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FOR GROWTH OF MULTI-ELEMENT SINGLE
CRYSTALS OF METALS AND METALLOIDS

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CRYSTALS OF METALS AND METALLOIDS

by

M. J. Murtha and George Burnet

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AN ANNOTATED BIBLIOGRAPHY FOR GROWTH OF MULTI-ELEMENT SINGLE CRYSTALS OF METALS AND METALLOIDS

M. J. Murtha and G. Burnet

ABSTRACT

A list of abstracted references specifically relating to the growth of binary and multi-element metal and metalloid single crystals is presented. These references provide a researcher with information required for preparing many compound single crystals, and is a guide for the preparation of new compound single crystals. Indirectly the bibliography also lists contemporaries working in specific areas of crystal research.
INTRODUCTION

Emphasis in solid state research during the past decade has shifted from single element materials to the study of compounds. An increasing need for research on these materials has resulted from substantial industrial use of crystals in low power solid state circuitry for applications ranging from the space program to many everyday devices. Most of the work has dealt with the production and characterization of semi-conducting crystals. Research on crystals can be expected to increase because of requirements for higher efficiency, and even more minute solid state circuits. Properties of entire new groups of crystals will be analyzed to optimize the efficiency of those circuits, in which they will be used as well as to maximize circuit reliability.

Single crystals of metal or metalloid alloys will be of special interest because of the unique non-linear properties many of them exhibit. Crystals which have unusual non-linear thermo-electric and thermo-magnetic properties are being evaluated now for use as gating or switching devices in computer and laser circuitry, as well as more conventional control devices. Some crystals of this type also have unique optical properties and are being used to focus and aim laser beams to the moon, for example. This same optical gating property could be used to increase machine computation speeds.

As the need for a given type of crystal becomes apparent, work on preparation of corresponding single crystals begins. Solid single crystals provide more meaningful research information because there are no grain boundary effects and properties can be measured along the different
crystallographic axes. As part of the work to date, there have been developed new non-destructive analytical procedures for crystal perfection (such as x-ray diffraction and magnetic resonance) and equipment for producing higher quality crystals, for example, ultra-high vacuum systems and levitation melting to eliminate crucible contamination. Solid state research is relatively new because it has been dependent on the development of these new and often highly sophisticated techniques. Besides meeting the immediate needs of industry, single crystal alloys are providing important basic information about bonding, electron spins, and nuclear properties.

Techniques of Growth

The same basic procedures as are used for the growth of elemental single crystals are used for production of compound single crystals. These techniques are listed in Table 1. Each procedure has been found to have unique advantages in the growth of certain single crystals. Physical properties of the multi-element system will usually dictate the best growth procedure. Some advantages and disadvantages of each procedure are also briefly listed in Table 1.

An apparent advantage for multi-element crystal growth by strain-anneal or from solution lies in the fact that constant composition crystals can be produced more readily. Homogeneity is more of a problem when the other methods are used because the higher melting component will solidify selectively. Unfortunately the number of systems to which the strain-anneal method of recrystallization from a homogeneous slug can be applied is limited. Other problems are also encountered in the growth of multi-element
Table 1. Procedures for Multi-Element Single Crystal Growth

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>From melt:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bridgeman</td>
<td>Oriented crystals can be produced.</td>
<td>Difficult to obtain uniform composition.</td>
</tr>
<tr>
<td></td>
<td>Crystal dimensions are predetermined.</td>
<td>Crystal strain and contamination from the crucible sometimes occur.</td>
</tr>
<tr>
<td></td>
<td>Growth rate and temperature gradient can be controlled.</td>
<td>Striations can occur due to mechanical movement.</td>
</tr>
<tr>
<td>Zone melting</td>
<td>Uniform composition can be obtained.</td>
<td>Cannot observe.</td>
</tr>
<tr>
<td></td>
<td>Oriented crystals can be produced.</td>
<td>Contamination from crucible can occur unless float-zoned.</td>
</tr>
<tr>
<td></td>
<td>Growth rate, temperature gradients and atmosphere can be controlled.</td>
<td>Striations can occur due to mechanical movement.</td>
</tr>
<tr>
<td></td>
<td>Wide temperature range available.</td>
<td>Large temperature gradient can cause strain.</td>
</tr>
<tr>
<td>Czochralski</td>
<td>Oriented crystals can be produced.</td>
<td>Control of growth rate is indirect.</td>
</tr>
<tr>
<td></td>
<td>Atmosphere can be controlled.</td>
<td>Temperature gradients occur in the melt.</td>
</tr>
<tr>
<td></td>
<td>Wide temperature range available.</td>
<td>Striations can occur due to rotation and convection.</td>
</tr>
<tr>
<td></td>
<td>No strain due to crucible.</td>
<td>Continuous feed of melt required to obtain constant composition.</td>
</tr>
<tr>
<td><strong>From solid:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strain-annal</td>
<td>Homogeneous crystals can be produced.</td>
<td>Crystals produced are often small, non-oriented and of random shape.</td>
</tr>
<tr>
<td></td>
<td>Lower-temperature process.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Minimum contamination.</td>
<td></td>
</tr>
<tr>
<td>From vapor:</td>
<td>Atmosphere can be controlled.</td>
<td>Crystals produced are often small thin plates, non-oriented and non-homogeneous.</td>
</tr>
<tr>
<td>From solution:</td>
<td>Crystals are of constant composition.</td>
<td>Crystals produced are of fixed shape and non-oriented.</td>
</tr>
<tr>
<td></td>
<td>Atmosphere can be controlled.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>No crucible is required.</td>
<td></td>
</tr>
</tbody>
</table>
single crystals, for example, significant component segregation even within single crystal grains.

The most popular methods for growing multi-element single crystals appear to be growth from the melt either by Czochralski pulling or by use of a zone-melt horizontal traveling furnace. These methods permit use of a controlled growth atmosphere and a large operating temperature range. Another advantage is the availability of units of commercial design which can be precisely controlled by proper instrumentation. A considerable amount of current research is directed toward improving the quality of pulled multi-component crystals. Critical evaluation of the relation of melt temperature gradient and seed or melt rotation to crystal segregation and perfection is underway. The use of microprobe analysis and etching techniques appear to provide useful data on local non-homogeneity.

Bibliography

Because alloy single crystal preparation work has been published more as an aside to research on crystal properties and important references are not always easily found, the following annotated bibliography of abstracted material on this topic has been prepared. Most publications of alloy single crystal preparation have appeared since 1960.

Several abstracting sources, Chemical Abstracts, Metallurgical Abstracts, and Solid State Abstracts, were used to obtain the references cited. The search covered all years back to and including 1955. The survey was limited to growth of three-dimensional crystals and thus omitted most research on thin films. Notation is made where the original article was published in a
language other than English. For these articles the English abstract was used to prepare the annotation. The abstracts are listed in alphabetical order by author.

The abstract sources used provide cross-indexing of articles but the authors realize that significant material quite likely has been overlooked or not yet abstracted, and encourage readers to call omissions to their attention.

Index

The information contained in the bibliography has been indexed by compound and growth method. The author's name is given, then the page on which the reference can be found. The index follows the bibliography.
Annotated Bibliography


Rod material, 1/8" dia., was rolled and recrystallized. A point was then acid shaped and lowered into a salt bath for recrystallization to large grains. Two to three cm single crystals of [112] axis orientation resulted.


A method for growing single crystals of germanium alloys is described. It was found that rotation of the seed strongly increased the probability of forming monocrystals, and the rotation was more necessary the greater the Si content of the alloy.


Methods for growing compound single crystals are reviewed, and a method is described for growing alloy crystals of constant composition.


An InSb crystal was pulled, without rotation, from a Se-doped melt. During growth, temperature fluctuations were induced in the melt. The crystal, after etching, showed segregation bonds corresponding to the temperature changes.


Preparation of ZnTe from a single phase eliminated the black spots usually present in these crystals. Crystals were produced in evacuated and sealed silica tubes at 850°C. The equilibrium and annealing time was one week.


An improved method of growing Al-Sb single crystals is described. Oxide in the aluminum was eliminated by vacuum heating which also removed volatile impurities. The crystals were grown by the Czochralski technique.

CuAu crystals were grown in such a manner that they did not enter the ordered tetragonal or orthorhombic phase fields during growth. This was achieved by growing the crystals in a 2-zone furnace. The graphite crucible was sealed inside a SiO₂ tube narrowed at the bottom to a fine capillary. The tube was then lowered through the furnace and after annealing the capillary tip was broken and the crystal quenched with water.


A method is described for growing GaSe single crystals from polycrystalline GaSe by using chemical transport reactions with iodine as the transporting agent. Single crystals were also grown directly from the elements in the same manner.


Single crystals of Al and its alloys were obtained by a somewhat modified method of recrystallization. The entire operation was carried out in one day, without complicated thermostat apparatus.


The growth of single crystals of peritectic-type intermetallic compounds was investigated for binary aluminum rich systems. Single crystals of MnAl₆ and NiAl₃ were grown.


Homogeneous crystals of Bi-Sb solid solutions are difficult to grow but are important in the study of electron-transport properties and band structure of these materials. A zone melting technique was used to grow the crystals with temperature gradients of about 60°C/cm and growth rates 1.6-0.4 mm/hr.


Single crystals of Ti, α-phase Ti-Al, and Zr can be grown directly from the melt, if the β→α transformation can be controlled. A growth technique using electron beam zone melting is described.

A kinetic model of crystallization is used to set up computer simulations of the growth of one, two, and three dimensional binary crystals. Different aspects and variables of crystal growth are analyzed. Results agreed qualitatively with parameters from other experiments.


The usual Pb-Te single crystal often contains mosaics of subgrains which alter its physical properties. Lead telluride is a non-stoichiometric semiconductor and the maximum melting point does not coincide with the stoichiometric compound. When a crystal grown by the Bridgeman method had the end which was last to crystallize removed and the remainder remelted, the melting point of the new crystal obtained was nearer the maximum temperature and the resultant crystal was free of mosaic substructure.


Single crystal GaAs having high resistivity ($10^8$ ohm-cm) was pulled by the Czochralski technique. Addition of a small amount of chromium allowed pulling of this high purity crystal which was bright and shiny, apparently free of oxides. Increased concentrations of chromium did not further improve the resultant crystal.


The effect of the polarity of the [111] directions on the growth of GaSb crystals heavily doped with Te and Zn was investigated. The crystals were grown by the Czochralski technique in a purified He atm.


Synthesis of Ge dichalcogenides is difficult for a number of reasons. Low thermal stability and high volatility of the chalcogenides together with the danger of explosion due to high expansion of S and Se vapors are examples. Crystals were synthesized in evacuated quartz ampules held in a temperature gradient for a length of time. This yielded polycrystals which were used to grow single crystals from the gaseous phase using a 2-zone vertical furnace.

A method is given for growing crystals of the $A^{II}B^{VI}$ type from a melt of pure components in stoichiometric ratio at 1500°C and under an argon pressure of 1000-1500 atm. An autoclave is described for growing crystals under a pressure of 2000 atm. at 2000°C. Crystals obtained have fewer imperfections and impurities than crystals grown from a melt of the commercially available compound. Crystals of non-stoichiometric composition can be grown.


A zone technique which should be applicable to many peritectic-type compounds was used to grow good quality single crystals of ZnSb. It consisted of moving a melted Sb-rich zone along a charge of stoichiometric composition.


Strains incurred during aging resulted in early fragmentation of the original grains in the polycrystalline material, and the subgrains in the single crystals indicated that grain-size refinement was a primary cause of early increase in hardness. This refinement was associated with a reconstruction of the material which proceeded at 200°C, as a short range order transformation characterized by a relatively high rate of nucleation and a low rate of growth and not as precipitate formation.


ZnTe/Al crystals were prepared under high argon pressure by cooling the Zn-rich melt from 1280°C to 1100°C and abruptly quenching to room temperature.


Single crystals of copper-aluminum alloys were obtained from a mother alloy prepared of 99.999% Cu and Al. These metals were melted under purified argon plus carbon monoxide in a high frequency induction furnace. By reducing the mother alloy with Cu, four Cu-Al alloys containing Al of 2.6, 5.7, 10.6 and 15.1 at. % were obtained. Single crystals were grown by the Bridgeman method in a 10⁻⁵ mm Hg vacuum. They were then homogenized at 1000°C for 24 hrs. in vacuum.

Single crystals to 1 cm dia. by 6 cm long of RbAg₄I₅ have been grown from nonstoichiometric melts by the Czochralski technique. Procedures for purification of starting materials and optimum growth parameters are discussed.


ZnTe was synthesized in evacuated and sealed optical-quartz ampules. Single crystals were grown by holding one end of the uncooled ampule at 1240°C and the other at 1230°C for 20-40 hrs. Lower temperatures resulted in more perfect structures.


Single crystals of V₅Si were prepared by a two-step process. The pure metals were melted by radiofrequency heating in an argon atmosphere, and the single crystal then grown by the floating zone process.


A metals handbook containing phase diagrams and crystallographic information about the phases for most binary systems containing metals or metalloids. Because of the quantity of data to present, the handbook has been published in three editions, and the third edition has three large supplements.


Single crystals of GaAs were grown by direct combination of Ga (99.999%) and As (99.9999%) in a carbon-lined quartz vessel at 1250-1275°C, followed by zone refining at 1260-1280°C and crystal growing at 1245-1270°C.


This article describes a simple apparatus for forming the zone in a zone melter by means of optical focusing. The method is far less expensive than other forms of zone melting, and no special equipment is necessary for operation of the apparatus. Though work has been restricted to Al alloys, growth of other single crystals seems feasible.

A method suitable for the synthesis and crystallization of $\text{Al}_{2}\text{VI}$ and $\text{AIII}_{2}\text{VI}$ and $\text{AIIIBVI}$ calcogenides is discussed. The compounds were synthesized from their elements in metallic Ga or In which were used as "solvents." After producing homogeneous solutions at 1000-1200°C, the crystals were formed in the melt during slow cooling.


A transport method used for uranium chalcogenides was applied for preparation of the above single crystals. Iodide was used as the transport agent.


Homogeneous mixed single crystals of ZnCd sulfide were grown from the vapor phase. Single crystals of about 25 mm$^3$ volume with Zn/Cd ratios of 0.4 to 0.7 were prepared.


The growth of single crystals by the strain-anneal technique presented many experimental problems. The strain required seemed critical and was different for each alloy. A table of strains is included.


Single crystals were prepared by strain-anneal techniques. Cr and Fe were arc melted several times in an argon atmosphere. Ingots 1 cm by 5 cm were annealed at 1100°C in evacuated silica tubes for 72 hrs. These ingots were then strained by a pressure of about 5 ton/cm$^2$ and annealed against 1600°C for 72 hrs. in an argon atmosphere. Usually two or three large grains grew in an ingot by this annealing.

When a rod of circular cross section was used to grow single iron-silicon alloy crystals by the floating-zone technique, the high specific gravity of the material caused the liquid zone to take a form unsuitable for transferring r.f. energy for induction heating. The volume of the melt periodically changed and the growth rate fluctuated. The result was a non-uniform distribution of solutes and variable crystal cross section. It was possible to maintain a constant melt zone volume by using a square cross section rod of starting material.


The possibility of using chemical transport reactions as a general method of growing comparatively large single crystals is examined. Only closed systems are discussed. Optically clear, 24 mm long, single crystals of Cd₄Ge₆ were grown by pulling quartz ampules in a vertical furnace. Low supersaturation was used to control the nucleation.


The preparation and properties of the above single crystals were studied. Single crystals of LaGaSe₃ were grown from polycrystalline specimens by the Bridgeman method. Single crystals of PrGaSe₃ and NdGaSe₃ were grown by the gas transport method using iodine as the transport agent.


Polycrystalline SmInS₃ was placed in an evacuated quartz ampule and heated in a gradient (1100°C-900°C) several days. Single crystal SmInS₃ formed in the cooler part.


Crystal growth from the liquid and from the vapor phase was investigated over the full range of concentration in the Se-Te system. Viscosity measurements indicated that single crystal growth should be possible at reasonable growth rates only at the high Te end. Constitutional supercooling calculations showed that viscosity would limit single crystal growth to high Se and high Te concentrations (~95 at.%).

Single crystals (Al-20 wt. % Ag) were obtained from the melt by a modified Bridgeman technique. Specimens were cut to shape from a rolled strip, packed in alumina and passed through a horizontal furnace with a steep temperature gradient. Crystals were then homogenized for 5-7 days at 560°C and quenched into water at room temperature.


The experimental procedure, methods for purifying the protective atmosphere (either Ar or H2), and the pretreatment of the alloy crystals (Al-Cu, 7.7% Al and Fe-Mo, 8% Mo) are explained. A diagram for the gas purification system and furnace construction is included. Single crystals were grown from Cu, Al, Al-Cu, and Fe-Mo. The inert atmosphere gave satisfactory results with all materials. The Fe-Mo alloy was found to be very sensitive to the purity of Ar. Growth rates and the temp. gradient are also discussed.


The preferential growth direction and the anisotropy of cleavage of HgTe single crystals grown by the Bridgeman method under constant growth conditions was investigated. Cleavage can occur only along the [110] planes and [111] is the preferred growth direction.


The preparation and properties of Mg2Ge were studied to determine feasibility and usefulness for electronic devices other than bipolar transistors, particularly for integrated electronics. The single crystals were produced by reacting stoichiometric amounts of the constituents in a graphite crucible inside a sealed Ta bomb followed by solidification of the molten compound to a single crystal by a Bridgeman technique.


For production of large single crystals of GaAs with dislocation densities of 10-100 cm-2, a polycrystalline ingot, sealed in an evacuated quartz tube, was melted at one end by a movable furnace. As the furnace moved, the free surface region became supercooled and a large single crystal formed.

Single crystals of barium telluride were grown in graphite crucibles by a Bridgeman technique. A procedure for seeding the melt is described.


Single crystal samples of ternary semi-conductors were prepared by zone leveling techniques.


Single crystal specimens of Mg and Mg alloys containing In, Cd, Ta, Al, Zn, Li, and Tl were prepared in both cylindrical and spherical form. Examination of stress-strain curves illustrated that the most important factor in solution strengthening of these alloys is an interaction between solute atoms and substructural boundaries in the crystals.


High quality GaAs crystals were pulled from the melt. Great precautions were taken to prevent impurities and moisture from entering the system. Crystals 20 mm dia. by 20 cm long were grown.


Notes and drawings of the altered furnace used are provided and the procedure for growing the crystals is discussed.


A review of crystal growth of the II-VI compounds starts with thermodynamic and phase equilibrium considerations from which growth methods are derived. Detailed descriptions are given of melt and vapor methods for II-VI crystals.

Crystal growth on the basis of phase equilibria in the Cd-Te system is discussed. Crystals were produced by slow cooling from the melt and the relative merits of the two starting compositions are discussed for CdTe and similar systems.


Large single crystals of CoSi were grown by the Czochralski technique over a pressure range of $10^{-5}$ torr to 300 psi.


Good crystals of II$_2$ IV$_5$ V$_2$ compounds were grown by either the vertical Bridgeman method or slow cooling.


Large single crystals of a semiconducting intermetallic compound ZnSnAs$_2$ were grown by the Bridgeman method. Electrical and optical properties were studied as a function of temperature.


This research was undertaken to find ways of preparing CdTe with as low an impurity content as possible. Single crystals were grown under a given Cd vapor pressure from a stoichiometric melt. When CdTe was grown in quartz boats it was greatly affected by the acceptor impurity. The use of graphite boats significantly reduced this. Changing the pressure $P_{\text{Cd}}$ made it possible to vary the type of conduction and the charge carrier concentration.


Sb and Ga mixtures containing about 10 at.% Sb were sealed in evacuated quartz tubes, heated to 650°C for 3 hrs., and cooled at 100°C/hr. to give 0.5 mm thick platelet single crystals.

An apparatus for preparation of single crystals of Ni and Ni-Fe alloys is described. The Bridgeman method was used and conditions for growing the crystals given.


Reaction on the surface of a polished specimen of single-crystal Fe of the respective vapor phase produced single crystals of Fe-75 at. % Al and Fe-25 at. % Si. The orientation of the alloy single crystal was identical with that of the initial Fe single crystal. The presence of the order disorder transformation was demonstrated.


Single crystals of InSb were pulled without rotation from the melt in the presence of Te or Se impurity. The formation of pronounced periodic and nonperiodic impurity striations were observed. The formation of these striations is the result of temperature fluctuations at the interface brought about by convection currents in the melt. The convection currents are primarily due to sharp temperature gradients in the growing crystal near the interface.


The basis of the liquid encapsulation technique is use of an inert liquid which completely covers the melt. Loss of volatile components from the melt is prevented by having inert gas pressure on the liquid in excess of the equilibrium vapor pressure. B₂O₃ is recommended as a suitable encapsulant.


Very high purity single crystals were produced by providing for impurity distillation from the closed system. Factors affecting crystal growth and perfection were studied.
Nester, J. F. and J. B. Schroeder, The preparation of oriented single
 crystal spheres of intermetallic compounds between the rare earth
 and iron group metals. Trans. AIME, 233; 249 (1965).

Methods used in growing relatively large single crystals of
YCo$_5$, NdCo$_5$, DyCo$_5$, and YFe$_9$ are described. The zone-melting
method of Mason and Cork was used. Procedures for preparing
the crystals are discussed. The largest crystal prepared by
the process was of sufficient size to permit fabrication of a
2.67 mm dia. sphere of NdCo$_5$.

Ovcharov, V. P. and O. P. Aleshko-Ozhevskii, Preparation of single-
crystal plates of a cobalt-iron alloy for the polarization of
neutrons. Kristallografiya 10; 96-98 (1965) (Russian).

A method is described for (1) growing large (100 mm x 45 mm dia.)
single crystals of Co-8% Fe by direct crystallization in an inert
atmosphere under carefully controlled conditions and (2) subsequent
cutting of plates and etching in aqua-regia. A neutron diffraction
investigation with white and monochromatic neutron beams disclosed
that polarization of the neutron beam at reflection from the
(111) plane was 95%, with sufficient intensity for structural
investigations.

Over'yanov, I. S., U. P. Marshina, F. P. Volkova, G. V. Pertseu, and
S. P. Shashchin, Preparation of single crystals of lead selenide

Preliminary data are presented on the preparation of PbSe single
crystals from the melt by a method other than the Bridgeman-Stockbarger
technique. A modification of the Czochralski technique is used in
which contact between the crystal and the crucible is minimized.
Highly perfect crystals were grown in this manner.

Pelohe, J. R., R. R. Stone, and L. R. Yetter, Statistical approach to
growth of single crystals of GaSb by horizontal growing techniques.
Solid-State Electronics, 8; 861-867 (1965).

The variables considered to be of importance in crystal growing
were tested statistically. Crystals to initiate nucleation were
produced in graphite crucibles with quartz tips, then the crystal
grown by zone melting in a vacuum. Radiofrequency heating was
used.

Single crystals of α-lebeauite, melting point 1220°C, were grown by the Czochralski method. The crucible was timed at 40 rpm and the seed crystal at 25 rpm. The rate of withdrawal was 1.3-0.6 mm/min.


A method is described of growing doped single crystals of compounds of elements of Groups II and VI a few cm³ in size. The crystals were grown from the vapor phase in a closed, moving crucible to permit efficient utilization of the charge and flexibility in the dimensions of the crystal. CdS, ZnS, CdSe, ZnSe, ZnTe, Zn_Cd_x were grown.


The breakdown from columnar growth to equiaxed growth for Al-Mg alloys was found to be dependent upon the rate of solidification, the temperature gradient in the liquid head of the solid-liquid interface, and the solute concentration. It is suggested that constitutional supercooling ahead of the dendritic interface promotes nucleation in the melt.


Lead selenide crystals were grown by sublimation using a technique in which almost the whole charge of a few grains was converted into only one single crystal. Control of the Pb:Se ratio in the resulting crystal was achieved by control of the partial vapor pressure of selenium during growth.


The preparation of crystals of the quaternary alloy system Bi_{24}Se_{65}Sb_{(60+x)}Te_{(150-x)} where -8 < x < 12 is described. The samples were prepared by a modified and carefully controlled Bridgeman process. Large crystals were obtained over the entire alloy system.

The influence of growth rate, quality of seed crystal, As vapor partial pressure, and impurities on dislocation density were investigated. The larger the diameter, the less the effect of growth rate. The seeding method used and Zn and Te impurities had no significant effect on dislocation density. Crystal perfection depended mainly on the precision with which the As partial pressure was held constant.


Single crystals of GaAs were tested with a number of different etchants. These crystals were boat grown. A description of the dislocations on the A face (111), B face (111), or both are given for each etchant.


Procedures for the preparation of the alloys and single crystals are mentioned. Major emphasis is given to analytical methods and results.


Dense samples of Se were prepared in an ultrasonic field. TlSe single crystals were also grown in the ultrasonic field in evacuated quartz ampules inside a rotating furnace.


The details of a sealed tube method for growth of zinc sulfide crystals is described and chemical purity of the crystals assessed. Influence of the following parameters is described: (1) ultimate evaporation temperature schedule, (2) temperature gradient, and (3) the pressure of the H₂S ambient. A model employing non-nucleated and surface-nucleated mechanisms is proposed.

Pure single crystals of Cu 1-30 mm dia. and 120-150 mm long were prepared by the Bridgeman method; the gas content of the crystals was 0.0004-0.0007% O, 0.0001% N, and 0.0001% H. A method was developed for the preparation of single crystals of α-brass, based on the method of Elam in which the loss of Zn is minimized by using sealed vertical ampules which are partially filled with molten brass. The vapor pressure of Zn prevents further loss of Zn. Single crystals, 10-30 mm in dia. and fairly uniform in Zn content, were prepared with little loss of Zn. The crystals were machined on a lathe and then annealed at 650° without disturbing the single crystal structure.


Single crystals of Mo-Nb solid solutions of given crystallographic orientation were obtained in an apparatus for electron beam zone melting, described by E. M. Savitskii, et al, (1961), by use of a nitrogen trap in a 10^-4-10^-5 torr vacuum. The alloys varied in composition from pure Mo to pure Nb. The components were melted directly in the apparatus. Two subsequent passings of the molten zone at 3 to 6 mm/min. were made in opposite directions for the production of single crystal alloys of homogeneous composition. Single crystals of high alloy composition (20% Mo or Nb) could be produced only with a seed crystal. All alloys of the system were grown with crystallographic orientations of [100] and [110]. Single crystals with the [110] orientation had the highest plasticity. The strength of single crystals of the Mn-Nb alloys increased and their plasticity decreased (although remaining at a sufficiently high level) with increasing Nb content.


A constant-current control with an electric thermal feedback loop was used to control an electron-beam floating zone melting furnace. A single-tube constant-current regulator utilizing W-filament lamps in the feedback loop is described. Numerous crystals of metals and alloys ranging from 10-20 in. in length were grown from 0.220-in. diam. starting electrodes.

A method is described by which single crystals of good quality Se and Se-Te alloys, as large as 25 mm length and 10 mm dia., were obtained. Amorphous Se pieces were placed on a cleaved surface of single crystal Te sealed in a Pyrex tube. The tube was placed in a Bridgeman furnace and lowered at 5-10 mm/day. A single crystal grew on the Te crystal base.


Homogeneous crystals of BiSb were obtained by positioning the traveling molten zone of a horizontal traveling furnace in a magnetic stirring field. This field consisted of passing a direct current through the molten alloy which was surrounded by four pairs of magnets. This induced stirring in the vertical direction and produced very homogeneous crystals.


An alloy ingot was made by melting weighed amounts of Cu and Au in a vacuum induction furnace. The ingot was homogenized by a vacuum anneal of 100 hrs. at 800°C. Thin rods were then cast from the ingot and single crystals grown in a vacuum by the Bridgeman technique. The crystals were homogenized for four hours at 900°C.


The growth of AlAgCu (20 wt. % Ag, 3.5 wt. % Cu) alloy single crystals by the strain-annual method is described. The effect of growth variables on alloys with limited solid solubility is discussed.


CdSb single crystals are prepared by zone melting in a boat with and without a seed crystal in a stream of pure hydrogen or in a sealed and evacuated tube.

A study was made of the affect of the structure of Ag-Cd, Ag-Zn, and Cu-Zn solid soln. alloys on the rate of evaporation of Cd and Zn. Alloys were prepared and single crystals grown. A technique was developed for growing single crystals without loss of zinc.


Dislocation-free GaAs single crystals up to 100 g were grown by the Czochralski method in a sealed system with additional As vapor, which must be held very constant. It was necessary to neck down very thin before pulling. Diffusion of groups II, IV and VI elements into this dislocation-free GaAs was achieved.


Single crystals of the above materials with $x$ up to 0.13 were grown from the elements by temperature gradient solution zoning with excess Te as a solvent.


CdSe single crystals were grown from Se solutions by temperature gradient solution zoning at 1050-1100°C, well below the melting point of 1239°C. As grown, the crystals were highly transparent and contained detectable Se inclusions.


Single crystals of Bi$_2$Te$_3$ were prepared by the Teal-Little method. Melting was affected in a quartz jacket under a He atmosphere. The rate of pulling was 2-3 in./hr.

Single crystals of 3.25% Si-Fe alloys were produced from comparative Si steel sheets by strain-anneal using a specially designed, high temperature gradient (500°C/cm) furnace. The specimens were strained by a slight rolling rather than by tension, chemically etched, then inserted into the furnace.


An unexplained small spherical projection of the solid phase into the liquid phase was detected at the interface of binary compounds at crystallization conditions. Stability of this interface was indicated when heat flow from the planar interfacial surface was equal to the heat flow at the interface of the spherical projection. Mathematical expressions for obtaining parameters to measure this heat flow are presented. Experimental results for conditions of stability vs. concentration at the interface of a Pb-Sn alloy compared favorably with conditions calculated from the mathematical equations.


A technique is described for the preparation of thin-rod specimens of brittle intermediate phases, and for the conversion of such rods into single crystals. Ingots of about 100 g and 11 mm dia. were made.


Vapor phase growth of ZnSe crystals was made by a modified Piper method in an argon atmosphere at relatively low temperatures, 1490° and 1400°K. Single crystals of size 1 cc were obtained at 1490°K. The growth rate was 10^-8 to 10^-7 moles/cm^2 sec. and was limited by the diffusion process of the vapors.


In the discussion of the experimental procedures, the preparation of alloy slugs and subsequent recrystallization of single crystals are explained. Crystals of 1/2 cm dia. and 0.1 cm in length were obtained.

The crystal was produced by direct fusion of ZnSe powder under high inert gas pressure (120 atm. argon).


Crystals produced by zone melting of previously mixed metal, melted in an evacuated bulb then annealed above 505°C for 15 hrs. A previously grown seed was used.


The Ta-Mo system was studied because of the large differences in x-ray and electron scattering values with composition, and the closeness of the melting points. Single crystals were produced at 10 at.% composition increments by electron beam melting.


Single crystals in the InAs-Cd Te system were prepared using iodine as the carrier. The growth procedure is explained in detail.


A wire of TiNi was strained by pulling. The ends were then spot-welded and vacuum sealed into a pyrex tube. Repeated temperature cycling between 500-900°C produced single crystal growth.


Single crystals of CdCr₂Se₄ were grown by reversible chemical transport, where CdCr₂Se₄ was the only deposited product. It was necessary to stabilize the CdCr₂Se₄ with an excess of Se to prevent partial decomposition.

A traveling solvent method has been used to grow GaP crystals from Ga solution. Growth rates of approximately 0.5 mm/hr. have been achieved at an average temperature as low as 850°C.


Single crystals of the above materials were pulled from the melt. Crystals up to 3/8 in. dia. were obtained.


ZnHg$_{1-x}$ Te and GaP$_{1-x}$ As$_x$ crystals were grown from solution by a traveling heater method. Homogeneous crystals were obtained by regrowing the crystals a second time, after removing the end sections.


A vapor phase method for producing boules of single crystal of zinc telluride. The product is usually about 10 mm dia. by 30 mm length.


Homogeneous slugs of alloy of liquidus and solidus composition were prepared by mixing the metals, then rapidly quenching. Two bars, a small section of liquidus composition and a longer bar of solidus composition were placed in a carbon coated quartz boat. The boat was positioned in a zone melter so that the liquidus charge was completely molten. Crystal growth at very slow rates, 7 x 10^{-6} cm/sec, with 40°C/cm temperature gradient produced highly homogeneous Bi-Sb single crystals.


Single crystals of Ge-Si were grown using the Czochralski technique. It was difficult to obtain these crystals and the crystals of low Si concentration were not homogeneous. Homogeneous crystals of 15 at. % Si were pulled by using a single crystal seed and by feeding the melt to maintain a constant composition.
<table>
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<th>Author (Page)</th>
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Fe-Mo
Fe-Ni
Fe-Si
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Ga-P
Ga-P-As
Ga-Sb
Ga-Se
Ge dichalcogenides
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Ge-Si
Ge-Te
In-Sb
Li-Mg
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Mo-Nb
Pb-Se
Pb-Te
Rare earth-Co
Rare earth-Fe
Rare earth-Ga-Se
Rb-Ag-I
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