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EAGLE-PICHER INDUSTRIES, INC.

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STUDY OF SINGLE CRYSTALS OF METAL SOLID SOLUTIONS

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INTRODUCTION

This paper is to report some of the findings of an analytical study of the parameters and requirements for growing single crystals of relatively high melting point metals in a zero gravity environment. The object of the complete investigation is to study the crystal growth of metals such as silver, copper, gold, and alloys with a melting point between 900 - 1100°C.

Applied space research can produce some important advances in material processing which can lead to space manufacturing. This applied space R & D effort can also produce materials with different properties than those produced on earth. These new or different properties would be totally due to the different environment in space, such as zero-gravity.

The ultimate purposes of the investigation are: to determine specific metals and alloys to be investigated; grow single metal crystals in a terrestrial laboratory; determine crystal characteristics, properties, and growth parameters that will be effected by zero-gravity; evaluate terrestrial grown crystals; grow single metal crystals in a space laboratory such as Skylab; evaluate the space grown crystals; compare for zero-gravity effects on crystal characteristics, properties, and parameters; and recommend either to produce or not to produce these crystals as a routine space manufacturing process.

Included in this report are experimental requirements to delineate briefly what needs to be accomplished and what equipment requirements are imposed by the process and materials. The effect of a zero-gravity environment is analyzed and discussed. A compilation of the metals and alloys that meet the selection criteria is added as appendices. A selection of materials for investigation is made and the reasons for the selection are given. An analysis is made of the crystal imperfection and parameters which are related to the specifically recommended materials. Some of the specifics are summarized and recommendations are made to investigate silver, germanium, and copper-gold alloy.

REQUIREMENTS FOR CRYSTAL GROWTH IN SPACE OF RELATIVELY HIGH MELTING METALS

Single crystals of metals that are grown in space have at least one growth parameter that is different from earth grown crystals. This parameter is zero-gravity which has a wide range of effects on the crystal growth and the resulting crystal. There are a number of evaluations that must be made in order to determine these effects. These evaluations are required in order to obtain usable information to manufacture routinely single metal crystals in space.

The experimental requirements for growing single crystals of relatively high melting point metals in space can be divided into three main categories. These are: the determination of properties, parameters, and other facts about space grown crystals; the comparison of data from earth grown crystals; and the specifications and design of a space manufacturing facility. Each of these are discussed in the following paragraphs.

The category which needs to be investigated first is that of the crystal properties. All of the crystal properties must be measured for both qualitative and quantitative variances, then a comparison of these properties must be made between terrestrial grown crystals and the space grown crystals. In these comparisons an analysis should be made to determine if there are any crystal properties that are better as grown in space. If there is at least one property that is improved or new in the space grown crystal it will become advantageous to manufacture such crystals in space. Some of the crystal properties are a function of the growth parameters and must be determined for growing single crystal metals in space. The initial values and limits will be the parameters as determined by earth based experiments and then modified to meet any requirements not anticipated. All of the final growth parameters in space must be compared to those parameters from the earth based experiments. These comparisons will give relative design information for a space manufacturing facility. Again if there is one parameter that varies widely from the earth based experiments, then a great advantage may exist in the space growth.

A scientific experimental study should be made to determine the exact zero gravity effects on the growth in space of metal crystals. All of the scientific facts, properties, imperfections, characterizations, and parameters of the experiment and crystals should be determined so that a comparison can be made between earth grown crystals and space grown crystals. These scientific studies should be extensive and exact. All facets should be studied in detail so that the subtle differences can be determined.

From all the above information a facility can be designed to accomplish space manufacturing of single metal crystals. This manufacturing facility should incorporate all of the earth based equipment with modifications for growing crystals in space. These modifications should be directed by the growth parameters and space laboratory limitations. From such a manufacturing facility, crystals may be routinely manufactured in space which can be accomplished only if the crystal properties and the growth parameters are known precisely. Other effects which have been studied on previous flights such as gas bubbles, settling, and surface tension, will try to be supressed or eliminated by experimental design. Thus only the zero gravity effects on crystal growth is utilized.

Space grown crystals may have more uniform properties because of the lack of thermal convection currents. Two such properties might be a more uniform dopant distribution and a more uniform stoichiometry in alloys. This would imply that more of the crystal would be usable because of the less variance along its length. Less variance could also result in unusual or even unknown properties such as electrical, I. R. etc., this is a function of the crystal lattice both microscopically and macroscopically. An example of this is the use of silicon and germanium after the purity had been increased.

CRYSTAL GROWTH METHOD

There are a number of methods which can be utilized to grow single metal crystals. A few of these methods are: Bridgeman-Stockbarger, Czochralski, zone leveling and vapor phase. Growing single crystals in zero-gravity precludes the use of some of these methods such as: Czochralski, zone leveling, any method that requires an open volume above the melt. Since metal single crystals are grown easily by the Bridgeman-Stockbarger method and a sealed capsule can be used in space, this is the method which will be used in this investigation. The Bridgemann-Stockbarger method directionally solidifies the melt by moving the crucible through the furnace from a hot zone to a cool zone. Usually this is done by lowering the crucible in the furnace which solidifies the crystal from the bottom up.

Historically, the method of freezing the melt from the bottom of the crucible has been used for many years by a few researchers. Previous to this the melt was frozen from the top as in normal cooling of an open melt. Bridgemann developed a crucible with a conical bottom, so that the melt would solidify first at the point. This method tended to produce a single crystal. Stockbarger modified this technique by making the cone much deeper and narrower, which starts the crystal growth in a narrow path that blocks some crystal growth orientations. In this way only a small number of seed crystals are formed. As the solidification proceeds, a faster growing seed usually dominates and a single crystal is produced. This method has been modified even further by forming a constriction in the bottom of the crucible. Thus, in the modified Bridgemann-Stockbarger method there is a seeding chamber at the bottom of the crucible and directly above this is a constriction. This neck allows only one small seed crystal to propagate into the bottom of the main crucible.

In order to cause a melt to solidify from the bottom of the crucible and continue smoothly to the top, the crucible must be cooled from the bottom. This can be accomplished in one of two ways. The crucible may be passed bottom side first through the furnace into a cooler region. Alternatively, the source of heat may be moved from bottom to top of the crucible. Either of these two means results in the melt freezing from the bottom of the crucible.

With either method of solidification the heat source or furnaces must have a temperature gradient. Ideally, this gradient is rather sharp, but not infinitely so. The two temperatures ranges on each side of the gradient must span the melting point of the material. Thus the hot zone is above the melting point and the cool zone is below the melting point, preferably with a centimeter or less between the zones. In order to achieve this gradient, a baffle is usually used between the two zones. A drawing of a typical Bridgemann-Stockbarger furnace is attached to this report.

CRYSTAL GROWTH PARAMETERS

In growing a single crystal of silver or gold-copper alloy there are a number of parameters that must be controlled. The parameters are discussed in the following paragraphs. Before these parameters are delineated it should be noted that there is a restriction on the crystal material; the Bridgemann-Stockbarger method can only be used for materials that shrink upon freezing. Both silver and gold-copper alloy meet this requirement.

The single crystal growth parameters may be separated into categories, those concerning the furnace and those dealing with the material. These will be treated separately.

The furnace parameters are zone temperature, temperature gradient, hold time at melt temperature, pull rate, cooling rate and furnace cut-off temperature. The hotter zone is maintained at a temperature 10 - 80°C above the melting point of the material. If the silver or copper-gold alloy melt is too hot, it supercools as solidification takes place, causing a polycrystalline ingot. The cooler zone is maintained at a temperature 50 - 80°C below the melting point of the material.

The optimum temperature gradient, as well as all other parameters is evaluated by experimental trial and error. A typical value is 30 - 300°C/cm. The temperature gradient and the pull rate are very closely allied. For a gradual gradient a faster pull can be used, and with a steep gradient a slower pull must be used. The pull rate must be such as to cause solidification of the melt while in the temperature gradient. Ideally, a planar solid-liquid interface is maintained. A typical pull rate is 1 - 10 cm/hour.

The material must be held at the melt temperature for a length of time to insure against cool or hot spots in the melt. Hot spots tend to supercool and cause the ingot to be polycrystalline. If the melt is at too high a temperature it tends to supercool upon crystal growth. With the melt lower than the freezing point solidification occurs through out the melt rather than at the seeding point. This polycrystalline solidification can be triggered by vibration or convection current. Thus the hold time is rather critical so that the melt is the correct temperature and has no hot spots. A typical hold time for the melt is 30 - 60 minutes.

The cooling rate of the lower zone is usually selected so that the crystal is not thermally shocked. This rate normally depends on the thermal insulation of the furnace and the effective insulation properties of the crucible and holder. Thus the cooling rate must be determined experimentally for each furnace-crucible-material system. The cooling rate may be such that the furnace can be turned off instead of cooled at a (50 - 100°C/hr.) programmed rate; in other circumstances, however, such as solid-solid phase transitions, the cooling rate is very important. In such cases as the solid-solid phase transition in the alloy 50% (at) gold-copper, the cooling rate must be determined by experiment.

The material parameters are melting temperature, preferred crystal orientation for growth, occurrence of solid-solid phase transitions, heat of fusion, tendency to supercooling, sensitivity to vibration during crystal growth, and the distribution coefficient of the dopant or impurity.

The melt temperature and solid-solid phase transitions have been mentioned in the discussion of furnace parameters. Usually a crystal will have a preferred axis for crystal growth purposes, since the atomic and electronic configuration of a certain crystal face may be more conducive to crystal growth. This preferred axis or face will grow at a more rapid velocity than other faces or axes. In the modified Bridgemann-Stockbarger method the crystal orientation surviving the crucible constriction has a high probability of being in the preferred direction.

The rate at which the heat of fusion can be removed from the solid-liquid interface determines the rate of growth of a crystal. This is one reason why the rate of pull must be determined experimentally, since an a priori assessment of the contribution of this effect to the pull rate for various materials would be difult, at best.

Silver and copper-gold alloy have a tendency to supercool if the temperature of the melt is considerably higher than the melting point at the time of crystal growth. This supercooling is a property of a number of metals and must be considered when melting the material. This tendency is avoided by keeping the hotter zone close to the melting point of the material and allowing the melt to stabilize at the desired temperature.

As the impurity or doping level in silver increases, it is usually harder to grow a single crystal. This is generally caused by the collection of impurities at dislocation faces. Thus, if an impurity is present that is deposited at the freezing interface, it will disrupt the normal silver crystal growth and possibly cause the ingot to be polycrystalline. Slower crystal pulling and vibration free growths may help alleviate this problem. Vibration can cause variations in the crystal such as striation and inhomogeneity because of the atomic kinetics at the freezing interface. The vibration pressure patterns may be radial, or longitudinal which will produce the same type of pattern in the crystal imperfection. The experimental apparatus for growing single crystals should be as vibration free as possible.

TYPICAL EQUIPMENT AND PARAMETERS FOR CRYSTAL GROWTH

In order to grow single crystals of pure silver, doped silver, or gold-copper alloy a specific set of equipment is needed. This equipment is described in general and is presented here only as being typical. The "Multipurpose Electric Furnace System for Space Experiments", proposed for Skylab can be used with a few modifications.

The typical design of the furnace is a resistance type, having two zones with the hotter zone at 1000°C maximum. The two zones should have 60 - 160°C temperature difference with a temperature gradient of 30 - 300°C/cm between the zones. It should have an inside diameter of 4 to 6 cm and a length of at least 25 cm. The inside diameter of the baffle should be approximately 2.5 cm. The ampoule is constructed of graphite sealed in quartz under a vacuum. The maximum diameter of the quartz envelope for the ampoule should be such that approximately 1 mm clearance on the radius exists at the baffle. The length of the graphite ampoule is 8 cm and the length of the quartz envelope just large enough to enclose the graphite and seal.

A smooth operating pull mechanism to pull the ampoule through the furnace, should have a velocity range of 1 to 10 cm/hr. and must be vibrationless. The pull rod must have an attachment for the bottom of the ampoule. A temperature programmed controller must be used to lower the furnace temperature at a steady rate or to hold the temperature at a desired temperature. The increase or decrease in temperature must be made at a steady rate and have a range capability of 20 - 2000°C/hr. This range is needed first for increasing the temperature at a rate of 1000 - 2000°C/hr. and a second decrease of temperature for annealing of a rate of 20 - 300°C/hr.

The equipment for analysis of the resulting single crystals is briefly noted in the section that relates parameters to materials.

CRYSTAL GROWTH IN ZERO-GRAVITY

The effects of a zero gravity environment upon silver, or copper-gold single crystal growth and crystal imperfection are discussed in the following paragraphs. A few comments are made about the general effects that are caused directly by the lack of gravity. These direct effects which are changes in the crystal growth parameters cause secondary effects in crystal perfection.

In a zero-gravity environment there is, of course, no relative mass acceleration. Density variations in a liquid that give rise to convection currents in a gravitational field have no such effect in the absence of gravity. Convection plays an important role in the production of some of the effects observed in the liquid-solid transition, particularly in the controlled solidification used in crystal growth, so one might expect some differences between crystals grown in a gravitational field and similar crystals grown in the absence of gravity.

A solid usually has a composition different from that of a liquid with which it is in equilibrium, except in the cases of pure materials such as pure silver and solutions exhibiting congruent melting such as 50% (at) Au-Cu. Progressive solidification of a liquid solution, then, usually produces a solid of non-uniform composition, i.e., when solidification is complete, the distribution of a solute in the solid is different from that in the initial liquid, even though the total amount of solute is unchanged. Thus, the effective and equilibrium distribution coefficients are useful in discussing solidification. The extent to which the component rejected from the solid is mixed with the main body of liquid determines the relation of the effective distribution coefficient to the equilibrium distribution coefficient. This mixing is done by two mechanisms, diffusion of the rejected component into the liquid and the stirring effect of convection currents. In terrestrial grown crystals both of these processes contribute to mixing in the liquid. In a zero-gravity environment, however, diffusion alone would occur.

Theoretically the two cases of mixing by diffusion alone and complete mixing by convection, lead to different predicted values of the effective distribution coefficient. When mixing of the rejected component with the liquid occurs solely by diffusion from a slowly moving planar interface, the value of the effective distribution coefficient is one in the steady state, i.e., the solid formed by a freezing liquid has the same composition as the liquid. Transient effects, caused only by diffusion in a zero-gravity process would produce segregation of impurities and non-uniform concentrations only near the ends of an ingot.

The above discussion applies primarily to alloys such as Cu-Au and to soluble impurities such as dopants in silver. Mixtures in which a component shows limited solubility in either or both phases of a solid-liquid system tend to segregate in the terrestrial environment, with the denser components settling to the bottom of the liquid. In the absence of gravity even mixtures of immiscible components would not segregate in the liquid phase. Thus macroscopically homogeneous composites and even alloys solidified from homogeneous atomic dispersions of immiscible liquid metals could be prepared in the zero-gravity environment.

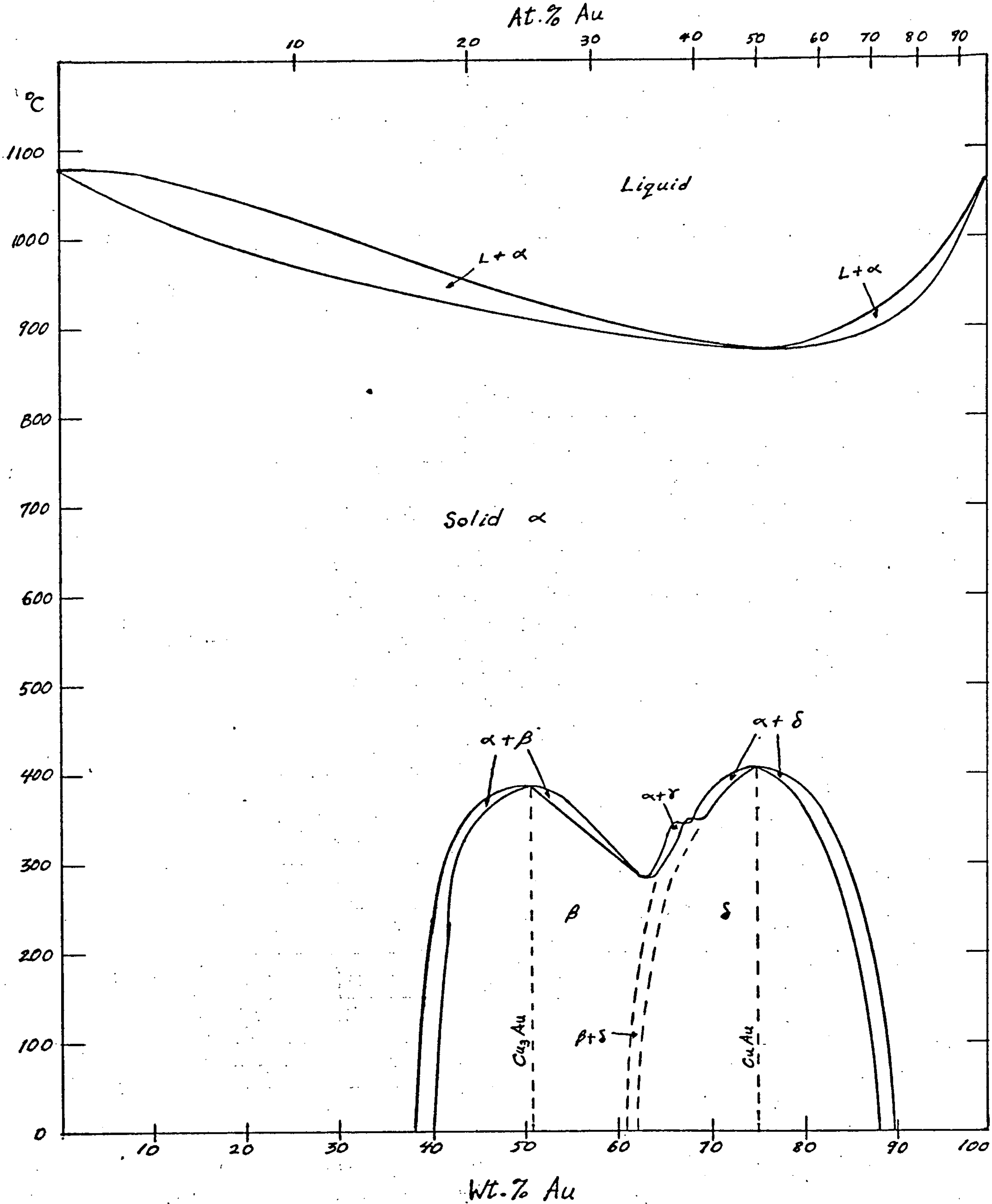
The absence of convection currents in a liquid would tend to favor a more stable liquid-solid interface for crystal growth experiments of either silver or copper-gold alloy. If, as is commonly supposed, an unstable interface favors striations and lack of perfection in crystals, crystal growth in zero-gravity should lead to more perfect crystals than those commonly prepared.

Solidification of alloys that exhibit a eutectic point in their phase diagrams often leads to a lamellar structure. This behavior is a result of properties of the alloy system rather than the particular conditions of solidification. A likely effect of zero-gravity solidification of such alloys is a more perfect lamellar structure rather than a non-lamellar structure. Similarly, if constitutional supercooling is responsible for striations in a crystal, growth in the absence of gravity would not be expected to yield an unstriated crystal. Supercooling of the melt is expected to become more prevalent for a zero-gravity environment.

One obvious disadvantage to crystal growth in zero-gravity arises from the fact that, in the absence of gravity, containerless liquids become spherical in geometry. Even a contained freely floating liquid would contact the crucible wall intermittently, making controlled seeding difficult. A proper container should remedy this problem. One advantage of growing single crystals in space comes not from the zero gravity environment but from the smooth vibrationless space laboratory. In a vibration free crucible the atomic kinetics at the freezing interface are not fluctuating which would yield a more perfect crystal. Vibration in the equipment tends to make crystal imperfections, but in the case of a supercooled melt it also raises the solidification temperature.

SELECTION OF MATERIALS FOR INVESTIGATION

The materials of silver, germanium, and copper-gold alloy were selected for investigation of zero-gravity effects on single crystal growth of relatively high melting metals. This selection was made after a review of all metals and metal alloys that have a melting point between 900°C and 1100°C. A compilation of these metals and alloys is given in Appendix A which gives the alloy, percentage of range for the constituents, and range of the melting curve for the alloy range. A number of candidate alloys were examined and the selection was narrowed to three: Au-Cu, Ag-Au, and Ag-Cu. These three were candidates because of the wider range of constituents. Comparing the phase diagrams for these alloys the Au-Cu has the advantage of a wider constituent range than the other two. It has the advantage of the existence of CuAu and Cu_3Au compounds and the other two do not have existent metal compounds. Each of Au-Cu and Ag-Cu have a point of the melting curve where the solidus and the liquidus lines meet. The advantage of growing a single crystal at this point allows an equilibrium state of equal alloy constituency in the melt and the freezing interface. Thus, no zoning of either constituent and a more uniform stoichiometry. The Au-Cu alloy at a composition of 50% (atomic) is the alloy compound of AuCu and it occurs at the stoichiometry where the solidus and liquidus lines meet. The AuCu compound alloy is an order-disorder alloy due to a lower temperature solid-solid phase transition. This solid-solid phase transition may be affected by a zero-gravity environment during single crystal growth.



PHASE DIAGRAM FOR COPPER GOLD ALLOY

With all of the advantages that the Au-Cu alloy has, it was selected to be the candidate alloy for investigation into the effects of zero-gravity crystal growth in space. The AuCu metal compound was further specified in order to gain all advantages possible from the alloy.

The selection of the elemental metals was greatly simplified since there are only three possible candidate metals: silver, germanium, and praseodyium (See Appendix A). There has been more investigation into the properties of single crystal germanium than the other two, so that far more data and growth parameters are known to a better degree of accuracy. These studies have included single crystal imperfections and defects which were related to impurities and growth parameters. The properties of silver are very well known, but those of single crystal silver have not been investigated as thoroughly as germanium. Silver can be easily grown into single crystals for investigation. Silver crystals differ from germanium in that they are soft, whereas germanium is hard, which makes the silver more difficult to cut and polish for an imperfection study. Germanium is a border line metal and is considered a semiconductor.

For the aforementioned reasons both silver and germanium are selected for investigation of zero-gravity effects on metal crystal growth. Silver is suggested for this initial investigation because of the abundance of data on earth grown crystals of germanium.

CRYSTAL PARAMETER MEASUREMENTS AS RELATED TO MATERIALS

There are a number of crystal properties and crystal imperfections that need to be analyzed for the effects of zero gravity. These properties are effective distribution coefficients, impurity segregation, alloy homogeneity, crystal perfection, and the liquid-solid transition. The defects which need to be analyzed are striation, lineage, slippage, lamella, and inhomogeneity. These properties of the crystal will be discussed in the following paragraphs.

In the following discussion there are suggested specific materials for investigation of alloys, pure metals, and doped metals. The specific metals and alloys were selected from the compilation in the appendix because of their characteristics and properties. These materials are to be used for the determination of crystal properties and imperfections which may be affected by crystal growth in zero gravity. These materials were selected from the list given in Appendix A because of a number of reasons which were stated in the previous section.

Alloy inhomogeneity can be macroscopic (about 10^{-1} cm) solute or solvent distributions which are produced in the crystal by various material and growth parameters. On a smaller scale (about 10^{-2} cm) inhomogeneities are produced by fluctuating growth conditions. This causes fluctuating solute concentrations in the crystal which are parallel to the freezing interface. If the freezing solid is supersaturated with one of the alloying elements, the concentration of that element in the crystal fluctuates with the fluctuating growth parameters. Thus, the inhomogeneities are usually longitudinal with isoconcentrations parallel to the freezing interface but can be random or change radially. To evaluate the homogeneity of a crystal, it must be sectioned vertically, polished, etched and examined visually with a microscope. The material that may be used to measure this property of homogeneity is the (50% at.) gold-copper alloy.

The effective distribution coefficient is a quantitative measure of the ratio of dopant left in the melt to the dopant that is deposited on the freezing interface. This effect is caused by the dopant lowering or raising the melting point of the material. The parameter,used to measure this,is the concentration of dopant along the freezing axis. The concentration distribution can be measured spectrographically and the coefficient calculated. Different spectrographs must be used for different impurity elements and different concentrations. The method to be used would be determined in each individual case. The materials which would yield the greatest amount of information are doped silver or doped germanium.

The impurity segregation in a crystal may be due to either the zoning effect or to convection currents and/or nonuniform thermal parameters. The effect of this leaves the crystal with a distribution of impurities that is nonuniform. This can be measured in the same manner as the effective distribtion coefficient with a mass, emission, or absorption spectrometer. The materials which are recommended to be used to determine impurity segregation are doped silver or doped germanium.

Crystal perfection is a function of all of the growth parameters and material properties. As the microscopic imperfections build up there are macroscopic imperfections that are produced. The macroscopic properties can be observed by lineage, slippage, lamella, and striations. The microscopic perfection of the crystal can be determined by x-ray backscattering patterns. The materials that can be used for this determination are pure silver, pure germanium, or either doped, or the copper-gold alloy.

The liquid-solid transition is observed by effects on the freezing interface. The morphology of the interface usually depends on: the free energy of the phases; mechanical equilibrium and density gradient of the surface; and the nucleation process of the new surface. The fastest growing crystal axis will dominate the freezing interface. All of the aforementioned points determine the shape of the freezing interface, however none of these can be determined from the interface geometry. The only information that can be obtained from the interface geometry is by comparison with other crystals grown with different parameters. Thus, a comparison between terrestrial grown crystals will yield comparative information about the growth parameters. In order to observe the solid interface the crystal growth must be stopped after the crystal has been partially grown. The only way that this may be accomplished, in this experiment, is to immediate-cool down the furnace so that the crystal becomes polycrystalline above the previously freezing interface. The crystal is sectioned and polished longitudinally and then examined under a microscope for comparison. The effects of zero gravity on the liquid-solid transition may include slower crystal growth, supercooling, and other effects. Materials which could be used for this study are silver, germanium (either doped or undoped), and the copper gold alloy.

Striations are macroscopic lines along which the composition or the growth rate has a variation. Striations are caused by thermal variances, fluctuations, mechanical variances, bands of impurities that are parallel to the freezing interface, and change in internal stress caused by two vying crystal orientations or compositions. Striations can be evaluated by microscope and etchpit count and geometry. The materials which would be used for striation determination are doped silver or doped germanium, or the copper-gold alloy.

Lineage and slippage are effects caused by internal stress which is due to growth parameter problems. They may be caused by crystal growth patterns (atomic kinetics), or thermal problems. Lineage is caused by thermal fluctuations that are radial across the freezing interface or too fast a cooling rate of the solidified crystal. Slippage is usually caused by vying crystal growth fronts that are secondary to the dominate front, but due to growth conditions are reinforced. Slippage may be caused by the geometry of the freezing interface, fluctuating thermal parameters, or slightly supercooling of the material before solidification. Each of these cause a plane of discontinuity in the crystal structure and along these lineage or slippage lines, impurities tend to concentrate. Thus, the discontinuity is propogated as impurities add to the internal stress. These lineage and slippage defects can be evaluated by etch pit arrangements. The crystal is cut perpendicular to the growth axis, polished, etched, and examined with a microscope. Lineage is identified by a connected line of evenly distributed etch pits with the same orientation. Lineage lines are usually radial from the central point of the crystal. Slippage lines are identified by a line of randomly distributed etch pits that are randomly oriented. X-ray analysis can be used to supplement the etch pit analysis. The materials that were selected to be used for the lineage and slippage determinations are silver and germanium, either doped or undoped.

Lamella is the layering of the crystal along the direction of the growth axis and can be caused by two phase alloys, thermal convection currents or large slippage planes. With a two phase alloy, one of the phases is continuous and the other has the form of plates in parallel array, or rods in parallel array. These can be caused by unsteady heat flow, freezing interface not flat enough, and characteristic of the material. The effect of this imperfection is a layering of the crystal usually perpendicular to the freezing interface and a periodically variance of the crystal properties. The crystal properties are usually consistent within a layer and the crystal usually has some of its impurities along the lamella surface. The lamella can be determined and evaluated by etchpit analysis and a microscope. The material to be used for the determination is doped silver, or copper-gold alloy.

These are but a few of the crystal imperfections that may be encountered in growing a single metal crystal in a zero gravity environment. These previous paragraphs have tried to describe each of the imperfections and how it is caused, and its effect. A brief statement has been made on how to measure and determine the imperfection, and a metal or alloy, was given as a first trial material. This alloy or metal should be investigated experimentally to determine if all of the above imperfections can be identified. This analysis should be done experimentally to verify this paper study.

SUMMARY

The findings of this analytical study of growing single crystals of relatively high melting point metals are summarized below in outline form.

The experimental requirements are:

- Determination of crystal properties and parameters
- Comparison between space grown and earth grown crystals
- Specifications of a space manufacturing facility

The typical furnace requirements are:

- Resistance type 1000°C furnace
- Two zones with baffle and 60 - 160°C temperature difference
- Temperature gradient 30 - 300°C/cm between zones
- Baffle hole diameter 2.5 cm
- Furnace length at least 25 cm
- Pull mechanism, 1 - 10 cm/hr vibration free
- Programmed temperature controller 20 - 2000°C/hr
- Ampoule - graphite crucible sealed in quartz under a vacuum - 2 cm x 8 - 10 cm

The material parameters for silver, germanium, and copper-gold alloy are:

	Ge	Ag	CuAu
Melting temperature °C	958	960	880
Latent heat of fusion, Kcal/mole	8.1	2.7	-
Preferred crystal orientation	111	-	-
Solid-solid phase transition	none	none	410°C
Tendency to supercool growth	yes	yes	yes

(continued)

continued

	Ge	Ag	CuAu
. Dopant distribution coefficient	known	Append.B.	N/A
. Shrink upon freezing	no	yes	yes

The zero-gravity effects on crystal property are:

Primary effects

- No density separation in the melt
- No convection currents in the melt
- Free floating melt

Secondary effects

- Diffusion mixing of constituents and impurities which causes the distribution coefficient to be one
- Homogeneous crystal from immiscible components
- Fewer striations
- More perfect lamella structure
- More tendency to supercool
- Difficult seeding because of free floating melt

Along with the zero-gravity environment in space there will be a vibrationless environment also, which will help produce a more perfect single crystal.

From the list of metals and alloys in Appendix A, silver, germanium, and (50% at.) gold-copper alloy were selected to be studied. These were selected by the following criteria:

Silver

- The only metal by all definitions

Germanium

- Best known properties and imperfections

Gold-Copper

- Wider constituent range (70% at.)
- Metal compounds exist
- Solidus and liquidus lines meet
- Order-disorder alloy due to solid-solid phase transition

The materials used to measure each of the parameters are:

- Distributive coefficient - Ag or Ge (doped)
- Impurity segregation - Ag or Ge (doped)
- Homogeneity - (50% at.) Au-Cu
- Crystal preparation - Ag or Ge (pure or doped), or AuCu
- Liquid-solid transition - Ag or Ge (pure or doped), or AuCu
- Striations - Ag or Ge (doped), or AuCu
- Lineage and slippage - Ag or Ge (pure or doped), or AuCu
- Lamella - AuCu

This summary has presented the findings of this analytical study. There are two appendices attached at the end of the report which gives the list of metals and alloys (Appendix A) that meet the selection criteria; and the distribution coefficient of dopants in silver (Appendix B).

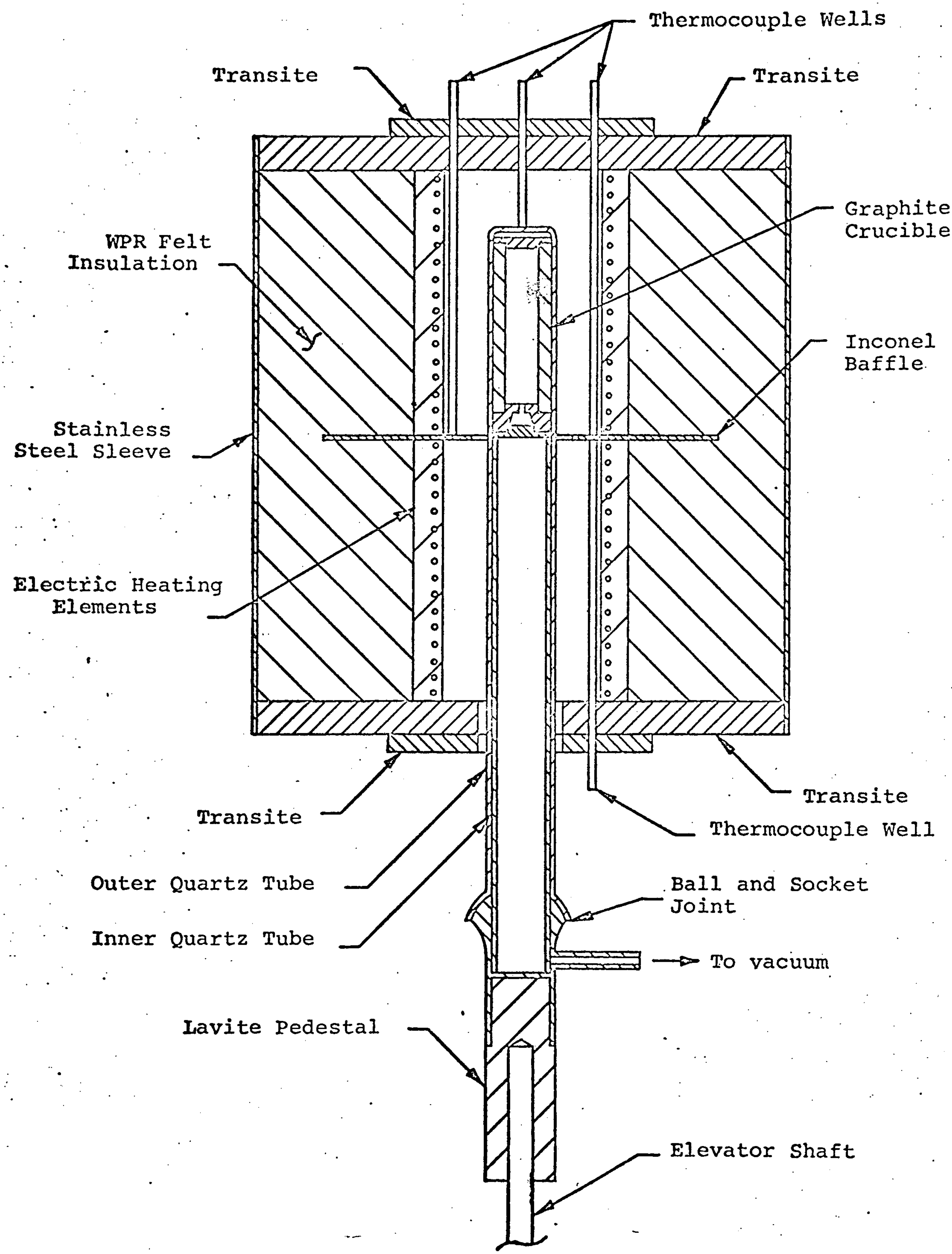
CONCLUSIONS AND RECOMMENDATIONS

An analytical study of the parameters and requirements for growing crystals of relatively high melting point metals was made and the results were presented herein. Also an analytical study of the possible effects of zero-gravity on the growth of these crystal system was made. The results of these studies has shown the feasibility of growing these single crystals in a zero-gravity environment and comparing them to terrestrial grown crystals in order to obtain useful information. The comparison of crystal characteristics and parameters would show the effects of zero-gravity upon crystal growth. The equipment requirements to grow these crystals has been shown to be a two zone furnace with a pull mechanism. A graphite crucible sealed in quartz must be used. The furnace parameters were stated with a value for each. The material parameters and the possible effects of zero gravity on the crystal growth were discussed. A list of metals and alloys that meet the criteria for selection was compiled and silver, germanium, and gold-copper alloy were selected. These materials were related to the crystal parameters in order that it can be possible to evaluate the comparison between terrestrial and space grown crystals.

The advantages of growing single crystals of silver, germanium, and gold-copper alloy in a space environment are no convection currents exists, no separation and settling out of immiscible mixture of metal liquids, and no vibration. These will produce different effects in the space grown crystal. The distribution coefficient would be approximately one, and inhomogeneity, lineage, slippage, and striation may be eliminated or reduced greatly; unless the increase in supercooling off-sets the advantages from not having convection currents. The lamella produced by some alloys would tend to be more pronounced and more perfect.

This analytical study of parameters, requirements and zero-gravity effects on single crystal growth of metals in space, concludes, there are definite advantages to space growth of metal crystals. There will be many crystal characteristics that will be changed for the better and the zero-gravity environment should enhance crystal perfection.

It is recommened that pure silver, pure germanium, doped silver, doped germanium, and (50% at.) gold-copper alloy be used as the materials for study. It is also recommended that crystals of these materials be grown in various orientations with respect to the gravatational vector. These crystals should be compared to the crystals grown vertically in order that gravity dependent crystal growth characteristics can be identified with more certainty. It is further recommended that this experiment be performed in space because of the good possibilities of a better single crystal.



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REFERENCES:

Brice, J. C. "The Growth of Crystals From the Melt", John Wiley & Sons, Inc., New York, 1965

Chalmers, Bruce, "Principles of Solidification", John Wiley & Sons, Inc., New York, 1965

Fabiniak, Thaddeus J., "Investigation of Zero Gravity Effects on Material Properties", Cornell Aeronautical Laboratory Technical Report No. KC-2862-P-1 on Contract No. NAS8-24952, April, 1970

Gilman, J. J., "The Art and Science of Growing Crystals", John Wiley & Sons, Inc., New York, 1963

Greenland, K. M., Proc. Phys. Soc. Lond. B. 65., 575, 1952

Lawson, W. D. & Neilsen, S. "Preparation of Single Crystals", Butterworths Scientific Publications, London, 1958

Menzies, A. C., Proc. Phys. Soc. Lond., B. 65, 576, 1952

Obreimov, J. & Schubnikov, L. Z. Phys. 25, 31, 1924

Schmidt, Paul H. "Purification and Crystal Growth of Gold", Journal of the Electrochemical Society, June, 1965

Smithells, Colin J., "Metals Reference Book", Vol. 1, 3rd. Ed. Washington Butterworths, 1962

Stemer, W. H. & Kaye, S. "Preparation and Evaluation of Apollo 14 Composite Experiments", Contractor Report NASA CR-61368, August, 1971

Stockbarger, D. C., Rev. Sci. Instmn. 7, 133, 1936

Tammann, G. Lehrbuch der Metallographic, Leipzig, 1923

Weiss, Richard J., "Solid State Physics for Metallurgists", Addison-Wesley Publishing Co., Inc. Reading, Mass.

Westbrook, J. H. "Intermetallic Compounds", John Wiley & Sons, Inc., New York

Wuenscher, Hans J., "Materials Processing in Zero-Gravity An Overview", NASA, June, 1972

APPENDIX

A - 1

APPENDIX A

COMPILATION OF METALS AND ALLOYS

The following metals and binary alloys were selected as meeting the crieteria for the crystal growth study of relative high melting metals and alloys. The selection criteria were that the melting point of an alloy fall in the 900 - 1100°C range for at least a 15 atomic per cent range of solute concentrations, or that a metal compound melting in the same temperature range exist. Pure metals having a melting point between 900 and 1100°C are also listed. True metal alloys were preferred, although systems containing Si, Se, As, and Te were also considered. The definition of a metal was taken to be that of the Bohr arrangement of elements.

Metals	Melt Pt. °C
Copper	1083
Germanium	958.5
Gold	1063
Praseodyium	940
Silver	960.8

Binary Alloy	Atomic %	Melt Pt. °C
Ag - As	0 - 80% As	900 - 1100
Ag - Ce	15 - 33% Ce	900 - 980
Ag - Au	0 - 100% Au	960 - 1063
Ag - Cu	0 - 12% Cu	960 - 900
	70 - 100% Cu	900 - 1083
Ag - Cd	0 - 15% Cd	960 - 900
Ag - Hg	0 - 11% Hg	960 - 900

Binary Alloy	Atomic %	Melt Pt. °C
Ag - La	16 - 33% La	900 - 955 - 900
Ag - Pb	78 -100% Ag	900 - 960
Ag_3Pr	25% Pr	956
Ag_2Pr	33% Pr	878
Ag pr	50% Pr	928
Ag - Th	0 - 20% Th	900 - 1100
Ag - Te	0 - 35% Te	960 - 871 - 958
Al - Au	10 - 47% Au	900 - 1060 - 900
Al - Ca	18 - 48% Ca	900 - 1079 - 900
Al - Co	80 - 96% Al	1100 - 900
Al - Cu	0 - 44% Al	1060 - 900
Al Mn	65 - 86% Al	1100 - 900
Al Sb	7 - 75% Sb	900 - 1050 - 900
Al Se	18 - 70% Se	900 - 970 - 900
Al Si	47 - 65% Al	1100 - 900
Au - Cd	0 - 18% Cd	1060 - 900
Au - Hg	0 - 15% Hg	1060 - 900
Au - Cu	0 -100% Cu	1060 - 880 - 1080
Au - Mn	0 - 37% Mn	1060 - 960 - 1100
Au - Na	0 - 52% Na	1060 - 876 - 900
Au - Ni	0 - 67% Ni	1060 - 950 - 1100
Au - Sn	85 -100% Au	900 -1100
Au - Te	0 - 22% Te	1060 - 900

Binary Alloy	Atomic %	Melt Pt. °C
Au - Tl	0 - 15% Tl	1060 - 900
B - Ni	47 - 56% Ni	1100 - 990 - 1100
Be - Cu	0 - 60% Be	1080 - 860 - 1100
Be - Si	33% Si	1090
Bi_2 - Ca_3	60% Ca	928
Bi - Cu	70 -100% Cu	900 -1080
Ca - Cu	76 -100% Cu	900 -1080
Ca - Na	35 - 63% Na	900 -1100
Ca - Pb	16 - 55% Pb	900 -1130 - 900
Ca - Sn	25 - 57% Sn	900 -1122 - 900
Cd - Cu	0 - 17% Cd	1080 - 900
Ce - Cu	80 - 100% Cu	900 -1080
Ce - Fe	15 - 33% (wt) Fe	900 -1100
Ce_3In	25% In	920
Ce - Ti	63 - 88% Ti	900 - 1100
Co - P	20% P	1022
Co - Sb	25% Sb	1088
Cu - Ge	0 - 18% Ge	1080 - 900
Cu - Ga	0 - 25% Ga	1080 - 900
Cu - Pr	0 - 70% Pr	1080 - 900
Cu - Li	0 - 40% Li	1080 - 900
Cu - Mn	0 - 70% Mn	1080 - 900 - 1100
Cu - Th	0 - 70% Th	1080 - 940 - 1100

Binary Alloy	Atomic %	Melt Pt. °C
Cu - U	0 - 20% U	1080 - 950 - 1100
Cu - Zr	0 - 18% Zr	1080 - 980 - 1100
Cu - Zn	0 - 36% Zn	1080 - 900
Fe - Ge	45 -100% Ge	1100 - 900 - 960
Ge - Pb	0 - 27% Pb	960 - 900
Hg - U	20 - 41% Hg	1100 - 900
In - Ni	18 - 66% In	1100 - 900
Mg - Si	11 - 64% Si	900 - 1100
Mn - Sb	13 - 41% Sb	1100 - 900
Mn - Ni	42 - 80% Mn	1100 - 1020 - 1100
Mn - Sn	58 - 83% Mn	900 - 1100
Mn - U	12 - 68% U	1100 - 1040 - 900
Na_2Te	33% Te	950
Ni - Ti	62 - 79% Ti	1100 - 940 - 1100
Ph - S	10 - 50%	900 - 1100
Pb - Se	20 - 57% Se	900 - 1080 - 900
Pr - Sn	18 - 36% Pr	900 - 1100
U_2Ti	33% Ti	900

APPENDIX B

DISTRIBUTION COEFFICIENTS FOR A SILVER MELT

Since doped silver was selected as a metal to be investigated, the following list of dopant distribution-coefficients in silver has been compiled. These were obtained from phase diagrams of the alloys. The distribution coefficient categories are k greater than one, k less than one, and k approximately one. The numerical values for the coefficients were not calculated because they were deemed not necessary for this study.

Distribution coefficient greater than one

Au	Pd
Cr	Pt
Ni	

Distribution coefficient approximately one

Mn (for less than 5% wt.)

Distribution coefficient less than one

Al

As

Ba

Be (less than 1% wt.)

Bi

Ca

Cd

Ce

Cu

Ga

Ge

continued:

Hg

In

La

Li

Mg

Na

Pb

Pr

Sb

Se

Si (less than 5% wt.)

Sn

Sr

Te

Th

Ti

U (less than 3% wt.)

Zn

Zr(less than 2% wt.)