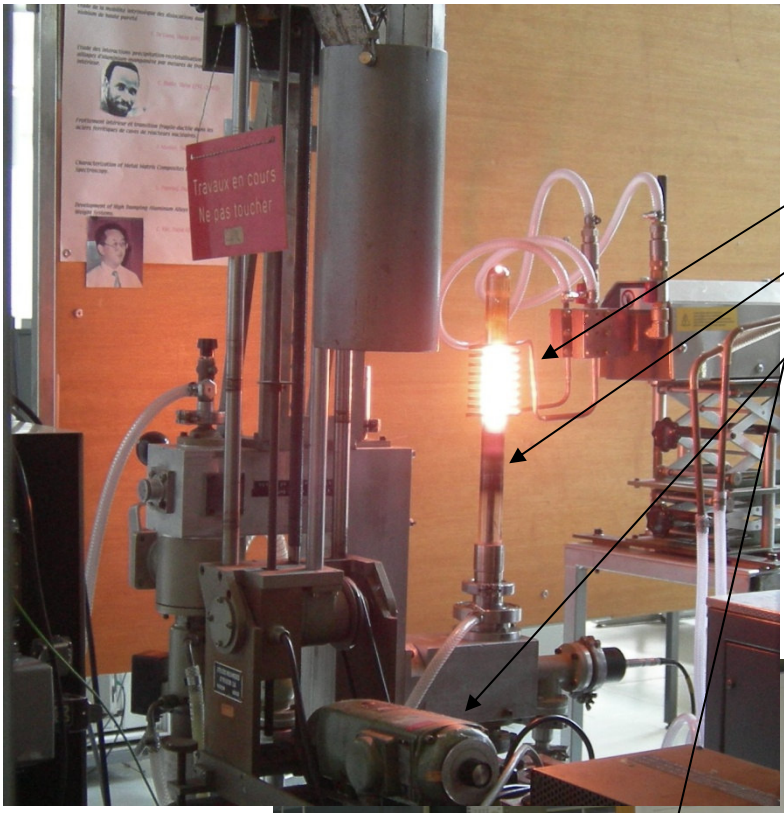




**SQUID:** The Superconducting QUantum Interference Device provides data regarding **AC susceptibility and DC magnetisation of the sample while varying temperature or field**. Traditionally, papers mention AC susceptibility v/s temperature measurements to determine the $T_c$ however this is partly because DC measurement wasn't a tool available then. It can be operated in a Zero Field Cooled (ZFC) and a Field Cooled (FC) mode, allowing a cool down to 2.5 K. The peaks of these curves and the points where they split indicates the transition from ferromagnetic to paramagnetic. Using the data available in various papers regarding **plots of Concentration v/s Critical Temperature, given the value of $T_c$ we can get a rough estimate of the composition**. The squid is a Non destructive Method, yet the size of the sample should be large enough to provide a signal but not too large that it will saturate. For our sample, Nickel being ferromagnetic, a sample of size 50mg is good enough.

**XRF:** X-ray fluorescence is a modern technique used for **elemental analysis and compositional measurements** where a sample emits characteristic X-rays on being excited by bombarding with X-rays/ Gammy rays. A highly polished (mirror finish) surface sample is required for the analysis. The XRF measurements were performed at PSI. The advantage is that it scans the entire surface providing a plot which gives an idea of the compositional gradients and variation.

# THE SETUP

The first Vertical Bridgman setup used consists of a graphite crucible mounted on a steel rod cooled by water in a quartz vacuum chamber which can achieve a pressure of $10^{-4}$ mbar. It is heated by water cooled induction coils of Copper which can have a max power of 3.5 kW. This can achieve a heating upto 1500'C but the setup is limited to a temperature of 1350 as the quartz cannot withstand much higher temperatures than that and there is a fear of the quartz tube cracking and imploding. An S type thermocouple is used due to the high temperature measurement. A motor is used to translate the crucible and the quartz tube through the coils at a minimum rate of 15mm/hour (0.25mm/min).

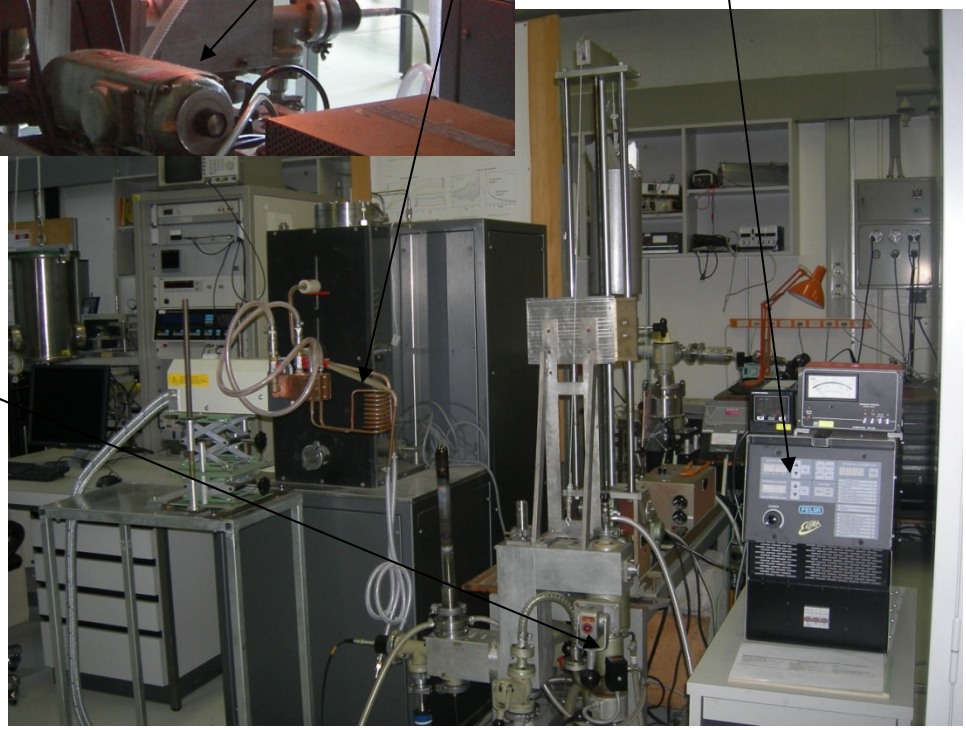



Induction coils

Quartz tube under vacuum

Motor for decent of crucible

Heating and water flow control, thermocouple reading and pressure gauge indicator.



Primary and diffusion type Secondary vacuum pumps and valves

**TRIAL 1:**

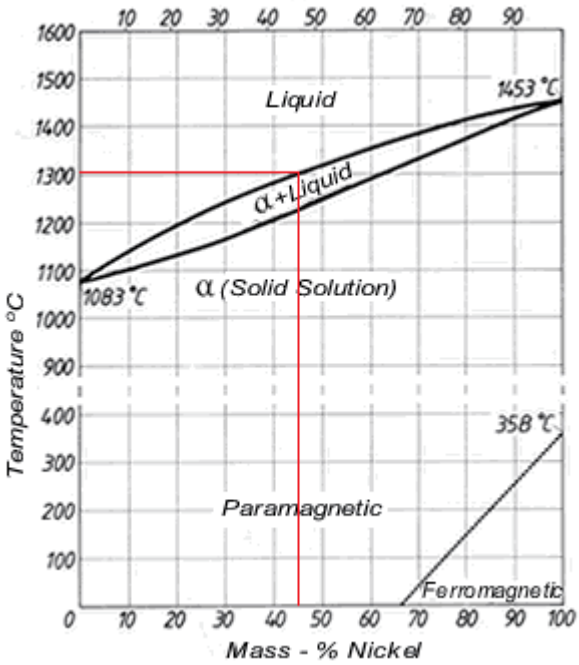
Although it was guessed that Ni alloyed with Graphite, as a preliminary trial, it was decided to use a split Graphite crucible of ID 2mm. Cu and Ni powders were weighed out and filled into the crucible.

Cu : -40+100 mesh, 99.5% metal basis. 55 wt%

Ni : -50+100 mesh, 99.7% metal basis. 45 wt%

As per the phase diagram it can be seen that the melting point at the required composition is 1300'C. Thus, the powders are heated upto 1340'C to ensure that it in completely above the liquidus and thereby provide no sites for nucleation to occur.

The decent rate is set at 0.5 mm/min.

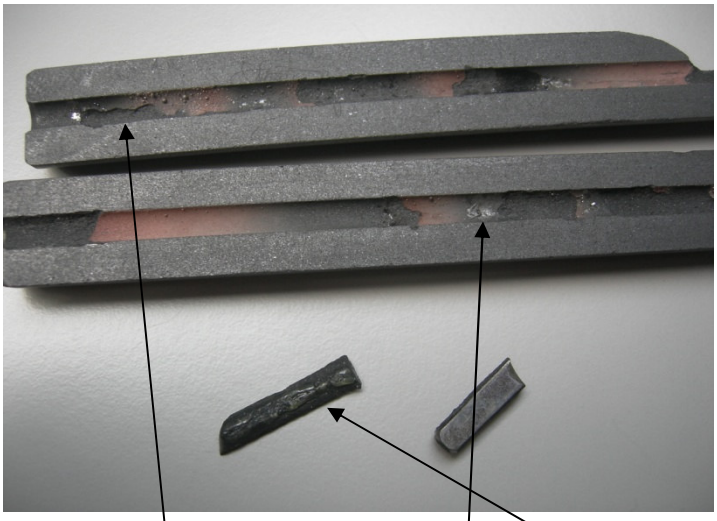


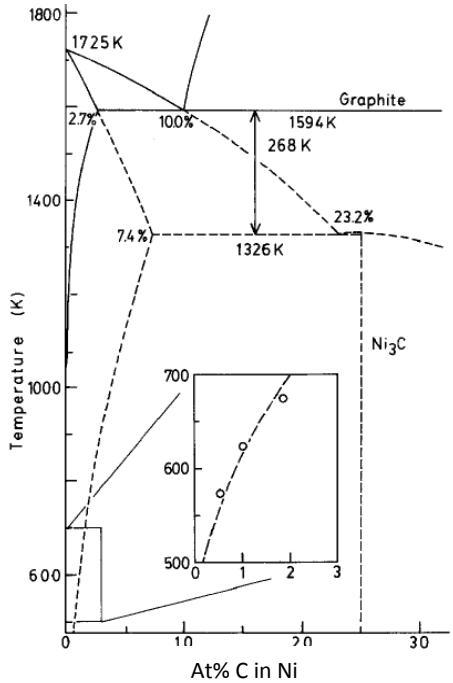

**OBSERVATIONS:**

As expected, there was a lot of **Nickel Carbide alloying** which made it difficult to extract the formed specimen. On being forced open, it was seen that the inner walls of the crucible were destroyed with a lot of Copper deposition and Nickel alloying. The surface of the specimen had a layer of carbide formed. The sample was polished and etched and photographs of the microsturcture taken. Although grains are not visible, there is carbide precipitation in the interior.

*>>As can be seen from the Ni-C phase diagram, C can dissolve upto 2.7% in Ni* [5].

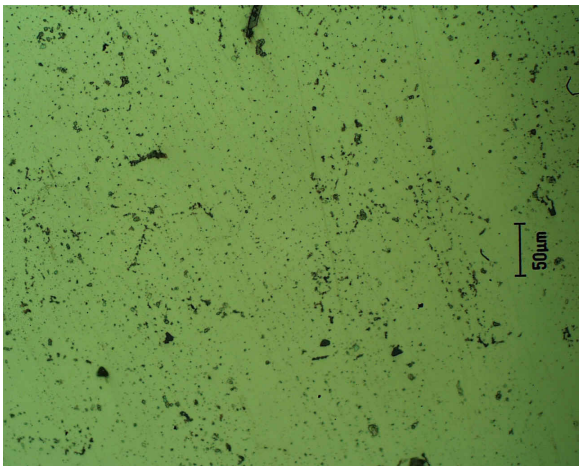
*C is negligibly soluble in Cu* [6].

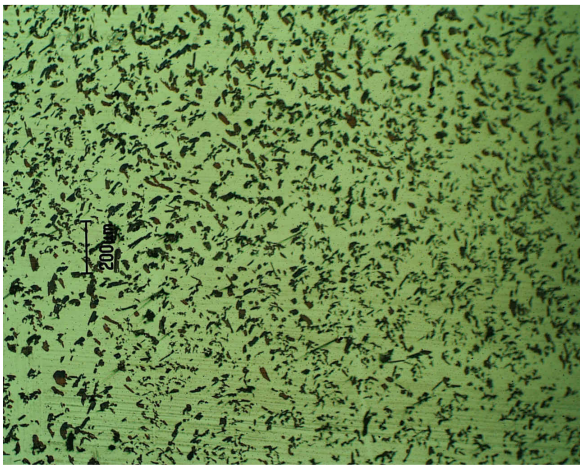





*^^The graphite crucible and crystal specimen. It is clearly visible that the inner surface of the crucible is corroded and Nickel is alloyed into it. The surface of the sample shows heavy graphite alloying.*

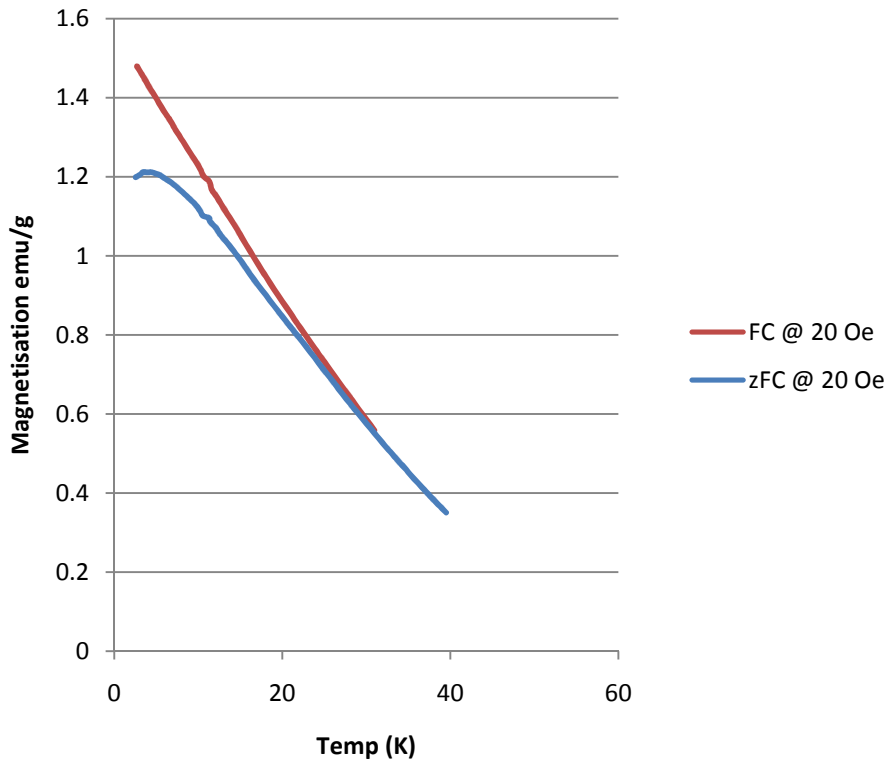
**Polish and Etch:**




^^*After polishing and etching, certain areas were free from possible Carbide alloying while other regions had a lot of "flakes" visible. However no grain boundaries were visible.*

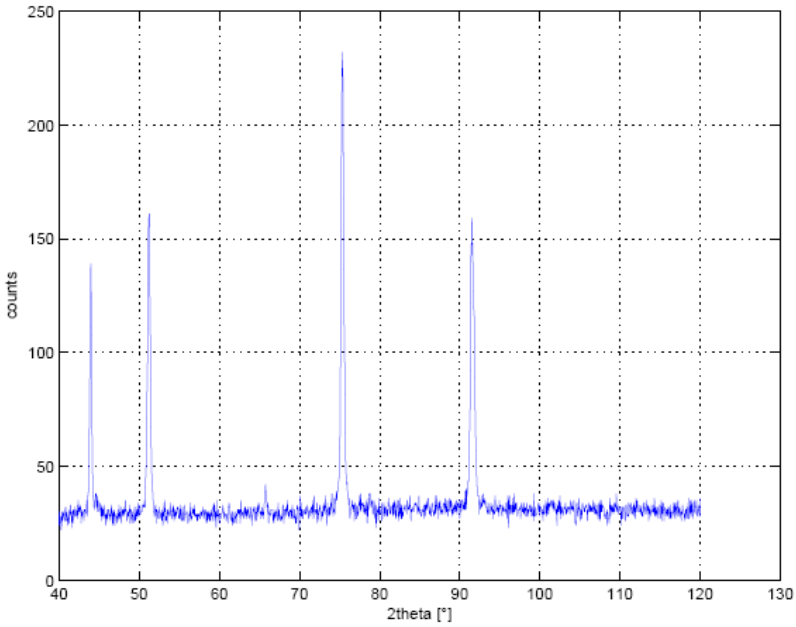
**SQUID:** DC Magnetisation (emu/g) v/s Temperature (K)

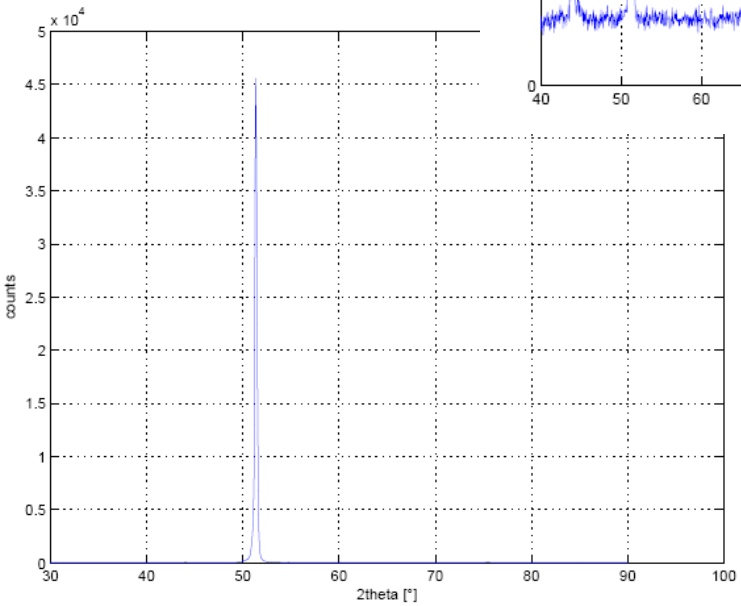



^^*The peaks of the FC and ZFC curves at ~5K indicate a Cu Ni ratio of 45-46 at.%* [7,8]. This roughly corresponds to a 43-44 % Ni by weight. This decrease can be attributed to the Nickel that has alloyed with Graphite. The decrease in Magnetisation is a result of ferromagnetic to paramagnetic transition in the alloy.

**XRD:**

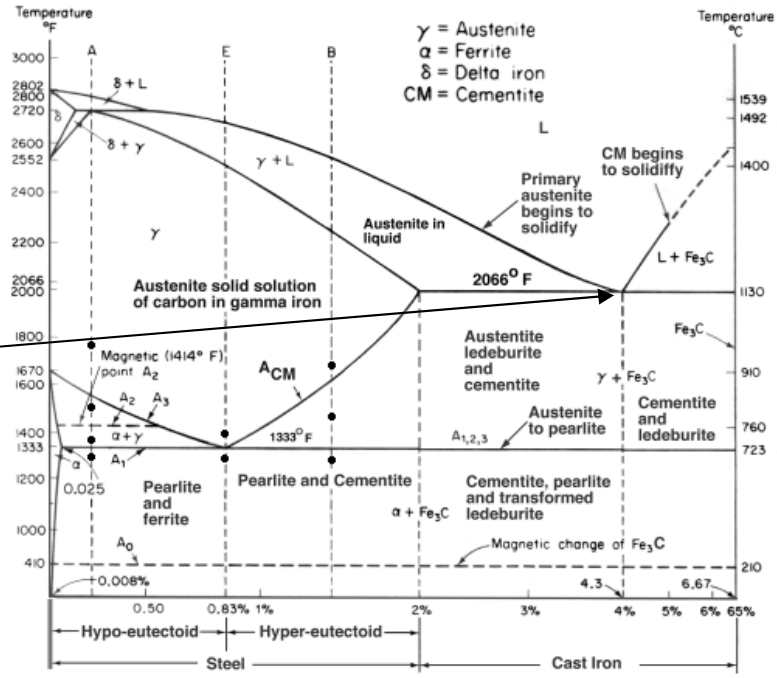
*>> The peaks seen are that of 111, 002, 022, 113. However the intensity values are not low when compared to a powdered sample. This indicates a slightly single crystalline nature.*



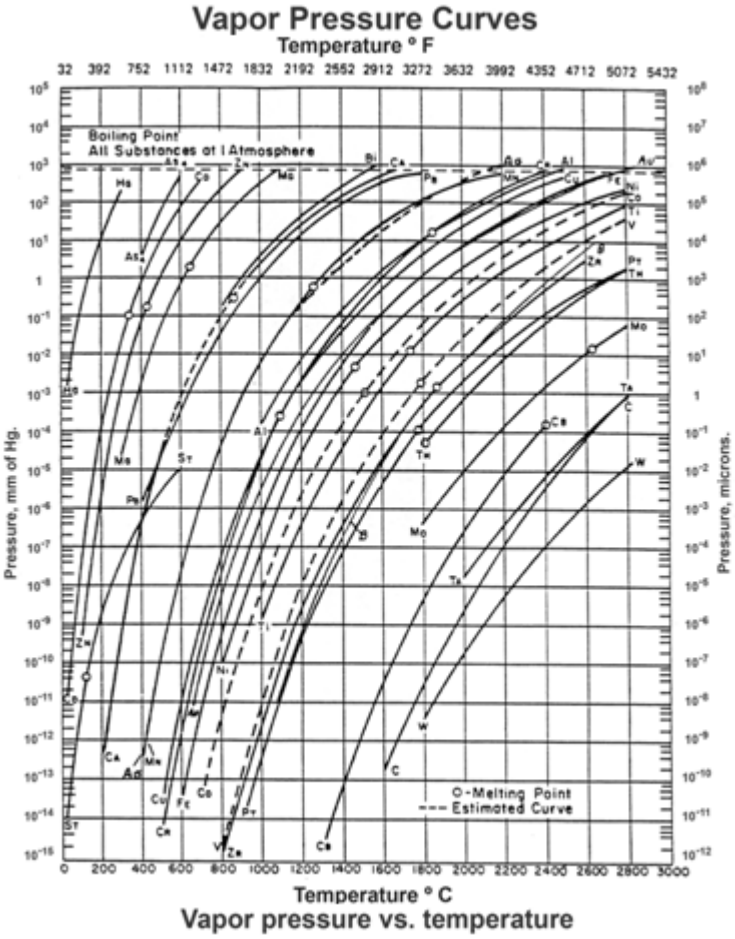

*<< In this measurement of the same sample a very high intensity is recorded for the 002 peak. (4.5 x $10^4$ counts as compared to 200 in the previous measurement.) By chance, the crystal may have been oriented and placed in with reflections occurring from the 002 plane (Bragg's law satisfied). This further shows its single crystalline nature.*

Modification to the machine: Going to 1300'C, the steel holder of the crucible completely melted. The reason for this is that, in the presence of the graphite crucible, *Carbon and Iron form a eutectic which melts at 1130'C* [9]. The steel base was then replaced my Molybdenum which melts at a much higher temperature.



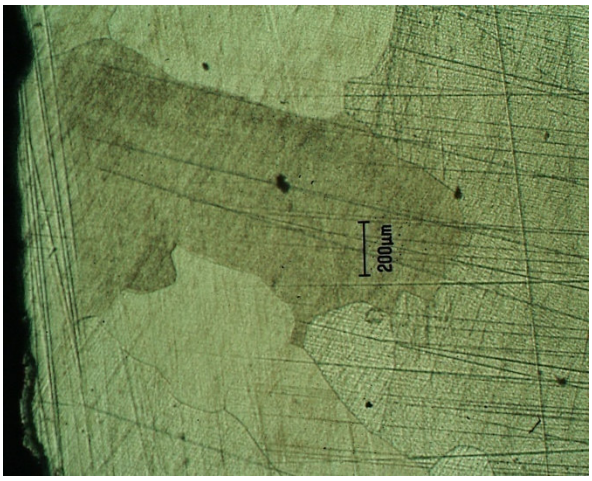
**TRIAL 2:**
Subsequent to the first trial, it is realised that it is not worthwhile to use Graphite Crucibles directly. Hence, Alumina tubes 10mm in diameter and 100mm long are used. They contain the powder and are placed inside a graphite crucible because graphite conducts, and is hence heated up by eddy currents.

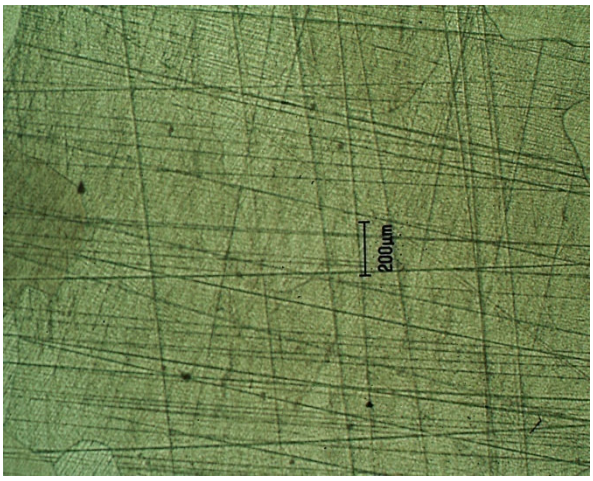
**One limitation of this apparatus is that the quartz tube is under vacuum. This leads to constant evaporation of the lower melting component of the alloy, Copper.** *The vapour pressure of Cu ($10^{-2}$ mmHg) is 30 times the vapour pressure of Nickel ($3x10^{-4}$ mmHg) at 1300'C and 1atm* [10]. At the low pressures that exist in the quartz tube, this value of Cu vapour pressure would only be higher. Thus, it is sought to cover the crucible to minimise the evaporative loss. We tried an alumina lid placed on top but that cracked due to possible thermal shock. It was also tried with a graphite cap but by the time the trial got over, the cap had popped out due to the overpressure of Copper and Nickel inside.

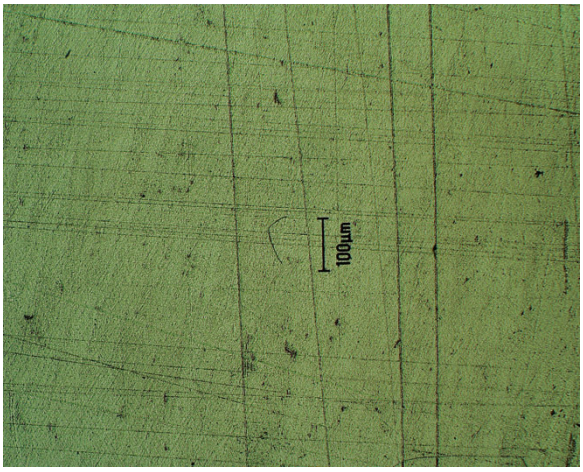



**OBSERVATIONS:**
The second trial was conducted without a cover and lead to huge losses. Starting out with 13g of weighed powders, the final sample obtained was a mere 5 grams. There was a lot of copper re-condensation on the walls of the crucible and more on the quartz tube due to the cooler surface.

Polish and Etch:





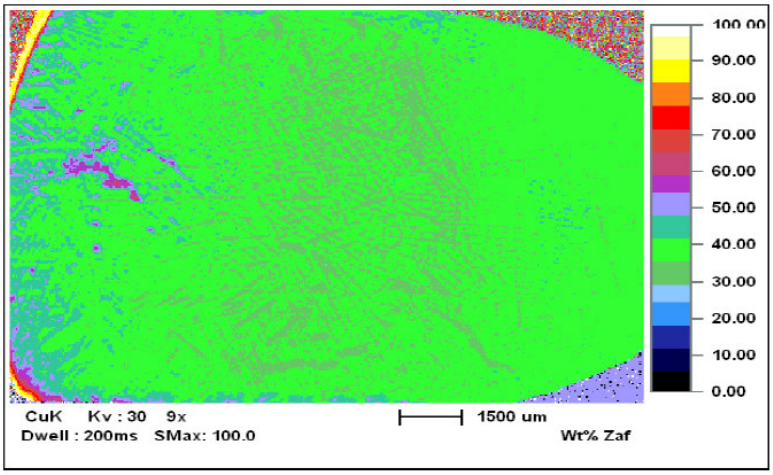

*<<As can be seen from the images, although not polished well, the grain boundaries in the first one are clearly visible. It was observed that there are columnar grains at the side and larger grains at the centre as seen in the other two images.* This can be compared to the sort of grain structure obtained in metal castings [11]. It also helps explain what is possibly happening. Note that our sample for this trial is much thicker than the previous trial. **If the sample cools from the side too, instead of from the bottom alone as we would require it, columnar grains to the centre would develop.** This leads us to conclude that for the given diameter of the sample with the material that we are using; our rate at which we pull down the samples is too high (0.5 mm/min). Owing to this fast rate, nucleation starts at the boundaries in accompaniment to the bottom.

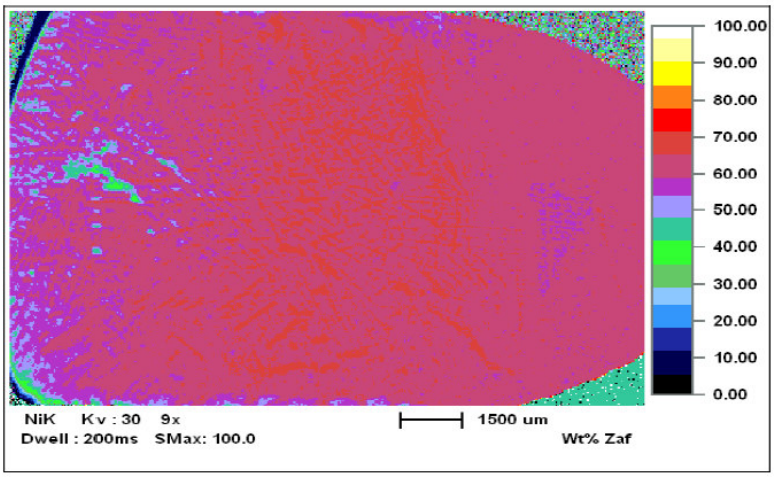
**XRF:** The sample was sent to PSI for compositional analysis. These are the results.

| Element | Wt % finally | Wt % initially |
|---|---|---|
| Ni | 56.19% | ~45% |
| Cu | 43.81% | ~55% |

Thus we see that immense amount of material has been lost with Cu having a higher tendency to evaporate.

*>>The composition gradient scans are provided alongside. It is visible that the % of copper as we move to the left of the sample (away from the pointed end) is increasing. At the very top, a layer of almost pure copper is obtained (seen in bright yellow). In the lower figure, the % of Ni goes on decreasing towards the left finally becoming almost nil (dark blue colour visible). Also the centre shows a higher Ni concentration. The cause of these axial and radial gradients is macro alloy segregation and will be explained later.*



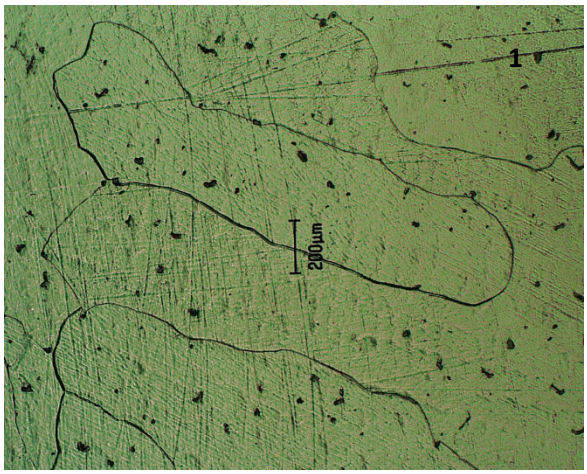



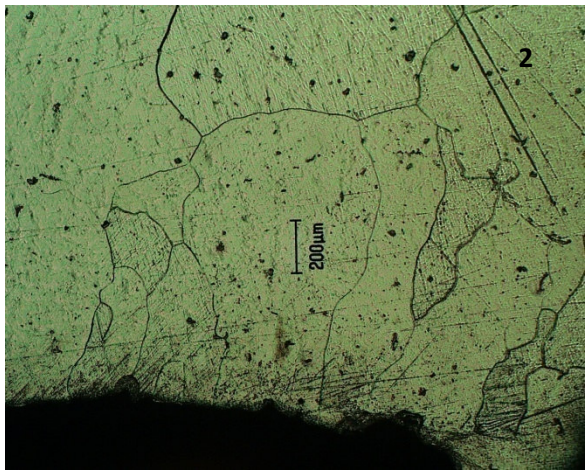

**SQUID:** The squid measurement did not give a meaningful result. The value of magnetisation was high (2.7 emu/g) and did not decrease in the range measured. This tells us that the composition is not close to where we started from, owing to a lot of evaporation.

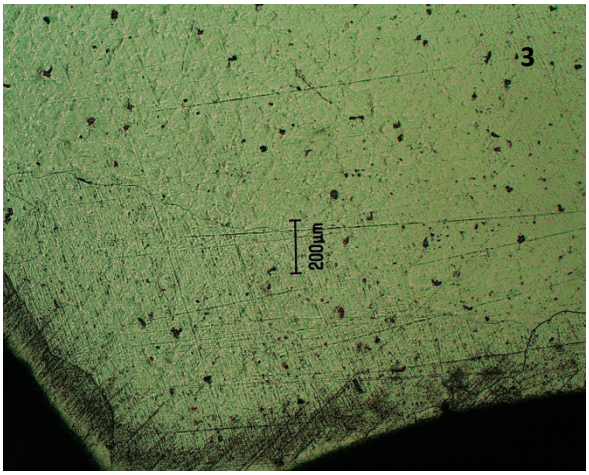
**TRIAL 3:**
In the second trial it was realised that a cap is essential to minimise evaporation to some extent. An air tight cap is not an option because the difference in pressure inside (due to vapours of Cu and Ni) and outside (vacuum) will force the cap out or may lead to an explosion. Hence something which did not let the pressure inside build up however also provided the Cu with a surface to condense on within the crucible was required. What finally worked for the third trial was stuffing the top of the crucible with carbon fibres. This allowed pressure to equilibrate in case of a pressure build up but also provided a surface for re-condensation of vapours. This protected the pumps and the quartz tube greatly and improved the sample to some extent but the copper re-condensed on the crucible walls, it did not go back into solution. Thus the change in composition still occurred.

**OBSERVATIONS:**
The procedure followed for this trial was a slow heating to 1300'C and cooling followed by a reheating to 1330'C and then the descent was carried out. The first step was intended to homogenise the constituents of the alloy, while the second one was to cause the actual single crystal nucleation. The recorded loss in weight was about 0.2g in the 8g sample. But there were a lot of droplets of copper on the wall of the crucible which were not ultimately part of the sample. The final sample lost 1.5g, most of which was copper.

**Polish and Etch:**



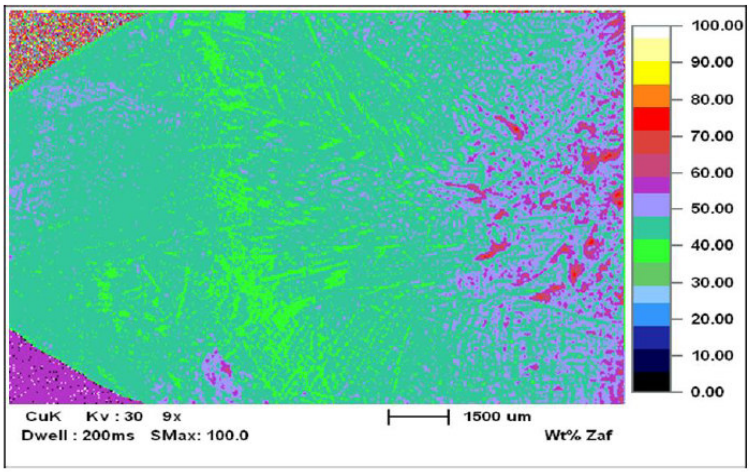

*<<(1, 2) show the same elongated columnar grains at the side of the crustal in a vertical section while at the bottom of the sample large grains are observed (3).*

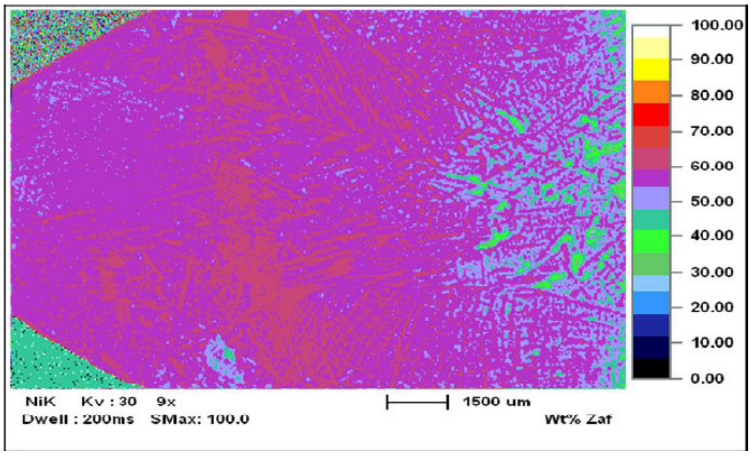
This again points to the fact **that translation speed is too high**. Different papers which talk about growing inter-metallic crystals talk of speeds of the order of 0.5 – 2 mm/hour.

Another contributing factor could be **nucleation sites provided by the crucible walls**. The inner surface of the crucibles is too rough and hence new crucibles were ordered to improve the overall quality. 15mm OD and 105mm tall Alumina crucibles with a point bottom were ordered from Almath Co., UK.

XRF: The sample was sent to PSI for analysis. These are the results.

| Element | Wt % finally | Wt % initially |
|---|---|---|
| Ni | 52.79% | ~45% |
| Cu | 47.21% | ~55% |



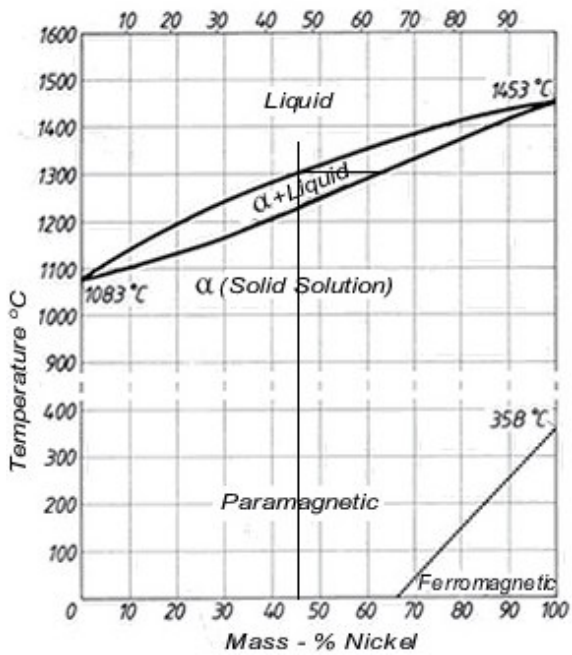



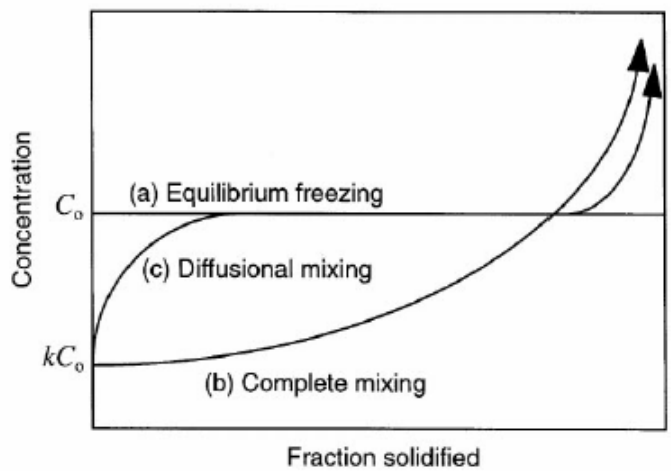

We see that although the change in composition is not as much as in the previous sample, there is still a significant change and this can be attributed to the loss of 1.5g, most of which is Cu.

*<<Exactly like the previous sample we observe that we have strong composition gradients, axial as well as radial. Copper is continuously increasing to the top, finally ending in a layer of 100% Cu (not visible well in this image) while Ni decreases.*

The reason behind this is **macro alloy segregation** as is a result of the fact that this alloy melts incongruently [12].

A look at the Cu Ni phase diagram reveals that at high temperatures Cu and Ni form a completely miscible melt. Cooling a melt of composition say 45% Ni (as that is the composition we are interested in), proceeds until the liquidus is reached when a solid of composition 62% separates out. Since the solid has a higher Ni content now, the melt would be deficient in Ni and richer in Cu. If convection currents are present in the melt, which are almost always there in the case of induction heating due to electromagnetic stirring, the composition of the melt homogenizes slowly to a different composition. If equilibrium exists in the melt, the liquid will follow the liquidus composition. In the case of casting, the composition of the solid also follows the solidus composition to end up at the required composition due to diffusion of the Cu from the liquid into the solid and Ni in the opposite sense across the solid-liquid interface. But in our case, the solid is not encapsulated by liquid as it is directionally solidified and very little change occurs in the solid composition. Hence, we end up with a **continuously changing axial composition**.






*<<The kind of composition obtained depends on the transport mechanisms operating within the melt as well as external conditions* [13].

If the alloy is cooled extremely rapidly (**quenched**), there is no time for diffusion of species and we do not obtain a composition gradient (a) if the melt was homogeneous. In this case we end up with a homogeneous but polycrystalline sample. If, as discussed, **complete mixing** occurs due to either convective currents or mechanical stirring due to rotation such as in Czochralski, we end up with strong concentration gradients as shown by the curve (b). If we manage to establish such conditions that **only diffusion** across the solid liquid interface and in the region just above it exists but there is not stirring in the melt we get transients at the start and end but homogeneous composition in between (c). Long rods can be prepared and their ends cut off.

Some of the **methods to ensure a homogeneous composition** are as follows:

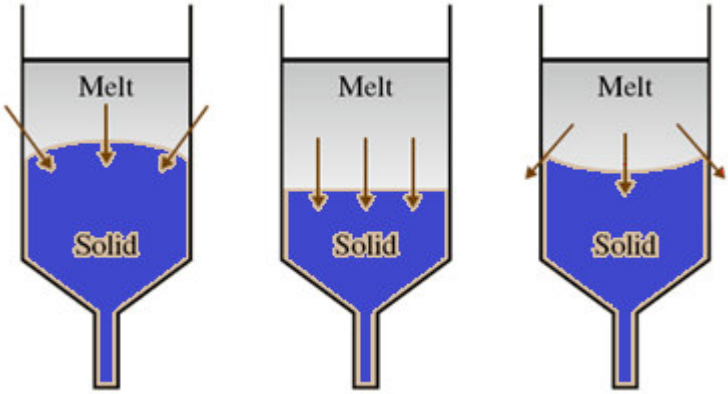
1. Have a **feed rod** which continually supplies the molten melt, **enriching it with the constituent which movies into the solid**. As the composition of the melt is stable, a crystal of fixed composition will be obtained [14].
2. Perform the experiment in space. Performing the experiment **in microgravity or a zero-gravity atmosphere removes the possibility of Convection**. Convection arises mainly due to thermal gradients which give rise to density differences and this leads to convection. Without gravity, there is no motion due to the difference in densities. The gradients due to electromagnetic stirring can be avoided by using a resistance furnace instead. (Experiments in such atmospheres ARE conducted.) Other ways to reduce convection are the application of magnetic fields and baffles in the melt.
3. Use Floating Zone method. This is probably the simplest method though only minimises the effect, It cannot be completely avoided. The procedure is as described section above dealing with Crystal growth techniques. The principle which prevents the solid from re-equilibrating as in cast solidification which leads to the composition gradients is used. In floating zone, both the rods at the top and bottom are solid (and cooler) and hence cannot homogenize. Only the thin zone in between which is melted has to homogenize, effectively the **upper and lower rods change very slightly to account for the change in composition of the thin floating zone**.

The reason why we cannot adopt the last method is, as stated before, that Copper being highly thermally conductive leads to a large melted zone (which anyway defeats this purpose) which cannot support itself between the two rods.

4. The speed of growth [12].

As already discussed, a **fast growth allows lesser time for homogenization of the melt. A slow speed ensures single crystallinity but also enhances composition gradients**. Hence, the drawing of the crystal must be done at the fastest rate which ensures the formation of a mono crystal. (Besides, it also saves power)

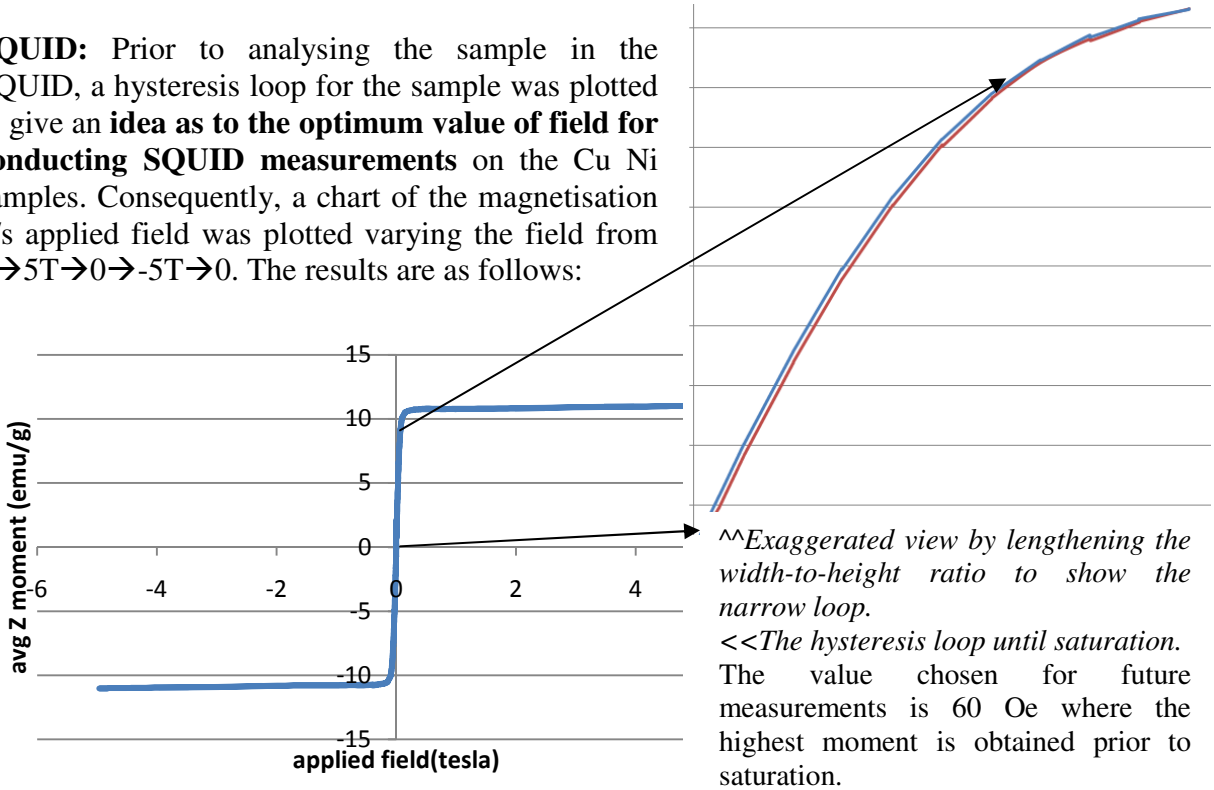
**Radial Composition gradients** are a result of **Interface shape**. The interface shape can be concave, convex or planar wrt to the solid and represents the Melting point isotherm. A convex Solid-Liquid interface wrt to the solid is created when the temperature gradient is low and heat extraction is primarily through the already solidified crystal. A concave interface implies that heat extraction is primarily through the walls of the crucible. [15]




*Interface shapes. The arrows indicate direction of heat flow>>*

A planar interface is most desired for a uniform radial layer without composition gradients. This can be obtained by rotating the boule at such a speed that the horizontal components of the centrifugal and surface forces cancel each other out.

**SQUID:** Prior to analysing the sample in the SQUID, a hysteresis loop for the sample was plotted to give an **idea as to the optimum value of field for conducting SQUID measurements** on the Cu Ni samples. Consequently, a chart of the magnetisation v/s applied field was plotted varying the field from 0→5T→0→-5T→0. The results are as follows:

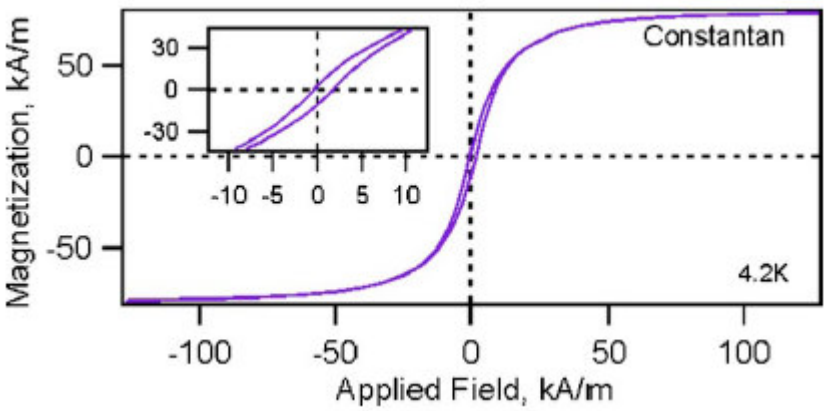


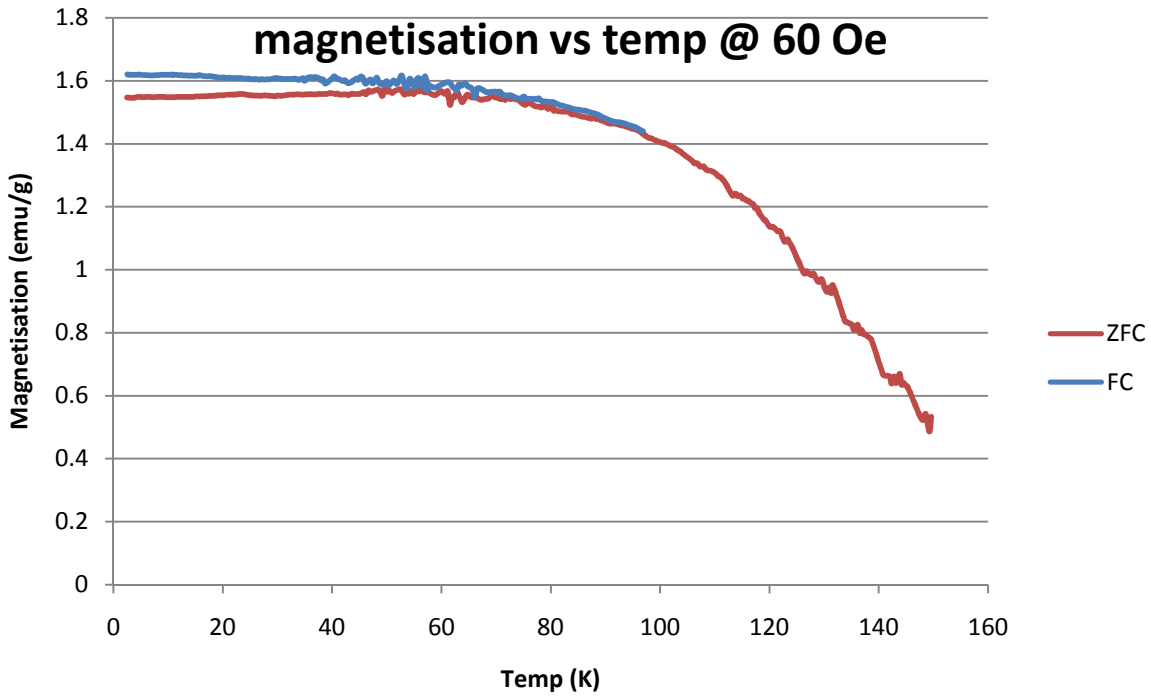

^^*Exaggerated view by lengthening the width-to-height ratio to show the narrow loop.*

*<<The hysteresis loop until saturation.*

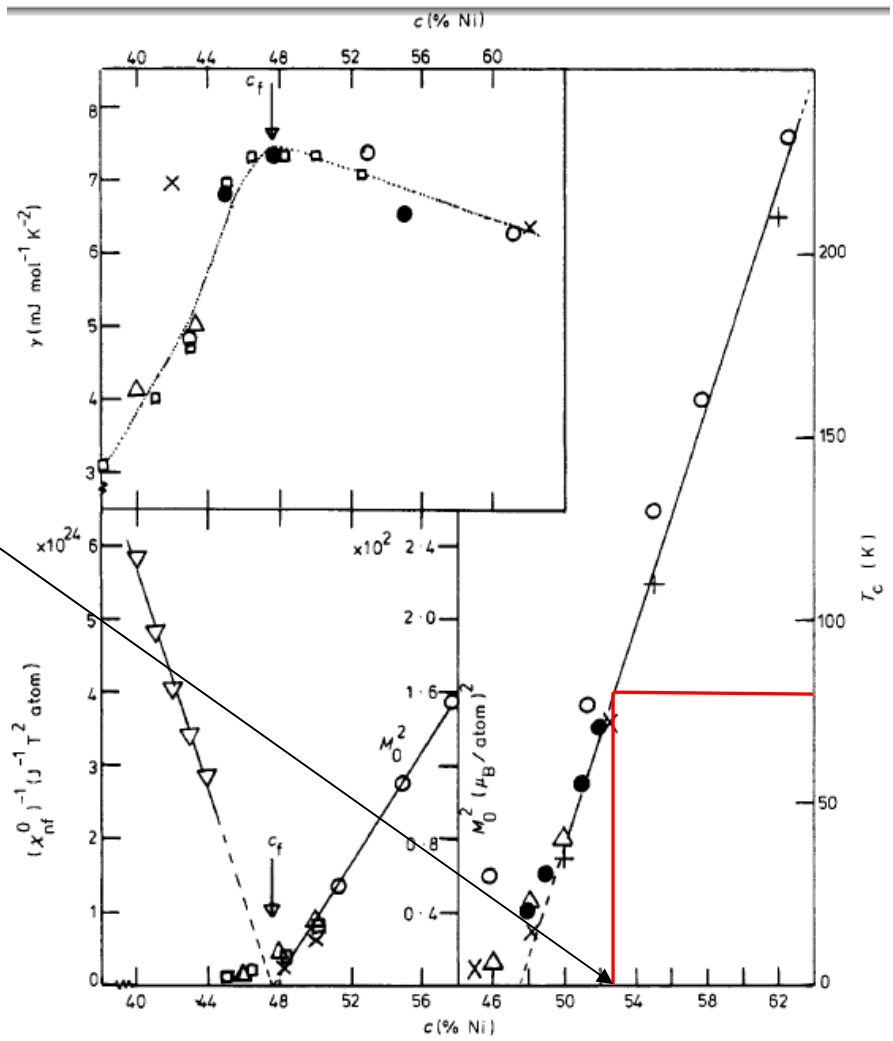
The value chosen for future measurements is 60 Oe where the highest moment is obtained prior to saturation.

The obtained result accurately matches the standard hysteresis loop [16] for constantan which more so confirms that our SQUID readings are accurate to a degree and reliable.





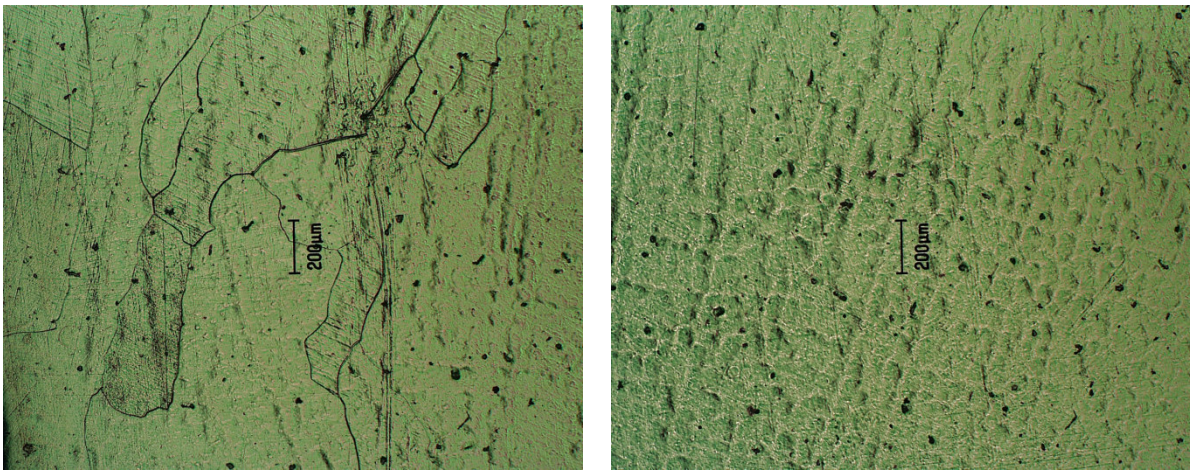

The split between the ZFC and FC curves gives the Critical Temperature for change of ferromagnetism to paramagnetism. The split is observed at ~80K and corresponds to a composition of approximately 52-54% Ni [8] and this corresponds well with that of the XRF, 52.79%.



**TRIAL 4:**
Before it was possible to conclude that it was really the above effect of which led to the composition gradient it had to be established that it wasn't due to something else like improper homogenization. Thus for the fourth trial, 13g of powders were taken and melted and cooled back down without pulling a crystal. This was reheated to 1340'C, held for a while and cooled again. This was to ensure proper homogenization of the constituents of the alloy. For the third time the obtained polycrystalline sample was heated to 1330'C and then it was made to descend at a rate of 0.25mm/min which is the slowest this setup can achieve.

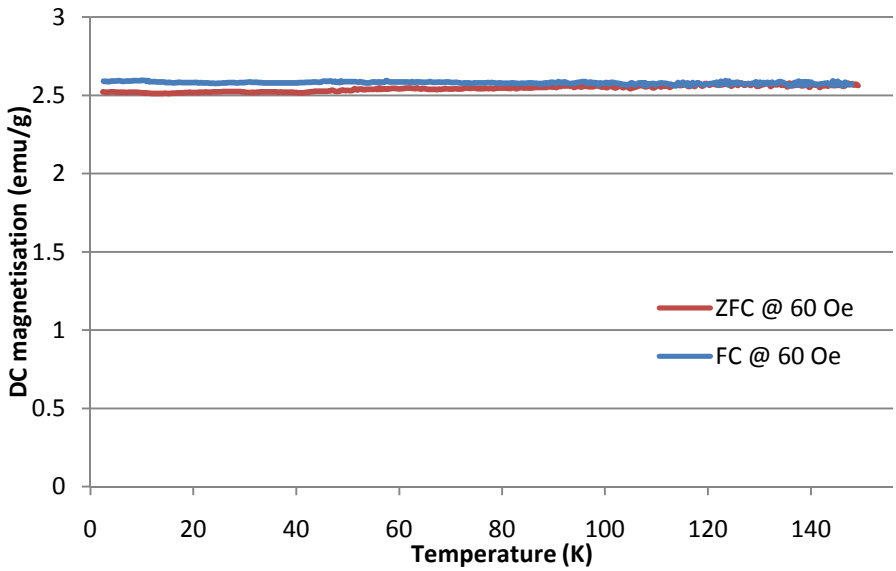
**OBSERVATION:**
The sample obtained was still very polycrystalline and a layer of copper was again obtained at the top. It is interesting to note that this layer is not because of re-condensation of vapours of copper which evaporate. The vapours which are within the crucible re-condense almost exclusively on the walls of the crucible and the carbon fibres at the top as these are the cooler regions and can be seen as tiny droplets. The 1mm layer of copper **confirms that convective currents exist within the melt** and the molten pool constantly gets enriched in copper, finally ending at the top.

**Polish and Etch:**




^^*Grains are observed and areas of larger grains are at the centre as expected.*

**SQUID:**



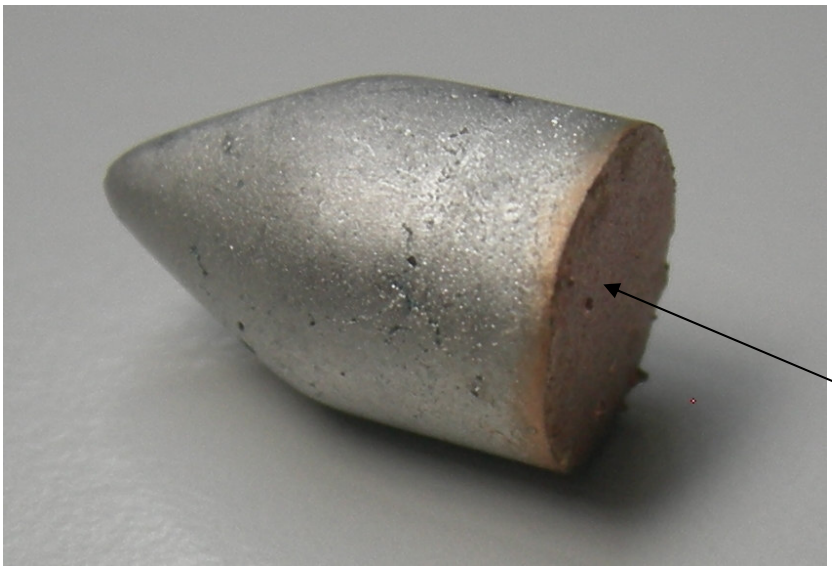

*<<As a result of 3 meltings before drawing the crystal, immense amounts of Cu have gone out of the crystal making it Ni rich and pushing the $T_c$ beyond the scanned temperature range. If we assume that that the transition occurs immediately after this region (i.e. 150 K) as the curves split just there, then to the estimated composition according to* [8] *is 58%!!*

# THE NEXT FEW TRIALS

The next few trials were aimed at investigating the problems that plagued our crystal growth process and circumventing them if possible.

There are two distinct steps to this process. The first is establishing a process to obtain a single crystal. The second is to be able to maintain the composition of the alloy as desired. Ending up with an overall accurate composition is a task because the composition gradients cannot be avoided. The speed of descent while growing a crystal is a double edged sword which, on one hand improves the single crystalline nature of the sample as it decreases, on the other hand enhances composition gradients as it allows sufficient time for complete mixing to occur. But there can be no compromise on the speed. The best that can be done is to choose the fastest speed which gives a single crystal. Since the composition gradient is a necessary evil in this case, we can at least aim at not deviating too much. This can greatly be curbed by reducing evaporative loss of copper.

The other issue is that the **entire setup is under vacuum** which causes a very high evaporation of Copper (about 30 times that of Nickel). Each constituent must maintain a partial pressure of its vapour in equilibrium with the molten liquid. Due to the vacuum, this vapour is constantly removed causing more and more of the material to evaporate. Thus an overpressure of Argon or any other inert gas would greatly reduce the evaporative loss. The apparatus used does not have a provision for Argon overpressure. If a connection of Argon is even made, it would be dangerous to take the apparatus to 1300'C as **Argon will ionise** and conduct and due to the induction heating will also achieve a temperature of 1300'C. Since the quartz tube is in direct contact with the plasma, it too will get heated up to 1300'C which is the limit of its safe operation temperature and there is a very high risk of it melting and leading to an explosion. Thus with a quartz tube exterior, Argon overpressure is a definite impossibility.

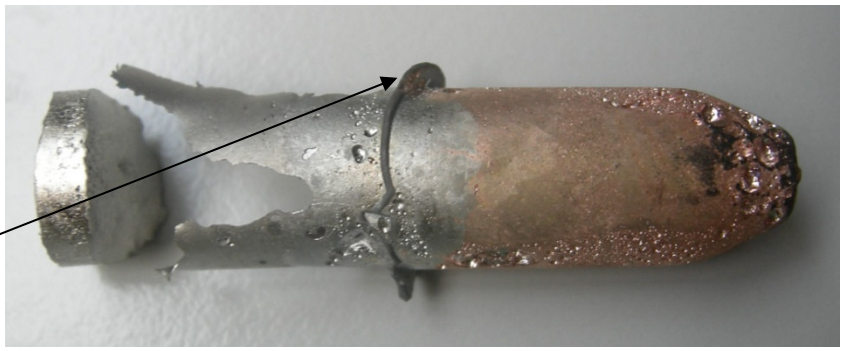


*<<The obtained sample. The layer of copper formed at the top confirms strong convective currents leading to macro alloy segregation.*

The **speed that this apparatus** can go to is a minimum of 1mm/4mins or 15mm/hour. We have seen that with the 10mm diameter crucibles, this speed is too fast and single crystals are not obtained. We would probably require much slower speeds of 0.5mm/hour or so to obtain single crystals. If we aim at thicker crystals, even slower speeds may be required.

Prior to the next trials, it was thought if it would be possible to modify the existing setup by adding a set of gears to achieve the required speeds. This modification was possible; however there was no solution to the vacuum issue. In the interim, trials were conducted with newer ideas, such as not mixing the powders but having Cu at the bottom and Ni at the top. The first

sample seemed fine and another one was prepared, but with larger amounts (net wt. 20g) and over-stoichiometric in Copper by an amount equal to the change in percentage of the previously observed samples. This did not work because the amount of powder filled the entire length of crucible and extended outside the induction coils. The Nickel powders were outside the coils and did not melt while the Cu powders melted and the volume reduction was significant. Ni did not fall down and become a part of the melt. It remained stuck to the top portion of the crucible walls and an inhomogeneous sample with voids was obtained. The crucible cracked due to either thermal shock or due to the difference in expansion coefficients of Cu Ni and Alumina.



*>>The in-homogeneity is visible with different shades of Cu and Ni. Large voids were formed. The fin like structure at the side is the molten metal which had flown in the crack in the crucible.*

Another perennial issue noticed is the fact that when starting with powders, a blue coating is obtained on the inside of the crucible. It can safely be assumed that since the **surface to volume ratio of the powders is high, they are very reactive and take up oxygen from the Alumina crucibles to form Copper oxide**. The powders themselves would also have their surfaces oxidised and this leads to contamination. A solution to this is to use crucibles of Tungsten and start from pellets or chunks of Cu Ni rather than powders.

*<< The inside walls of the broken crucible after a sample has been prepared in it. The droplets on the walls are that of Cu which has recondensed from its vapours on cooling.*

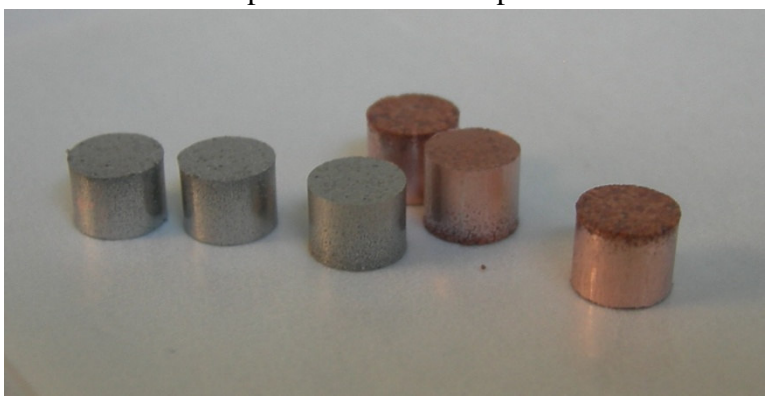
*<<The bluish colour on the walls is as a result of Copper oxidation using Oxygen from the Alumina crucible.*

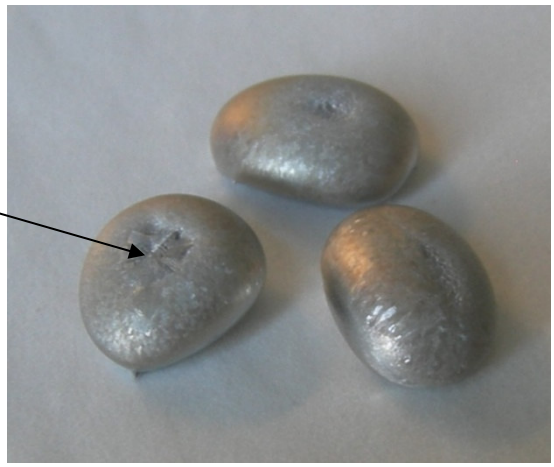
Keeping these problems in mind, the next trial was done using the vertical Bridgman setup at the University of Geneva.

# TRIAL AT THE UNIVERSITY OF GENEVA

Prior to describing the setup used, I would like to mention the changes that were attempted at while preparing the crystal.

Firstly, this sample does not have powders as its precursor. As previously mentioned, the intention here is to minimise contamination and oxidation and reduce evaporation too. Moreover, if it is **decided to use chunks of Cu and Ni** in the setup, they must be made from the powders in the arc furnace. Although the arc furnace operates in an overpressure of Argon to minimise oxidation, it still occurs in the case of powders. Another issue faced, which is more critical, is that the powders fly when they are struck by the arc in the furnace. This leads to variation in composition/ and also spoils the inside of the furnace. Therefore, the **powders are first compressed into pellets** of roughly 1g each using a hydraulic press with a 2 ton load. These pellets are then **melted into chunks in the arc furnace**. A good vacuum is prepared in the furnace first which is followed by washing with Argon twice. Finally, the melting is done in an Argon overpressure to obtain chunks about 6g each which are stiochiometrically of the required composition. It was attempted to break these chunks into smaller pieces since they were now homogeneous, however the alloy is ductile due to the presence of copper and not brittle to be smashed. The chunks were directly fed to the crucible.





^^*The compressed pellets of Cu and Ni*

>>*The formed chunks. The puckered mark at the top is a collection and agglomeration of impurities that melts at a temperature higher than the alloy (>1300'C) which as floated to the top. The purity of the samples was ~99.5% for Cu and 99.7% for NI. Also possible are the particles of oxide layer formed at the surface of powders.*

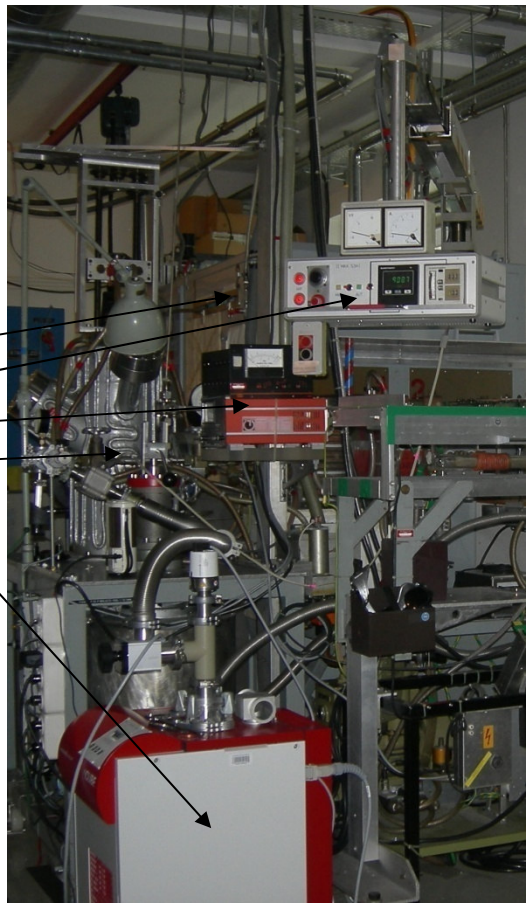
Secondly, the entire process of drawing the crystal was carried out **in an overpressure of Argon**. This greatly reduced any evaporation of copper.

Thirdly, the **descent rate was kept low**. This was to ensure that a good single crystal is obtained. In case of polycrystallinity, the descent rate would have to be slowed down further. This is a possibility as a much thicker crucible is used and as a rule of thumb the speed of descent is inversely proportional to the crucible diameter due to the increased nucleation sites and larger radial gradients which make nucleation from the walls more pronounced.

What **couldn't be avoided is an RF induction furnace**. It is an advantage in most situations but in this case an induction furnace leads to convection currents. This could not be avoided due to the setup available.

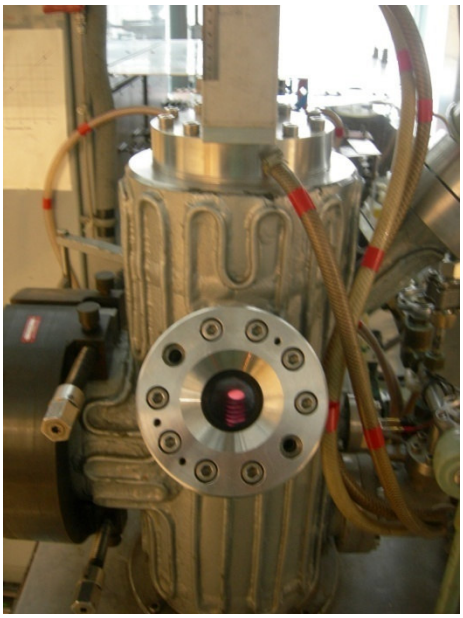
**THE SETUP:**

It is a self-built apparatus which is capable of performing Czochralski, Zone refining as well as Vertical Bridgman. The trial can be conducted in either vacuum or an overpressure of an inert gas to avoid evaporation. It consists of a water-cooled Steel exterior with a wide variety of induction coils for heating available in different diameters and number of turns. It can have a traversing speed as slow as 1µm/hr and allows rotation of the sample. The power which can be supplied for melting is upto 40kW. Different thermocouples are available and can be used depending on the application. The melt can be magnetically levitated. This setup addresses most of our previous concerns, primarily those of a slower descent speed as well as availability to conduct the trial in Argon.

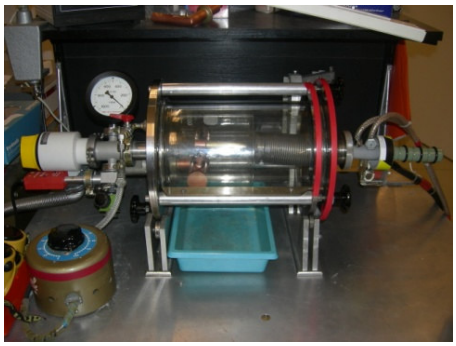


*>>The generator setup*
*The temperature sensor*
*Pressure gauge*
*The water cooled steel exterior*
*Vacuum generator*

The sample chunks are put inside the Alumina crucible which is then placed in a Zirconia flat bottom crucible for support which has a hole drilled in at the bottom for the thermocouple to pass through. The Tungsten-Rhenium thermocouple sits at the tip of the alumina electrode bottom and is capable of measuring temperatures upto 2000'C. The sample weight is 24g and it is expected that when melted will fill up the 10mm conical bottom and an additional 0.7mm of the cylindrical portion. The apparatus is kept under a good vacuum for a day and flushed with Argon several times prior to the actual trial. A pressure of 3 bar is established and the sample gradually melted and taken to a temperature of 1360'C. After a dwell time of 20 minutes the descent is started at a speed of 2.3mm/hr.



*>>The arc furnace*



*<<The induction furnace of the setup with the water cooled exterior. The glowing sample crucible is visible with the induction coils.*

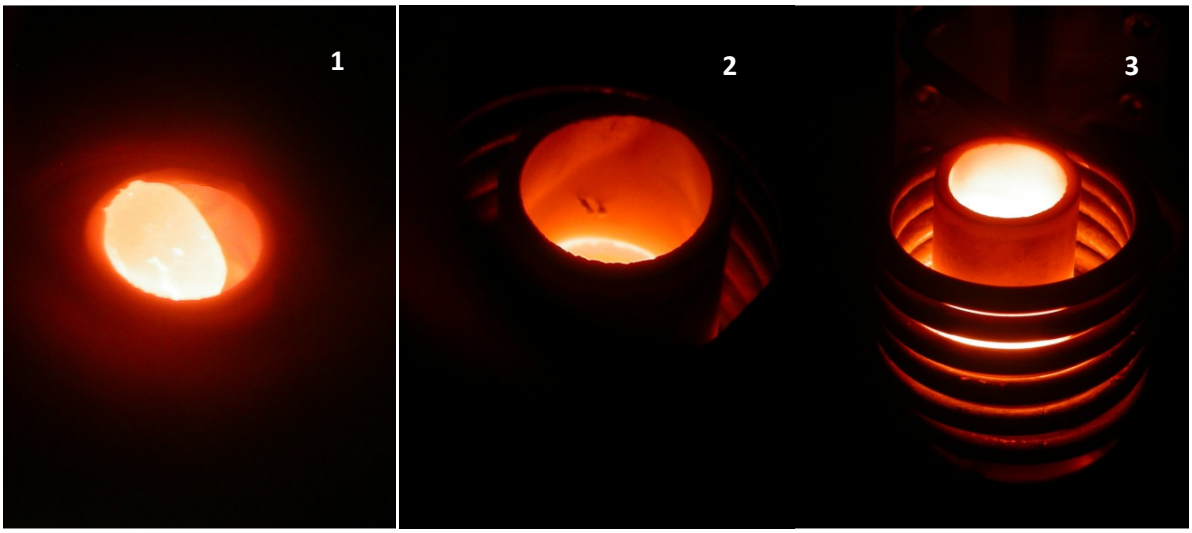
**OBSERVATION:**

During the first trial, we were not successful in melting the sample. Unlike the experiments at EPFL where the Alumina crucible is placed in a Graphite crucible which supports the eddy currents and heats up the Cu Ni powders inside, here we did not place the samples in a conducting sheath. Since Cu Ni also supports Eddy currents, we wished to heat it directly.

*>>The point bottom crucible was made to stand in a flat bottom Zirconia crucible which had a hole drilled in it for the thermocouple to sit.*

The walls of the crucible being long, we were unable to look inside. The sample was heated till the thermocouple read 1360'C in a static 3 bar pressure of Argon. On descent and cooling we discovered that the *chunks hadn't melted at all*. This implied that the thermocouple heated up by induction much easily compared to the sample although it was out of the coils. The temperature it displayed was not the actual temperature of the samples but much higher. The sample was red hot, but below the solidus temperature of 1220'C.

In the next trial, in order to heat effectively, a **tungsten susceptor** was used as a sheath. The tungsten would first heat up and then radiate to heat up the sample. However it was observed that this didn't work as the mutual induction of the inductor coils and the tungsten susceptor was not good and it did not achieve the heating as desired. Instead, the previous method was used with a much higher power now. The crucible was cut at the top so that the molten metal was visible to indicate completion of heating. The thermocouple reading was completely disregarded. The required power was twice as much but it heated effectively.




^^*the chunk before melting (1); on melting, the visible level of the melt (2); while descent (3)*

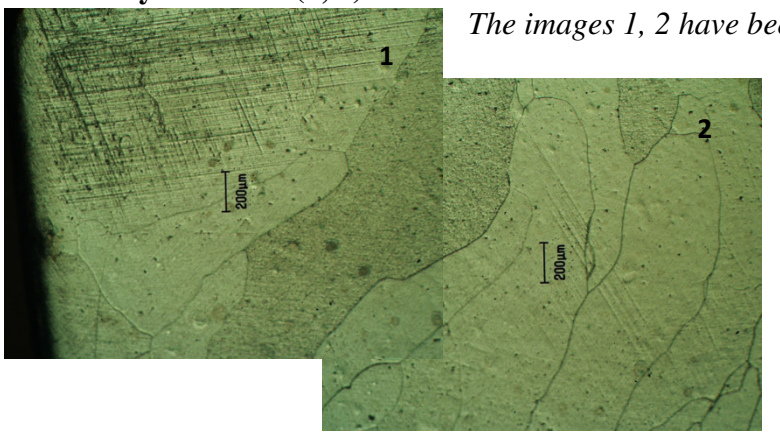
- The obtained **sample is still poly-crystalline**. A **bubble is again obtained at the bottom** (*visible as the brown patch at the bottom*)**.** This has been observed in a lot of samples. It can be attributed to the **high surface tension** of the melt and possibly the **oxygen eliminated by the Alumina** crucible which gets trapped there. This prevents a single nucleation site and a lot of grains therefore develop.
  One way to counter this could be to go to a much **higher temperature ($T_{liquidus}$+300'C)** which would significantly reduce the viscosity and surface tension and prevent the bubble from forming.

- >>*There is still a **layer of condensed copper** on the side of the crucible walls.* The pressure in this trial was 3 bar which improved the situation greatly. Although evaporation does occur it is very much reduced. The recondensed droplets are not present anymore. A higher pressure might further reduce it.

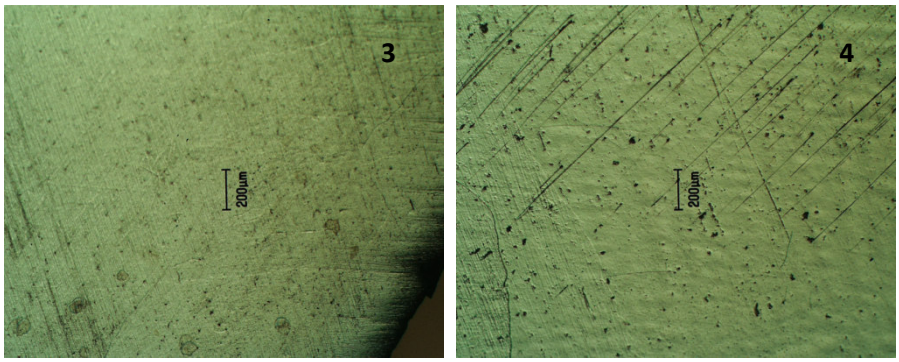
- In order to complete the trial in a day, a higher speed of 2.4 mm/hr was used. A slower speed is instrumental in obtaining a single crystal as the dimensions of the sample aimed at are much higher this time. The diameter is 20 mm which is significantly higher than previous samples attempted. A speed of **1mm/hr should be tried first** and the sample examined. Further trials should be conducted based on this. The presence of **columnar grains at the boundaries (1, 2)** further confirms this.

The sample on polishing and etching revealed a polycrystalline structure but the **grain size is higher** than the previous samples **despite the larger diameter**. This is extremely good and we can aim at higher sized grains using slower descent rates and ensuring nucleation from the bottom of the crucible. The quality of the sample will greatly improve. **Several large grains are already observed (3, 4).**

*The images 1, 2 have been overlapped to show continuity*




One half of this sample will be annealed at 1180'C for 10 days which will serve to even out the composition gradient. This sample can then be compared to see the effect of the post anneal with the other half.



# THE NEXT STEPS TO BE TAKEN

After having gone through a large number of trials, some unsuccessful so as not to give any learning, but a lot of them pointing to what went wrong and where an improvement could have been made, I conclude with a list of definitive steps and probable ones which should be tried out to yield a single crystal.

- **Always use chunks or pellets as a precursor**. If you have powders, pelletize them.

- A **slower speed (<1mm/hr) is a must** for the given size of sample (20mm diameter). Start trials with 1mm/hr and analyse the microstructure obtained. Especially note the shape of grains (whether columnar at the boundary or equiaxed or if large grains are obtained), and the grain size. Go to progressively slower rates.

- **Maintain an over pressure of Argon**. Do not conduct trials in Vacuum. With 3 bar of static Argon pressure some evaporation was still observed but much lesser than in vacuum. A higher pressure would be effective in reducing evaporation.

- A **composition gradient will always result** if the vertical Bridgman is used for an incongruently melting sample. One definitive thing to do with each sample is to do a **post anneal ~20'C below the solidus in vacuum for ~10days**. This will even out composition gradients and also lead to grain growth. After making a sample, it can be cut along the length longitudinally, with one half polished and etched and the other half annealed. Then a composition analysis should be conducted to observe the gradients before and after annealing.

- Another thing to try out is using **another material for a crucible** instead of Alumina or Zirconia (which evolve oxygen and contaminate the sample). A smooth **tungsten** or **molybdenum** crucible would be optimal. It would work well with an induction heater. Since it can be machined to a much smoother finish, it can provide much fewer nucleation sites and result in a better crystal. Moreover, it can be reused whereas an alumina crucible must be broken at each trial. In case it manages to remains intact, the thermal shock that it receives after 2 trials causes it to crack. But this is not a necessity.

- Once a single crystal is obtained, **the radial gradients should also be analysed by cutting transverse sections of the sample** and polishing/ etching it.

- The composition gradients could be lowered by using other methods of **controlling the interface shape** by using a setup that allows rotation of the sample.

All this said, **a better method to yield a single crystal of the said alloy (Cu-Ni or any other incongruently melting composition) is the floating zone using an electron beam to melt the zone.** However, it is more complicated, with a lot of parameters which have to be fitted to succeed.

# CONCLUSION

In conclusion, I hope that this report has been as interesting a read as it has been for me to prepare this material.

I have structured it such that it not only summarises the observations and results derived out of the trials conducted over the three months of my internship, but also serves an a starting point reference to anyone who intends to continue with the project of growing single crystals.

In the process of conducting these trials, reading up volumes of papers and books and discussing them with my guide and colleagues, to conclude the results that I did, has been a great learning experience at each step.

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