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# GROWTH OF ZINC SINGLE CRYSTALS AT A CONTROLLED RATE FROM THE MELT

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# GROWTH OF ZINC SINGLE CRYSTALS AT
# A CONTROLLED RATE FROM THE MELT

by

Robert John Wienert

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# TABLE OF CONTENTS

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Robert John Wienert

## ABSTRACT

The equipment and procedure for controlled rate growth of zinc single crystals by the Bridgeman technique were developed. Crystals 1.0 inch in diameter and 8.5 inches long were grown under different conditions of temperature gradient, growth rate, and radial heat loss.

It was observed that two variables, growth rate and radial heat loss, had to be controlled to assure a high probability of single crystal growth.

Sparkcutting to obtain the necessary surfaces for determination of crystal perfection appeared to cause nucleation of a large number of dislocations. The method of cutting crystals needs to be examined and possibly modified or replaced by a new method such as the use of an acid saw.

# INTRODUCTION

Every real crystal contains a certain amount of imperfection and many methods have been investigated to obtain more perfect crystals. One of the more widely used techniques is growth from the melt. This method is easy to perform and gives good results if a large number of crystals are to be grown. Consequently this technique would be preferred if high quality crystals can be obtained.

One means of measuring the perfection of a crystal is by determining the dislocation density in the bulk of the material. The dislocation density varies with different materials. For some semiconductor materials this value is of the order $10^2$ $cm^{-2}$ and Dash (1) has reported growing silicon and germanium crystals which appear to be dislocation free. However in metals a dislocation density below $10^6$ $cm^{-2}$ for strain-annealed crystals is considered good, with lower values being obtained in the growth of single crystals. For zinc the lowest value reported is by Chyung and Taylor (2) and is of the order of 4 to 9 x $10^4$ $cm^{-2}$.

These values may be lowered by use of special equipment and careful control of the critical growth parameters. The special equipment includes crucibles with very smooth walls, crucibles which are shaped so that any dislocations in the seed or produced in an expanding section cannot grow directly into the bulk of the crystal, and methods of cutting and polishing which will not cause mechanical stress to be placed on the crystal during analysis. The growth parameters which may need to be carefully controlled are temperature gradient in the melt, the growth rate, and the radial heat loss or gain.

The experimental work reported here is concerned with finding which of the growth parameters are important and must be controlled to grow more perfect crystals. In addition the need has been demonstrated for a strain-free method of cutting and polishing to prevent a large number of dislocations from being formed when the crystals are analyzed. Finally an attempt is made to correlate the results of the perfection analysis to the growth parameters to find which are important.

The metal used in this work is zinc because it has a fairly low melting point, others have investigated this metal and the results from this work may be compared with their results, zinc may be safely handled in graphite containers, and it is fairly cheap and readily available in 99.99% purity.

## LITERATURE REVIEW

Many experimenters have investigated various growth parameters to find which ones must be controlled to obtain a more perfect crystal. Some parameters have been investigated quite widely but others by only a few people. The parameter included in the largest number of research projects appears to be the growth rate, while the temperature gradient, crucible conditions, and metal conditions have been included in only a small number of cases. Radial heat loss has been acknowledged by many as being a critical parameter but no one has actually done work to find just how important it really is.

Growth rate is generally agreed upon as being very important in attempting to grow more perfect single crystals. Deo and Marya (3) reached the conclusion that as growth rate decreases the perfection of the crystals obtained increases. The range of growth rates used was from $1.39 \times 10^{-3}$ cm/sec to $2.78 \times 10^{-2}$ cm/sec. This same conclusion was reported by Zasimchuk and Ovsienko (4) at growth rates from $4.1 \times 10^{-4}$ cm/sec to $3.5 \times 10^{-3}$ cm/sec, Iwauchi <u>et al</u>. (5) at ranges of $5.0 \times 10^{-4}$ cm/sec to $1.12 \times 10^{-2}$ cm/sec and Goss and Weintroub (6) at rates between $8.33 \times 10^{-4}$ cm/sec and $2.75 \times 10^{-2}$ cm/sec.

Goss and Weintroub (6) also investigated the importance of temperature gradient. The range of their investigations was from 2°C/cm at a growth rate of $8.83 \times 10^{-3}$ cm/sec to 45°C/cm at a growth rate of $2.50 \times 10^{-3}$ cm/sec. These values should be large enough to cover most practical cases in growth from the melt experiments. From their work, Goss and Weintroub concluded that changing the temperature gradient had little effect on the perfection of the crystals.

Radial heat loss probably has not been investigated because it is very difficult to obtain a record of the amount of heat flow in a radial direction as a function of axial position. Consequently most workers have not investigated this parameter. Chyung and Taylor (2) report that by growing a seeded crystal in an S-shaped crucible, and carefully controlling radial heat loss, crystals with dislocation densities of 4 to $9 \times 10^4$ $cm^{-2}$ have been obtained. This value is very low and would seem to indicate that growth in an S-shaped crucible is a very valuble technique for obtaining more perfect single crystals and also that the amount of radial heat loss must be very closely controlled to prevent the formation of large quantities of dislocations during growth.

# EQUIPMENT

The equipment described here has been developed over a period of years. The work was begun in 1963 by David W. Arnold and Edwin H. Olson. They designed and constructed the first equipment and began to locate and correct problem areas. They did not publish any of the work done by them. After their departure this work was continued by Marlyn J. Murtha and finally the author.

## The Unit of Arnold and Olson

The work of Arnold and Olson was concerned mainly with the type of crystal growth unit shown in Figure 1. With modifications it is still in use today. The apparatus was designed to grow cylindrical crystals 1.0 inches in diameter and 8.5 inches long with a $50^{\circ}$ cone tip. The three parameters capable of investigation were thermal gradient, growth rate, and radial heat loss. The gradient was controlled by the amount of heat generated by the immersion heater, the growth rate by the flow of air to the cooling chamber, and the radial heat loss by control of the growth of the guard ring so that the height at which the guard ring was solidifying was also the height at which the zinc specimen was solidifying.

The growth chamber assembly consisted of the specimen metal, the heating elements, the cooling elements, the insulation, the sensing elements, and the recorders and controllers.

The metal specimen and the guard ring were either cast to the desired shape or machined from a larger piece of metal. The metal used was 99.99% pure zinc. The total weight of the specimen was about 700 grams.

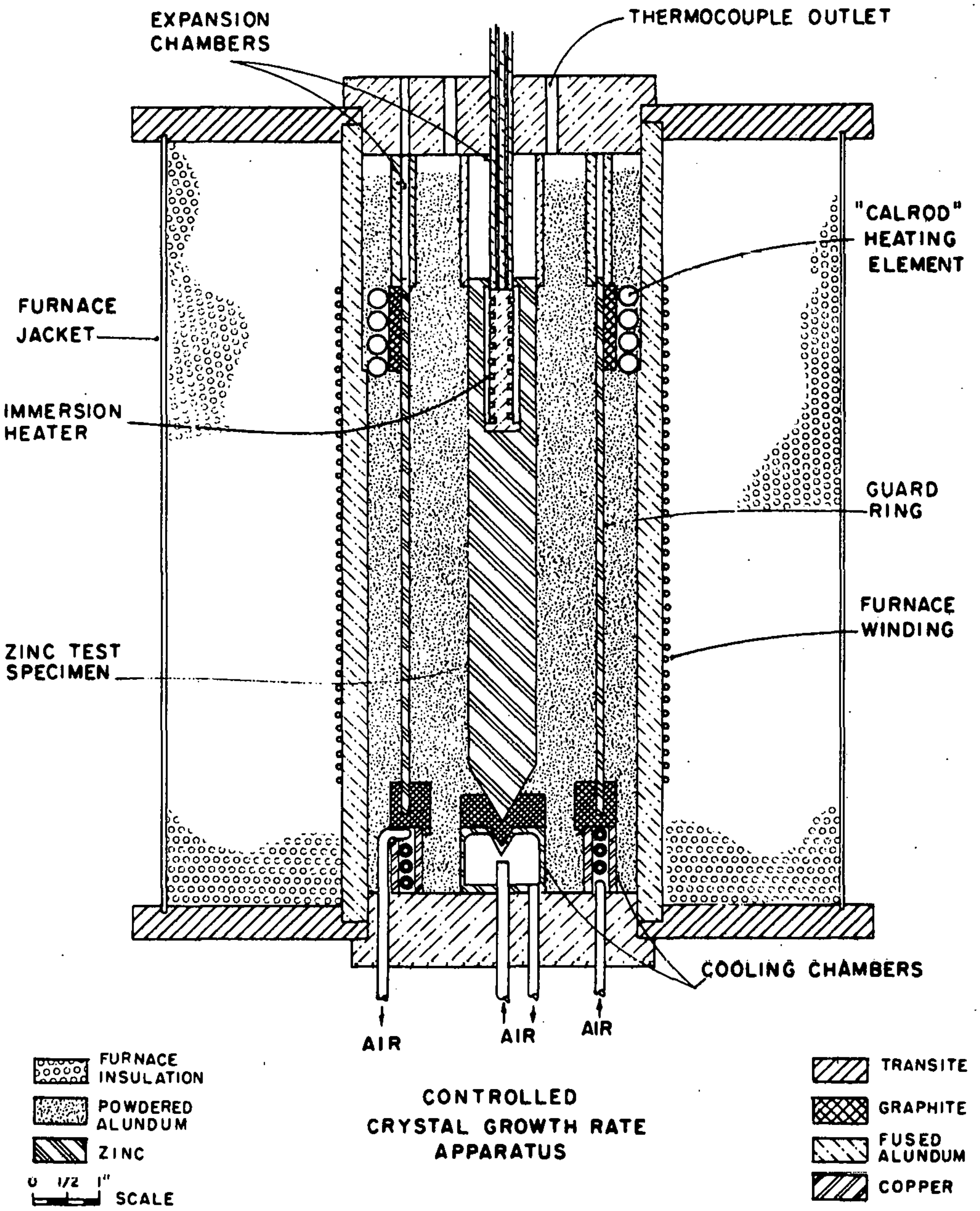

Figure 1. The unit of Arnold and Olson

A hole was drilled in the top end to allow the immersion heater to be inserted into the slug. The guard ring had a thickness of 0.25 inches and an inside diameter of 3.75 inches. The height was also about 8.5 inches and the weight about 3000 grams. The cone of the slug was inserted into a graphite spacer which had a cone hollowed out to receive the cone of the slug. This was then placed on top of a copper cooler with a matching cone for a cone on the bottom of the graphite spacer. The guard ring fitted into a graphite ring which rested on top of the copper cooling coils designed for the guard ring. Expansion chambers were found at the top of the metal to allow expansion when the metal melted.

The heating elements were the outside heaters and the immersion heater. The outside heaters were divided into three sets of windings, the first near the bottom of the slug, the second in the middle, and the third near the location of the immersion heater. The windings were capable of carrying from 2.0 to 6.0 amps at 110 volts. This required 7.0 amp powerstats. The guard ring heater was near the top of the guard ring but was kept from coming in contact with the metal by means of a graphite spacer. This heater was able to carry 3.63 amps at 110 volts which required a 5.0 amp powerstat. The immersion heater consisted of a buffer heating element carrying 4.3 amps, 110 volts from a 5.0 amp powerstat and a control heating element operating at 1.73 amps, 110 volts from the motor operated powerstat of the gradient controller. The powerstat of the controller was limited to a maximum of 3.0 amps to prevent overloading the furnace. The outside case was made of tantalum and nichrome windings are wound onto a fused alundum core before it was slipped into the tantalum case. The case was finally filled with alundum powder, the top welded on, and the area around the leads sealed with sauereisen cement.

The copper guard ring cooler was hollowed out and filled with copper tubing to form a spiral through which air may be passed to remove heat from the bottom of the guard ring. The cooling chamber for the specimen was also copper with a cone machined into the top and extending down into the center cavity of the cooling chamber. The inlet air tube extended into the cooling chamber and blew the air directly onto the bottom of the cone.

The insulation used for the solid parts was either transite or fused alundum. These parts included the top and the bottom of the furnace, the furnace core onto which the windings were placed, and the thermocouple support between the zinc test specimen and the guard ring. The loose insulation was Nortons No. 220 alundum powder. It was used to fill the rest of the chamber and was packed down to hold all of the main parts firmly in place.

The sensing elements used with this equipment consisted of all chromel-alumel thermocouples. Seven were mounted on the inside of the alundum thermocouple support tube and were spaced 1.0 inches vertically and 45° angularly. These were bent inward so that the junctions were 0.0625 inches from the surface of the zinc slug. Another thermocouple was placed in the graphite spacer at the bottom of the slug. Corresponding thermocouples were mounted on the outside of the support tube with the junctions 0.0625 inches from the inside surface of the guard ring. A thermocouple was also inserted in the graphite spacer at the bottom of the guard ring. These provided the absolute slug temperature and the radial temperature differences between the slug and the guard ring. In addition two thermocouples were mounted on the inside of the support tube, 1.181 inches (3.0 centimeters) apart, with the top one 0.25 inches below the bottom of the immersion heater and the junctions located 0.0625 inches from the surface of the slug. These provided information on the temperature gradient for the control of the heat input by the immersion heater. There were also two thermocouples in the slug air system and two in the guard ring air system to measure the difference in temperature between the incoming and outgoing air.

The thermocouples for the slug and guard ring were passed through an ice bath to give a reference temperature of $0^{\circ}C$ and then wired to a rotary switch. This switch was motor driven and resulted in the absolute temperature and differential temperature being output sequentially to the proper recorders. The thermocouples for the thermal gradient control were passed through an ice bath and wired directly to the controller. The thermocouples for the air flow were inserted into the tubes by means of Swagelok tees so that the thermocouples were inserted into the air flow from right angles. These were wired so that the difference between the two thermocouples was input to the controllers for the coolers and to the recorders for the rate of heat removal.

The slug cooler also had a Schutte and Koerting Model S transmitting rotameter with a range of 3.0 to 30.0 liters/minute and a signal range of 0.0 to 50.0 millivolts connected in the air flow inlet line. In addition a Brooks rotameter tube R-6-15-A or R-6-15-B (depending upon flowrate) with stainless steel floats was in the air line flowing to the guard ring cooler. The flow rates were multiplied by the temperature differences of the incoming and outgoing air. This value was recorded and when multiplied by the heat capacity of the air would give the amount of heat removed by the cooling air.

Also each of the furnaces was equipped with a voltmeter and an ammeter to help monitor the rate of heat input and prevent overloading the furnaces when the powerstat settings were increased.

The controllers used to control the heat flux in the crystal growth assembly were two General Electric type 524 three-mode controllers. One of these controlled the current to the slug heater and thus the heat input and the other controlled the rate of heat removal from the slug. The controllers had a General Electric Type 521 two-pen strip chart recorder which recorded the temperature gradient and the rate of heat removal. This recorder had 2.0 to 20.0 millivolt scales for each pen and was equipped with set point potentiometers and transmitting slidewires to transmit the error signals to the controllers. The black pen on this recorder recorded the product of the flow rate and the temperature difference of the cooling air to the slug cooler on a 20.0 millivolt scale. The red pen recorded the vertical temperature gradient on a 2.0 millivolt scale.

Also necessary were a Sargent Type SR recorder with a multiplying potentiometer to record the temperature difference from the guard ring air system, a Bausch and Lomb VOM-6 for the temperature difference of the cooling air for the slug, a Sargent Type SR for the absolute temperature of the slug, and a Sargent Type MR for the radial temperature differences.

Following construction the equipment was calibrated and the assembly used to make a number of unsuccessful crystal growing runs. Several shortcomings were noted and corrections made where necessary. Shortly afterward Arnold and Olson left and the equipment was idle until taken over by Marlyn J. Murtha in 1967.

## Modifying and Improving

The main problems with the apparatus at this point were that once the zinc melted it would often leak out through the alundum powder and the amount of heat that had to be removed by the coolers was very large. In addition there were also problems with the immersion heater burning out or being corroded by the molten zinc.

To eliminate these problems a new design for the controlled rate crystal growth apparatus was prepared. The guard ring was eliminated, a graphite crucible was designed to hold the zinc specimen, and a graphite core was placed on top of the slug to conduct heat from the furnaces on the sides to the top of the metal and thus establish the temperature gradient. The crucible walls were 0.125 inches thick so as to be strong enough to contain the metal and suitable to mount the thermocouples on. The graphite core was 2.0 inches high and extended to the outside edges of the growing chamber so as to be as close to the outside furnaces as possible. This assembly was placed in a double-walled metal cylinder.

The two walls were 3.0 inches apart and the space between the walls was filled with alundum powder and the ends sealed. This annulus was then evacuated to about 15 microns to provide good insulation and prevent heat loss through the sides of the chamber. The cooler for the zinc guard ring was retained and was used mainly to help remove heat from the outside and thus reduce the cooling load on the slug cooler.

When this apparatus was tried, some necessary changes became evident. The diameter of the graphite core was decreased to slightly larger than the top of the crucible and the heating wire wound directly on this to give a better means of establishing the temperature gradient. The crucible walls were found to be conducting a fairly large quantity of heat to the slug cooler and consequently were reduced in thickness to 0.0625 inches to decrease this flow and still have the required strength. To help control radial heat flow an arrangement for holding coils of copper tubing to remove heat and also support the outside thermocouples was designed and constructed.

## The Present Unit

At this point the author began work on this project. The equipment was used on a number of occasions and a few more changes found necessary. Temperature controls were constructed for the outside furnaces to give better heat control during the preheating and final heatup. The rotary switch for the thermocouples was found to be defective and had to be replaced by a better unit. In addition an arrangement was designed and constructed which would allow part of the air flow to the cooling chamber to be bypassed around the controller so that the changes in flow rate would not be large enough to cause the controller to become unstable. The amount of flow through the bypass may be adjusted as desired by means of a needle valve installed for this purpose.

The equipment at this point worked satisfactorily and the growth chamber is shown in Figure 2. The size of the specimen and the growth parameters are the same as previously mentioned. The apparatus for casting the slug is shown in Figure 3. The cooling chamber consists of a hollow center surrounded by an insulating shell through which the cooling air is passed. A graphite stem extends into the center of the chamber and is the means by which heat to be removed enters the cooling chamber. A graphite extension for the stem is used to lift the casting and the melting crucibles higher into the furnace so that they may be more thoroughly heated. A ring of insulation causes heat removed by the cooler to flow down the graphite stem. The casting crucible is the same as is used in attempting to grow a crystal and in fact may be one that has been used previously as any oxide will be removed by cleaning the cast slug with 6N hydrochloric acid. The melting crucible should be large enough to hold all of the metal to be cast and should rest on top of the casting crucible so that the metal will drain directly into the bottom chamber. The plug rod is also graphite with a $2^{\circ}$ taper at the lower end and long enough to extend above the top cover of the furnace. There are four thermocouples used in the casting furnace. The three for the casting crucible have their junctions at the bottom, middle and top and are spaced angularly at $120^{\circ}$ intervals. These are used to indicate when the metal has solidified and to lower and center the casting crucible in the furnace. The thermocouple for the melting crucible is used to

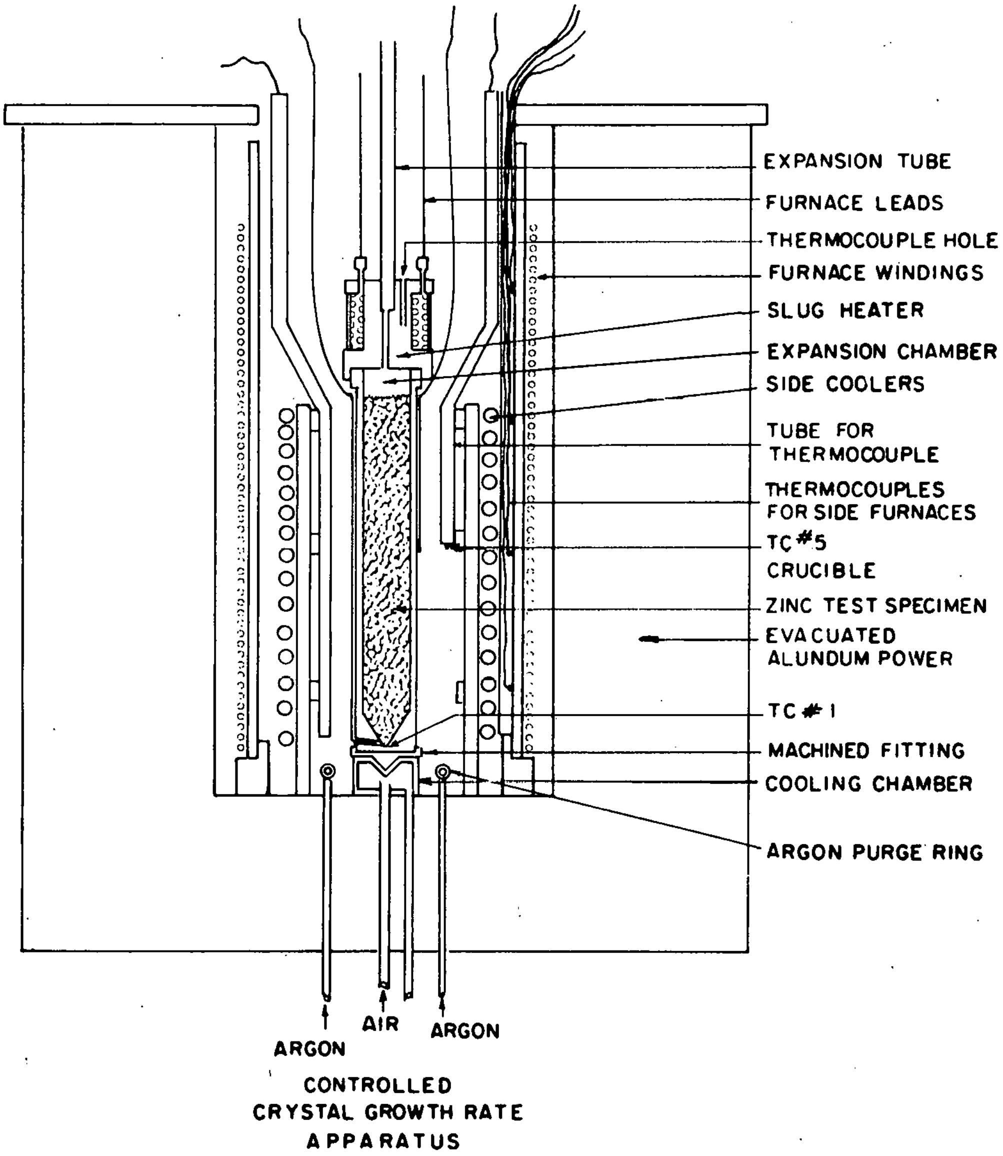

Figure 2. The present unit

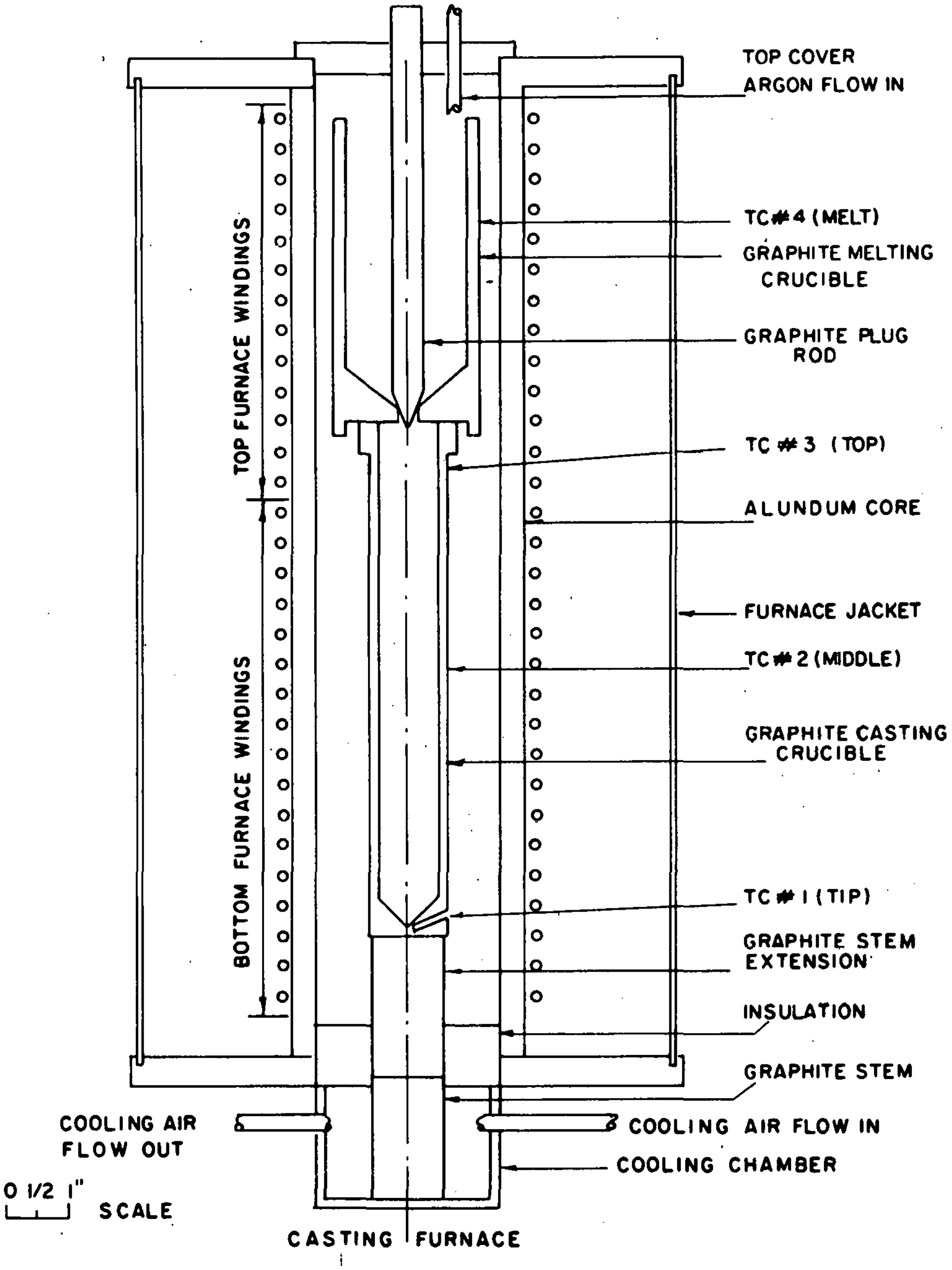

Figure 3. The casting furnace

indicate when the metal is melted and ready to be poured. These are connected to a switch which will enable the selection of desired thermocouple signal and this will be output to a Sargent Type MR recorder. The tubing to introduce the argon purge is 0.25 inches stainless steel tubing. The top cover is made from transite with holes for the plug rod and the argon purge tube. The windings for the side furnaces are in two sets, one near the casting crucible and one near the melt crucible. The windings and the powerstats for them must be able to carry 5.0 amps maximum.

The cast specimen is placed in a graphite crucible 9.625 inches long with an outside diameter of 1.125 inches. This results in a wall thickness of 0.0625 inches. The top and bottom of the crucible are slightly larger in diameter to give more strength in the areas where threads must be made. The point of the cone is 0.125 inches from the lower end of the crucible. An expansion chamber is left at the top of the specimen for the metal to fill when it is heated and expands.

The machined fitting that screws onto the bottom of the crucible is made from copper. The face of this cap is 0.125 inches thick. The threads that hold it onto the bottom of the crucible are found on the inside edge of a lip extending upward from the outside of the face of the cap. From the center of the bottom a cone extends downward which will exactly fill a cone found in the center of the top of the slug cooler. The matching of these two cones will insure that the bottom of the crucible is exactly centered on top of the cooler. Before this piece is attached to the crucible a small amount of powdered graphite is placed in the cap to fill any gaps where the bottom of the crucible and the face of the cap are not perfectly flush.

The slug cooler is also copper. The top and sides are machined from a single piece of copper. The outside diameter of the cooling chamber is 1.125 inches with a height of 1.0 inches. The thickness of the walls is 0.125 inches. The cone is cut into the top face and extends down into the middle of the chamber. The bottom piece is made from another piece of copper and is also 0.125 inches thick. There are holes drilled in this piece for the inlet and outlet air tubes. The tubes are 0.25 inches outside diameter stainless steel tubing. The inlet tube is directly in the middle and extends into the chamber 0.25 inches to blow the air directly onto the inside cone. The outlet tube is located near one edge and is flush with the bottom. This piece is soldered to the sides and top.

The slug heater is made from a graphite core 2.0 inches in diameter and 2.25 inches high. The middle part of the core where the furnace windings are is 1.5 inches in diameter and 1.5 inches high. The lip extending down from the outside edge of the furnace has threads on the inside of it to match those on the top of the crucible so that the furnace is firmly attached to the crucible. An expansion hole is drilled in the center of the core and a length of 0.25 inches stainless steel tubing extends this expansion area above the top of the core. This tubing must extend above the top of the alundum powder used for insulation also. A hole for the thermocouple to record the furnace temperature is drilled into the top of the core. The furnace windings are made from

7.50 feet of 1.6 ohms/foot heating wire to give a total resistance of 12.0 ohms. Two notches are filed in the edge above the windings to serve as outlets for the furnace wire. The ends are stripped of insulation and inserted into the ends of 0.0625 inches copper tubing. These are held together by means of Swagelok fittings. The copper leads again must extend above the final level of the alundum powder and are used as a location to connect the wires from the gradient controller. A strip of sheet metal is wrapped over the windings to hold them in place and protect them from damage.

The outside furnaces consist of four sets of windings. These are located near the top, middle, and bottom of the slug and near the slug heater. The windings are made on the outside of a fused alundum shell. The wires and powerstats must be able to carry up to 7.0 amps at 110 volts. Each furnace is equipped with a Honeywell Brown Protect-O-Vane Controller to allow the maximum temperature attainable by the furnace to be regulated. Each of these controllers requires a thermocouple to report the temperature of the furnace. The thermocouples are placed in a 0.375 inches stainless steel tube which is sealed at the bottom. This is inserted into the growth chamber just inside of the fused alundum shell with the bottom resting on the graphite ring that supports the shell. The junctions are placed so that they are in the middle of the respective furnace. Each furnace is controlled for maximum power by a powerstat with a voltmeter and an ammeter included in the circuit.

The argon purge ring located near the slug cooler is a hollow ring with a number of small holes in the bottom side. The argon is introduced by means of two lengths of tubing through the bottom of the assembly and passes out through the holes. Since the argon is more dense than the air and oxygen, in particular, it displaces them from the growth chamber and thus reduces the amount of oxidation.

The assembly for the side coolers and the outside thermocouples is constructed from four stainless steel rods and three stainless steel rings. The rods are 0.25 inches in diameter and 10.0 inches long. The rings have an inside diameter of 2.50 inches, are 0.50 inches high; the wall thickness is 0.0625 inches. The rods serve as legs and are evenly spaced and welded to the outside edges of the rings with the side coolers being soldered to the outsides of these legs. The rings serve as cross pieces and the thermocouple support tubes are welded to the inside edges of the rings. The bottom ring is located 2.0 inches from the foot of the assembly and the top ring at the top of the support legs. The middle ring is spaced between these two. The side coolers are made from 0.25 inch copper tubing that is bent into four to five turn coils to fit the outside edge of the assembly with the inlet and outlet tubes bent upward to extend from the top of the growing chamber. Three sets of coils are made in this manner. The first coil is next to the top of the slug and the top three thermocouples found on the crucible. The second coil is located near the middle of the slug and the last near the bottom of the slug. The inlet tubes rise from the bottom sides of the coils and are attached to an air source for the cooling flow which may be regulated by means of manually controlled values. The thermocouple support tubes are made from 0.25 inch stainless steel tubing. The tubes are spaced $45^{\circ}$ angularly except for number 9 which is immediately next to number 8.

The tubes extend downward to the point where the thermocouples will extend just below the end of the tube when properly placed. The tubes extend upward to rise above the level of the alundum powder. Just above the top ring, the tubes are bent outward 30° from the vertical as the tubes approach the sides of the growth chamber, they are bent again so that they are once more vertical. The thermocouples are inserted into these tubes and adjusted to the desired height.

The insulation used to fill the growth chamber is Nortons No. 220 alundum powder. The insulation around the growth chamber is formed by the double-walled metal cyclinder mentioned previously.

The thermocouples are all chromel-alumel. The numbers required are ten each for the inside and outside locations near the slug, four for the side furnaces, two to find the change in temperature between the incoming and outgoing air, and two for the gradient controller.

The switch for the inside and outside thermocouples is a motor powered rotary switch which outputs both the value for the inside thermocouples and the difference between the inside and outside thermocouples. This switch is specially constructed for low voltages.

The rotameters are the same except that the Brooks rotameter is used to regulate the flow rate to the argon purge ring.

The controllers and recorders are the same except that the guard ring recorder has been eliminated, as has the guard ring, and a Honeywell Brown Electronik is used to record the absolute temperature.

The bypass in the air system is constructed using two tee connections and a valve to regulate the flow in the bypass.

# PROCEDURE

## Casting a Slug

The first step is to weigh out 700 grams of 99.99% pure zinc; slightly less is required for the higher gradient runs to allow for more expansion. The metal is next cleaned in 6N hydrochloric acid for about 30 seconds to remove oxide from the surface, then rinsed in distilled water, finally in acetone, and allowed to air dry.

The cleaned zinc is placed in the upper chamber of the casting furnace, the cover put on, and the tube to bring in the argon gas put in the hole in the cover. The argon flow is turned on and the plug rod lifted slightly to allow the argon to flow into the crucible and the lower part of the furnace to displace as much oxygen as possible. After a few minutes the furnaces are turned on and the current flowing through the windings set at 4.0 amps. After a short time the plug rod is pushed back into position to retain the metal in the top chamber when it melts.

The metal is next allowed to heat up and melt. When the metal is superheated by 25°C to 50°C above the melting point and the crucible is at a temperature where the metal will remain liquid when poured, the plug rod is removed. The current in the windings is then reduced to 1.0 amps, the bottom cooler turned on, and the argon purge turned off. The metal will begin to cool and after a time solidify. As soon as the metal is completely solidified, the furnaces and cooler are turned off, the top cover removed, and the top chamber taken out to allow the slug to cool.

When the slug is cool enough to handle, it is removed from the casting furnace, taken out of the crucible, again cleaned in acid and placed in a new crucible. The procedure for placing in a new crucible is to hold the crucible upside down, slide the slug up into the crucible completely and then turn the assembly over. The top of the crucible is filled with tissue paper and a furnace core screwed on to hold the slug firmly in place during handling.

## Preparing a Slug for the Run

The thermocouples must be checked for any defects in either insulation or welds. In addition the thermocouples for the gradient controller must be insulated with sauereisen cement so that they will not pick up any voltages from the other thermocouples. Thermocouple number 1 is located at the point of the slug and each consecutive thermocouple is on the outside of the crucible, 1.0 inches higher, and rotated at an angle of $45^{\circ}$ around the slug except that number 9 is directly above number 8. It is necessary to drill a hole into the lower part of the crucible in which to insert number 1 to be near the point. It may be found desirable to place a drop of sauereisen cement over the heads of the thermocouples to insure that they are reading the wall temperature and not a temperature in the alundum powder.

The growth chamber is prepared by vacuuming out the alundum powder so that the slug may be set onto the top of the cooler and no powder will be between the fitted pieces. At times it may be necessary to vacuum out all of the powder to accomplish this. The layer of oxide on the fitted pieces can be removed by placing a small amount of abrasive on the top of the cooler and rubbing the piece that fits on the bottom of the crucible against it to wear them both down slightly. The abrasive used is the same alundum powder that is used for insulation. An extension that will hold the fitted piece for the crucible and enable it to be rotated against the face of the cooler without completely disassembling the growth chamber has been found desirable.

When the sauereisen cement is dry, the furnace core and paper packing are removed and replaced with an operable furnace. A small amount of powdered graphite is placed in the fitted piece that screws onto the bottom of the crucible and, while holding the crucible upright, the fitted piece is screwed onto the bottom. The slug is now ready to lower into the growth chamber. The main problem when lowering the slug into the chamber is that the alundum powder may fall from the sides onto the top of the cooler. If this happens the chamber must be vacuumed out again. The cones of the fitted piece and the cooler will assure correct placement at the bottom and the slug may be rotated so that the inside and outside thermocouples are next to each other. The thermocouple wires must now be separated and laid out so that they will not cause the slug to twist while the alundum powder is being added. A piece of tape is placed over the top of the stainless steel expansion tube and the inside thermocouple for the furnace inserted in the prepared hole at the top of the slug heater. The powder is added to the chamber and packed down until the chamber has been filled in this manner. The tape can now be removed from the expansion tube and furnace leads for the slug heater and the thermocouples connected. A check must be made to see that all of the recorders and controllers are working satisfactorily.

## Preheating

Since the slug cannot be heated up fast enough to allow a crystal to be grown the same day without putting in some very long hours, it has been found desirable to partially heat the slug to about 300°C overnight and to then finish heating up and grow a slug the next day.

To begin heating up the side coolers are turned on slightly and the argon flow started. At this point the side furnaces may be turned on and the current through the windings set at 4.0 amps. The controllers for the outside furnaces are set so that the slug will heat up to about 300°C. By turning on the motor that rotates the switch and the recorder for the temperature of the slug, the heating up of the slug is followed. The slug heater may be used to partially heat the slug to check to see that the thermocouples are working. The powerstat controlling the maximum current to the slug heater should be set at 4.0 amps and the controller set to deliver only 2.5 amps to the slug heater. This will cause the top of the slug to heat up faster than the bottom and should cause the recorded thermocouple temperatures to become separated on the recorder. The power to the slug heater is left on long enough to check everything out but not long enough to melt any part of the slug. At this point the motor for the switch, the recorder, the controller and the powerstat are turned off.

## Growing a Crystal

Prior to beginning the final heating and melting of the slug, all of the recorders and the motor that rotates the switch for the thermocouples are turned on. The three ice baths, two for the thermocouples and one for the air flow to the cooling chamber, are filled with crushed ice. The set points for the outside furnaces are selected and the slug heater turned on to help heat the slug in the manner mentioned previously. The controller for the slug cooler is set so as to have the rate of heat removal low to remove some heat to help establish a gradient but not enough to hinder the slug seriously from heating up and melting. The recorder for the temperature difference is operated on a large enough scale to include all of the points except possibly that of number 10 as the thermocouples at the slug heater need be of little concern. Using a potentiometer the input to the switch by each thermocouple (both inside and outside) is read and the values obtained compared to the values recorded on the recorder for horizontal temperature difference and the recorder for the actual temperature of the slug at the various axial positions. When the gradient approaches the desired value, the controller for the slug heater is switched to automatic.

The slug is allowed to melt completely and the metal at the point to become superheated by about 25°C above the melting point. Then by adjusting the side furnaces and the side coolers the differences between the temperatures of the inside and outside thermocouples are brought as near to zero as possible. The controller for the cooler is set to the desired rate of heat removal and switched to automatic to allow the controller to adjust the air flow rate to hold this rate of heat removal. As the horizontal temperature differences decrease, the range of the recorder is also decreased so that changes may be seen more readily.

The above should cause the metal to stop heating up and to begin to cool. Using the potentiometer, the input to the switch from thermocouple number 1, at the point, is checked so that the moment the metal solidifies may be more accurately known than from the recorder for the axial temperature. As soon as one thermocouple shows that the metal has solidified, the potentiometer leads are moved to the next higher thermocouple. The times that the metal at each thermocouple solidifies are recorded so that the growth rate may be more accurately known. The main concerns at this point are that the heat removal rate remains about the same and that the horizontal temperature differences remain small.

Growth of the crystal is continued until all of the metal that will possibly solidify has solidified. Not all of the metal will solidify because after the metal at number 8 has frozen the gradient will begin to decrease and the slug heater will begin to supply heat to the slug faster than the cooler can remove it. At this point the slug heater and the side furnaces are turned off, the side coolers turned down to only a small flow of air through them, and all of the recorders and the motor for the thermocouple switch are turned off. The controller for the slug cooler is also turned off as the flow will be maintained with the controller off but will not be maintained to get a constant heat removal. The slug is now allowed to cool enough so that it can be safely handled. This usually takes about 20 hours.

## Unpacking the Crystal

After the crystal has cooled sufficiently it is removed from the growth chamber. The thermocouple wires and the leads for the slug heater are first disconnected. Then all of the coolers and the flow of argon are turned off. Most of the alundum powder is vacuumed out so that the crucible assembly can be lifted out. The thermocouples are removed. The fitted piece from the bottom and the slug heater are removed by unscrewing them from the crucible. The crystal should now be removed by merely turning the crucible upside down and allowing the crystal to slide out slowly. The crystal is examined to see that the point is sharp and that a large layer of oxide has not built up on the surface of the crystal. This is done to check the construction of the crucible and to see if any of the coolers have developed a leak. The crystal is cleaned in 6N hydrochloric acid for about 20 seconds. This should cause any grain boundaries present to become visible and remove the oxide from the surface of the crystal. If the crystal is single the flash planes can be observed as the crystal is rotated.

If the crystal is single it must be handled very carefully so that stresses will not cause dislocations to be nucleated. The crystal is wrapped in paper and stored in a place where it will not be jarred or strained until it is to be analyzed.

## Analysis

To analyze the crystals the 1.0 inch desired section must first be cut using a sparkcutter. The section grown at the desired rate is placed on a goniometer and the crystal orientation found. Knowing the orientation the section may be sliced in any manner desired. The plane chosen for cutting in this case was the prism plane of the zinc crystal, that is the $\{10\bar{1}0\}$ plane. Figure 4 shows the operations previously described in analysis and in addition one face of the slice has been polished on the acid polisher. The crystals cut along the prism plane are smoothed by polishing the faces on a polishing cloth saturated with 8N nitric acid. The acid polisher was modeled along the lines of one described by Young and Wilson (7). These faces were then further polished and etched using the manner described by Brandt *et al.* (8). This method will cause mercury to be deposited where dislocations intersect the surface. Under a microscope the dislocations may be examined for any patterns and the dislocation density determined.

In addition sparkplaning of the surface and elongation of the tensile specimens were both tried briefly.

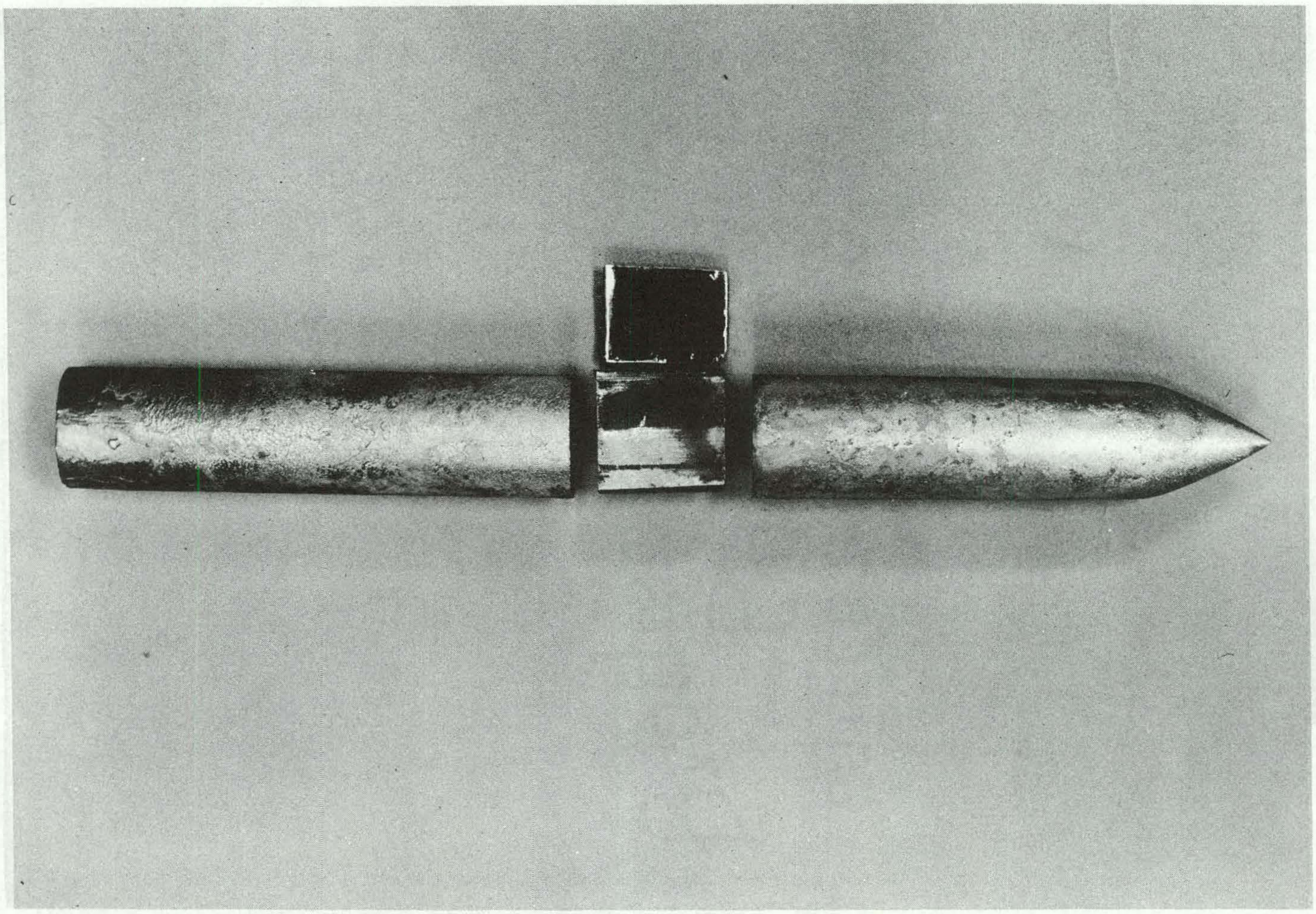

Figure 4. A zinc crystal cut for analysis showing the chosen section sliced on the prism plane and one of these faces after acid polishing

# RESULTS

Using the equipment and the procedure previously described, seven single crystals have been grown. From these crystals, eight sections have been chosen for analysis. The data for these are shown in Table 1.

Table 1. Crystal sections for perfection analysis

| Number | Growth Rate cm/sec | Gradient °C/cm | Heat Flow Direction | Heat Flow Quantity |
|---|---|---|---|---|
| Zn - 20 | 0.00141 | 6 | out | small |
| Zn - 21 | 0.00081 | 6 | in | very small |
| Zn - 23 | 0.00192 | 6 | out | very small |
| Zn - 25 | 0.00249 | 6 | out | small |
| Zn - 26 | 0.00132 | 9 | in | very small |
| Zn - 29 | 0.00065 | 9 | in | very small |
| Zn - 29 | 0.00157 | 9 | in | very small |
| Zn - 30 | 0.00235 | 9 | in | very small |

The growth rates reported are the average values for growth from one thermocouple position to the next higher position and are determined by dividing the distance by the time for the interface to travel this distance. This value is probably accurate to within 5% as the temperatures of all thermocouples on the crucible are recorded at 5.0 minute intervals to observe if their cooling rates are linear and these temperatures may be plotted as a function of position as in Figure 5 to approximate the position of the interface and observe how constantly it advances upward.

The heat flow direction is determined by the radial temperature

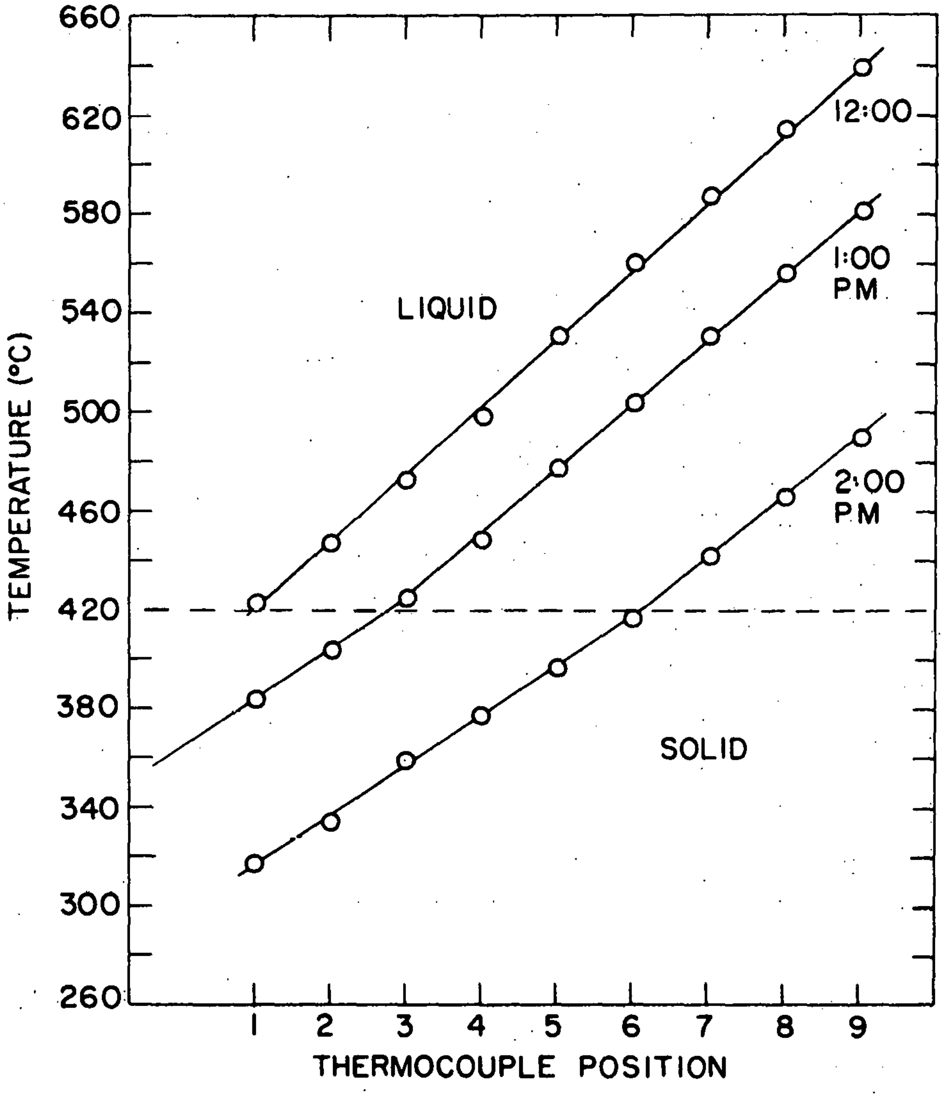

Figure 5. Temperature-position comparison for Zn - 30 to show the temperature profile in the solid and the liquid and show the means of determining solid-liquid interface position

difference. For instance if the specimen is hotter than the surrounding material the heat will flow to the surroundings. When the radial temperature difference at the nearby thermocouples was less than 5.0°C (0.2 millivolts) the quantity of heat flow was said to be small and if it was less than 2.5°C (0.1 millivolts) heat flow was said to be very small.

The results of the analysis do not appear here as the preliminary indication is that the sparkcutter used to obtain the surface to be examined for imperfections has caused the nucleation of a large number of dislocations. The zinc crystals had a large number of visible cleavage cracks present after sparkcutting and when these crystals were analyzed dislocation densities of the order $10^9 cm^{-2}$ were found. These values are felt to be too large for the single crystals grown. This will have to be further investigated and, if true, modifications made on the sparkcutter or a means of cutting the surfaces will need to be devised. Palatnik et al. (9) report that the crystal will be damaged less if the crystal is used as a cathode rather than an anode when cut on the sparkcutter. Turner et al. (10) report that cutting in a 100°C oil bath and at angles of 10° or 80° from the basal plane decrease the damage done to the crystal. The acid saw, if necessary, will be modeled after the saw discussed by Young and Wilson (7).

In addition some zinc crystals that were not single and some that were only partially single have provided some valuable information. Some crystals were grown at a high rate and as a result were polycrystalline. The crystal numbers and positions that correspond to high growth rates and showed the nucleation of additional crystals are Zn - 17 in the cone and Zn - 24 in the cone. The growth rates were $2.82 \times 10^{-3}$ cm/sec and $2.49 \times 10^{-3}$ cm/sec respectively, and the radial heat losses were small in both cases. These rates have not been too fast to grow crystals successfully in the bulk but are too fast in the area of the cone. Additional crystals may be nucleated because at faster rates projections from the crucible wall that the crystal would otherwise grow around become nucleation sites for additional crystals. Some of the additional crystals may be only surface blemishes while others grow into the bulk of the crystal because they grow faster than the crystal nucleated at the cone.

Some crystals were grown at slower rates but with a large radial heat loss and later found to be polycrystals. This is the case in Zn - 15 at the cone where additional crystals had also nucleated. The growth rate was $1.36 \times 10^{-3}$ cm/sec. The large radial heat loss would cause a concave interface and crystals nucleated on projections from the wall would grow and become larger in cross-sectional area because at the center of the specimen at the height that they are solidifying the zinc is still liquid. Therefore the second crystal does not have to compete with the main crystal for the atoms from the liquid.

In addition a combination of radial heat loss and fast growth rate has resulted in polycrystals. When Zn - 25 and Zn - 30 become polycrystalline at about the position of thermocouple number 6, a high rate of growth and a large amount of radial heat loss were present. The growth rates were $2.49 \times 10^{-3}$ cm/sec and $2.35 \times 10^{-3}$ cm/sec respectively. Previously single crystals has been successfully grown with one or the other of these conditions present but not with both present at the same time.

## CONCLUSIONS

1. If a single crystal of zinc is grown too fast a number of additional grains will nucleate. This is especially true for growth in the area of the cone.
2. A large amount of radial heat loss from a zinc single crystal at the solid-liquid interface may cause the nucleation of additional grains. The critical area of growth is again the cone.
3. A combination of radial heat loss and fast growth rates can also cause the nucleation of additional grains under conditions where only one of these would normally not have this effect.
4. The method of obtaining surfaces for examination must be made less damaging if it is shown that this was the reason for the large numbers of dislocations in the crystals. This will be done by improving the performance of the sparkcutter, construction of an acid saw, or use of other means to cut the crystals without straining them.

# RECOMMENDATIONS

1. A number of zinc crystals will have to be grown to replace those damaged in analysis to analyze for perfection as a function of the growth parameters.
2. The conditions of the growth parameters may be enlarged by using one more value for the temperature gradient, larger amounts of radial heat loss or gain, and possibly slower or faster growth rates.
3. Crystals of zinc may be grown so that two sections may be obtained from the same crystal as was done with Zn - 29. This is so that the effect of radial heat loss may be compared both within crystals as well as in different crystals and to see if crystals grown slowly first and then more rapidly will result in more perfect crystals than those grown at the faster rate throughout the whole crystal. This may also be done by slowing down the growth rate to see the effect on perfection of the crystal.

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